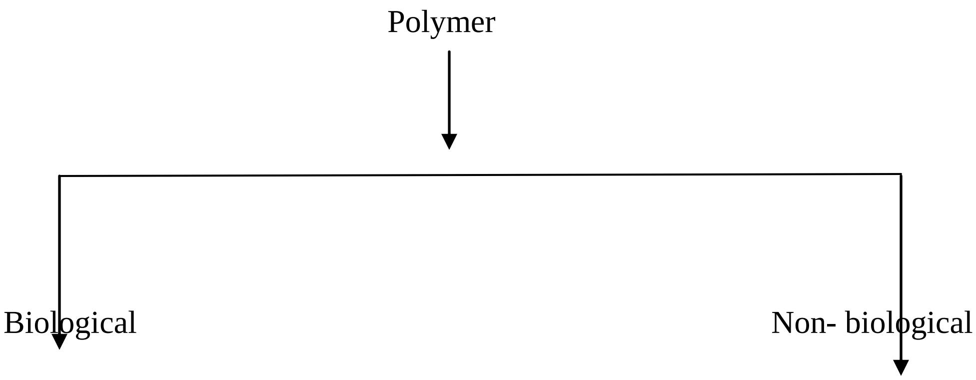
MODULE-1

Introduction: -The macromolecules are divided between biological and non-biological materials. The biological polymers form the very foundation of life and intelligence, and provide much of the food on which man exists. The non-biological polymers are primarily the synthetic materials used for plastics, fibers and elastomers but a few naturally occurring polymers such as rubber wool and cellulose are included in this class. Today these substances are truly indispensable to mankind because these are essential to his clothing,shelter, transportation, communication as well as the conveniences of modern living.



Proteins, starch, wool plastics, fibers easterners

Note: Polymer is not said to be as macromolecule, because polymer is composedof repeating units whereas the macromolecules may not be composed of repeating units.

Definition: A polymer is a large molecule built up by the repetition of small, simple chemical units known as repeating units which are held together by chemical covalent bonds. These repeating units are called monomer

Polymer – ---- poly + meres

Many parts

In some cases, the repetition is linear but in other cases the chains are branched on interconnected to form three dimensional networks. The repeating units of the polymer are usually equivalent on nearly equivalent to the monomer on the starting material from which the polymer is formed. A higher polymer is one in which the number of repeating units is in excess of about 1000

Degree of polymerization (DP): - The no of repeating units or monomer units in the chain of a polymer is called degree of polymerization (DP) . The molecular weight of an addition polymer is the product of the molecular weight of the repeating unit and the degree of polymerization (DP).

$$DP=\frac{Molecular\ \ weight\ of\ the\ polymer}{Molecualr\ \ weight\ of\ the\ monomer}$$

Note: The term plastics have been derived from the Greek word “Plasticos” which means “Fit for mounding”. Hence plastic may be defined as organic on inorganic substances, natural or synthetic which can be molded into articles of different shape and size. Hence it is noted that all plastics are polymers and all polymers are not necessarily plastic.

Classification of polymers: There are several ways to classify polymers. The classification is based on several considerations. The source of polymer i.e. natural on synthetic, the type of polymerization process used in the synthesis, nature and type of chain and the solid state behavior of polymer chains etc.

Again polymers may be classified on the basis of the following.

(i) Their reaction of stress and temperature.

(ii) Their mechanical strength and behavior

(iii) The ways by which they are produced

(iv) Their molecular arrangement

(v) The type of monomer involved in the polymer.

(vi) The morphology of the polymeric substances.

The different classification schemes can be outlines as follows.

- → Natural and synthetic polymers.
- → Addition and condensation polymers
- → Homochain and Heterochain polymer
- → Organic and inorganic polymers and element- organic polymer
- → Homo -polymers and co-polymers
- → Linear, branched and cross-linked polymers
- → Charged or uncharged polymer/ ionic or non- ionic polymer
- → Thermoplastics andthermosetting polymers
- → Fibers, plastics and Elastomers
- → Crystalline and Amorphous polymers.
- → Isotactic, syndiotactic and atacic polymers.

Note: Polymers with three different types of nonnumeric units are sometimes called as ‘terpolymers’

The repeating units constituting the polymer molecule are called as constitutional repeat units or ‘CRU’.

Comparison between Thermoplastics and Thermosetting Polymer

Thermoplastics Polymer

i. They are often formed by addition polymerization leading to long linear chain polymers with no cross-links.

ii. They soften readily on heating because secondary forces between the individual chains can break easily by heat, light or pressure.

iii. They can be reshaped and reused from waste

iv. These are usually soft, weak and less brittle.

v. They can be reclaimed from wastes.

vi. They are usually soluble in suitable solvents.

vii. Adjacent polymer chains are held together either by vanderwaals forces on dipole-dipole interaction or by hydrogen bonding.

viii. During molding there is no change in chemical composition occurs.

ix. These aregenerally tough materials

Example: PF, PP, PVC, PMMA, PS Nylons etc.

Thermosetting Polymer

i. They are often formed by condensation polymerization with three dimensional network structures.

ii. They do not soften on heating and on prolonged heating, however charring of polymers is caused.

iii. They cannot be reshaped and reused.

iv. They are usually hard, strong and more brittle.

v. They cannot be reclaimed from wastes.

vi. Due to strong bonds having inter and intra-chain cross-linking, these are insoluble in almost all organic solvents.

vii. Adjacent polymer chains are held together only by strong covalent bonding.

viii. During molding further polymerization and cross-linking occurs.

ix. These are brittle materials.

Example: Epoxy resins, silicones, Bakelite etc.

Natural and Synthetic polymers:

Natural polymers: Obtained from animal and plant origin.

Examples--Cellulose, starch, protein, wool, silk, leather.

Synthetic polymers: Synthetically prepared in the laboratory.

Examples-- Plastics, resins, synthetic fibers like Nylon and Terylene, adhesives, paints etc.

Homopolymers and Copolymers: - (i) If a polymer is formed from a single monomer unit, then it is called as a homopolymer.

A-A-A-A-A-A-A-A-..

Example: PE, PMMA, PS, PAN ,PVC etc.

(2) Polymeric compounds which are built up of two different types of monomer units in their chain are called "Copolymers" or "Mixed polymer" polymers with three different types of nonnumeric units are sometimes called as "ter-polymers" copolymers are further classified as alternating copolymers or statistically regular (where both repeating nonnumeric units are joined side by side) and random copolymers or statistically irregular (where there is no regularity in the joining of units of two different monomers)

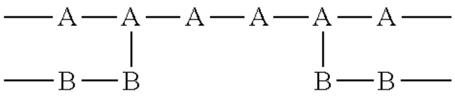
Copolymers are again classified as block or graft copolymers.

(a) Alternating Copolymer ….. ABABABABAB……..

(b) Random Copolymer …. ABBABAABAABA……

(c) Block Copolymer … AAAAABBBBBAAAA…..

(d) Graft Copolymer



Graft Copolymer

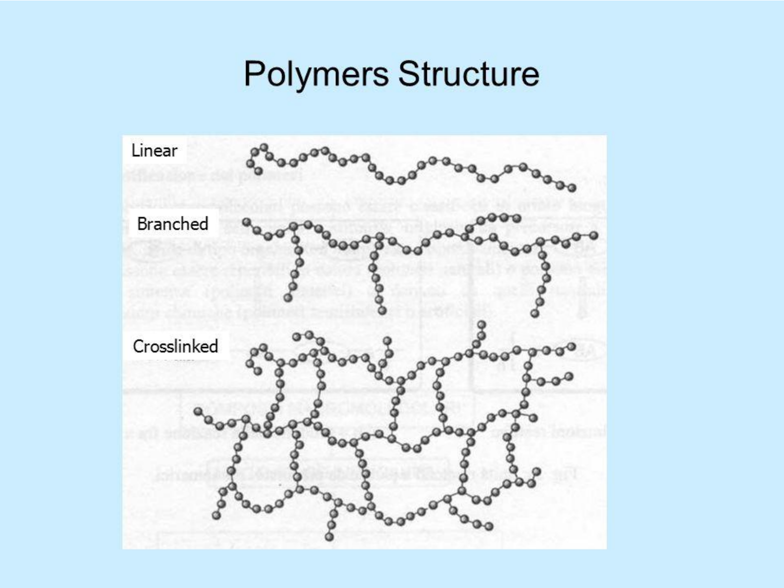
—A—A—B—B—A—A—

Block Copolymer

Oligomers: The chain like molecules with a few (8-10) structural units are called “oligomers” aligo means few and mers means parts. These are low molecular weight products. Many organic compounds are of fairly high molecular weight, yet these are not considered as polymers. It is the complexity of their molecules and not the multiple repetitions of the monomers which accounts for their molecular weight and size.

Again polymers can also be classified as linear or cross linked polymers.

- Linear polymer
- Branched Chain polymer
- Cross linked polymer


Polymers Structure

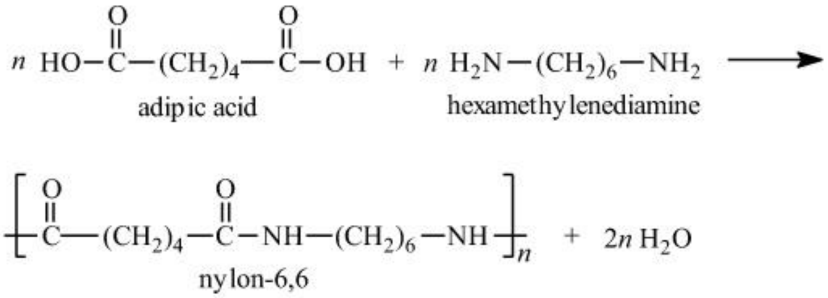
According to the structure of their main chain, all polymers can be broadly classified as homochain and heterochain polymers. In case of homochain polymers the main chain is made up of linkages between the atoms of same elements.Polymers are divided into two principal classes on the basis of the constitution of the main chain. Homochain polymers are those in which the main chains are constructed from atoms of a single element; heterochain polymers are those in which the main chains are constructed from atoms of two or more elements

Example: Carbon in organic polymers

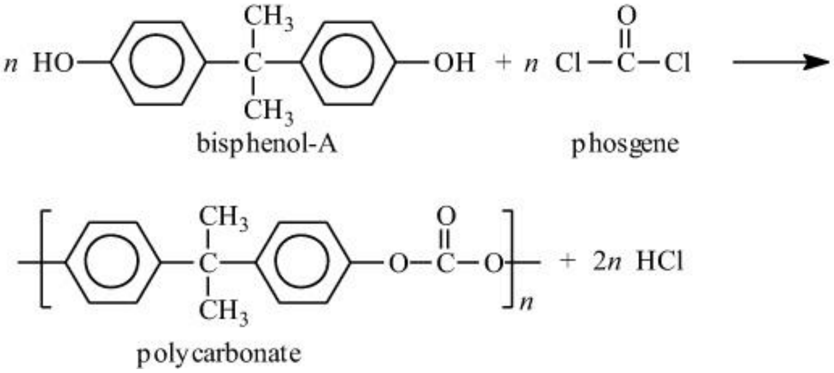
$$\begin{array}{c} \vdots \\ -c \\ \vdots \end{array} \quad \begin{array}{c} \vdots\ \ \vdots\ \ \vdots\,\vdots\,\vdots \\ -c-c-c-c-c \\ \vdots\ \ \vdots\ \ \vdots\,\vdots\,\vdots \end{array} \ \begin{array}{c} \vdots\ \ \ \vdots\ \vdots \\ -c-c \\ \vdots\ \ \ \vdots\ \vdots \end{array}\text{-----------------}$$

In heterochain polymers, the main chain consists of linkages between different atoms i e between carbon and oxygen in polyesters and between carbon, Nitrogen and oxygen in polyurethanes etc. Again polymers are also classified as organic, Element-organic inorganic polymers etc.

A



B



Organic Polymers: (i) The polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer. The atoms attached to the side valencies to the backbone carbon atoms are however usually carbon, hydrogen, oxygen, Nitrogen, siphon and halogen, atom. The majority of the synthetic polymers are organic.

(ii) The no. and variety of organic polymers are so large in number that when we “refer” to polymer we normally mean organic polymer.

(iii) They fall under aliphatic and aromatic compounds, which can be further classified as homo-chain polymers and hetero- chain polymer.

The homo- chain polymers are polyethylene, polybutadiene, PVC, polyvinyl alcohol, PMMA, polybutadine , while hetero -chain polymers are polyethers , polyesters, polycarbonates, epoxy polymers, polyurathanes, polyamides, poly sulphides etc.

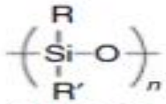
Elemento-organic polymers: This type of polymers includes the following.

(i) Compounds whose chains are composed of carbon atoms and hetero atoms (Except N, S, O)

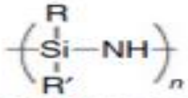
(ii) Compounds with inorganic chains, containing side groups with carbon atoms connected directly to the chain.

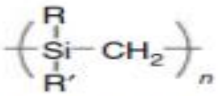
(iii) Compounds whose main chain consist of carbon atoms and whose side groups contain hetero atoms (except N, S, P and halogens) connected directly to the carbon atom of the chain.

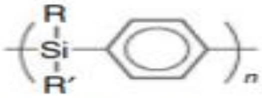
Example:Polysiloxanes


Silicones
(polysiloxanes)


Polysilanes
(polysilylenes)


Polysilazanes


Polycarbosilanes


Polysilphenylenes

Other **examples** are poly titanozanes and poly stananoxares.

Inorganic Polymers: Inorganic polymers are polymers containing no carbon atoms but have si-si, si-o, N-Px, P-C and B-O linkage i.e. polysilanes , polyphosphazenes , polyphosphonic acid on polyphosphates and polyboron oxides .Inorganic polymers studied a little extent because it is difficult to provide a classification.

The inorganic polymer possesses superior thermal, electrical and mechanical properties over the organic polymers.

The polymers contain largely elements of IV-VI groups of the periodic table.

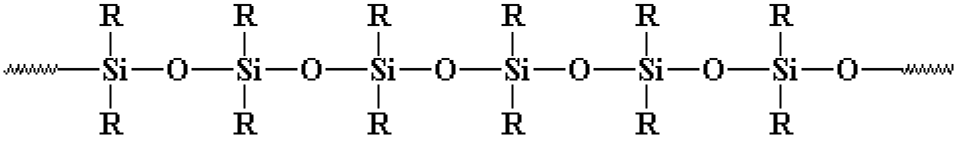
The elements of group IV can form linear polymers, Group-V usual form Low molecular weight compounds. Sulphur and selenium (Group VI) have a high tendency to form linear homochain polymeric compounds. On most of these cases we are talking about polymers whose backbone chains are made mostly of carbon atoms, if not entirely of carbon atoms. These we call *organic* polymers. But now we're going to leave convention behind and talk about some polymers that don't have any carbon atoms in the backbone chain. These are called, as if you couldn't guess, *inorganic* polymers. Here's a menu if the inorganic polymers on this page to help you navigate:

Silicones
Polysilanes
Polygermanes and polystannanes

Polyphospahazenes

Silicones

You've seen inorganic polymers before -- if not on these pages, at least in everyday life you've probably seen a silicone polymer somewhere. Silicones are the most common inorganic polymers. They look like this:

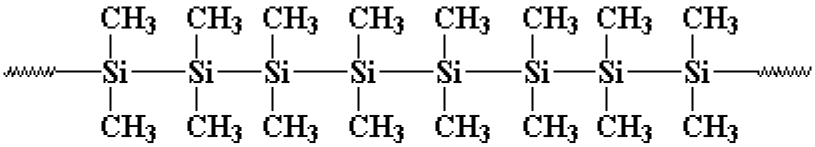


They really should be called *polysiloxanes*. The bond between silicon and oxygen is very strong, but very flexible. So silicones can stand high temperatures without decomposing, but they have very low glass transition temperatures. You've probably seen rubber or caulking made of silicones somewhere before.

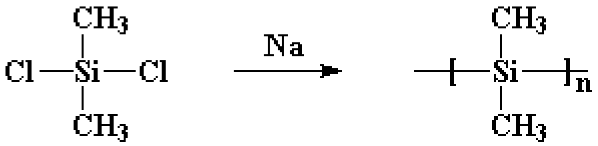
Polysilanes

Let's take a look at the element silicon for a moment. You can see that it's right beneath carbon in the periodic chart. As you may remember, elements in the same column or *group* on the periodic chart often have very similar properties. So, if carbon can form long polymer chains, then silicon should be able to as well. It took a long time to make it happen, but silicon atoms have been made into long polymer chains. It was in the 1920's and 30's that chemists began to figure out that organic polymers were made of long carbon chains, but serious investigation of *polysilanes* wasn't carried out until the late seventies.

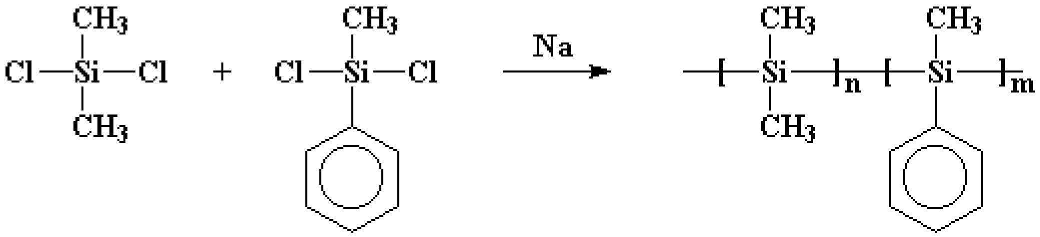
Earlier, in 1949, about the same time that novelist Kurt Vonnegut was working for the public relations department at General Electric, C.A. Burkhard was working in G.E.'s research and development department. He invented a polysilane called polydimethylsilane, but it wasn't much good for anything. It looked like this:



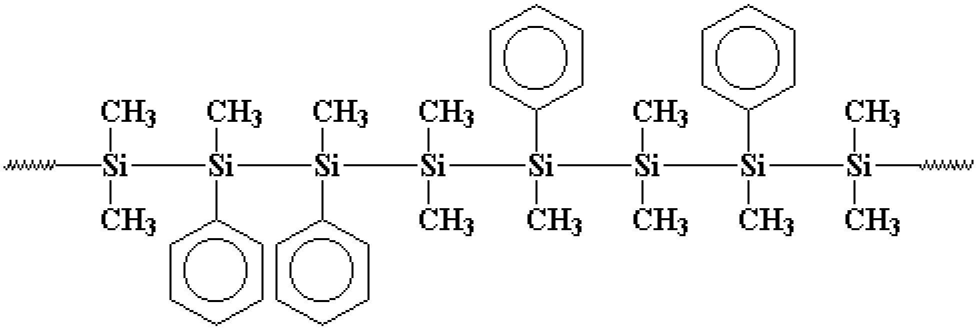
It formed crystals that were so strong that nothing could dissolve them. Burkhard tried to heat it, but it wouldn't melt below 250°C, when it decomposed, without melting. That made polydimethylsilane pretty much useless. He made it by reacting sodium metal with dichlorodimethylsilane like this:



This is important, because in the seventies, some scientists got the notion that they were going to make small rings of silicon atoms. So unwittingly did something similar to what Burkhard had done. They reacted sodium metal with dichlorodimethyl silane, but they also added some dichloromethylphenylsilane to the brew. And guess what happened! I'll give you a hint: they didn't get the rings they wanted. What they got was a copolymer, like this:



Maybe that polymer is more clearly drawn like this:

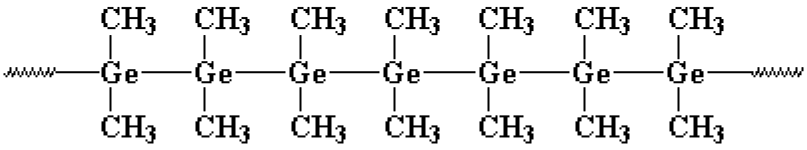


You see, those phenyl groups get in the way when the polymer tries to crystallize, so it isn't as crystalline as polydimethylsilane. This means it is soluble and can be processed and played with and studied.

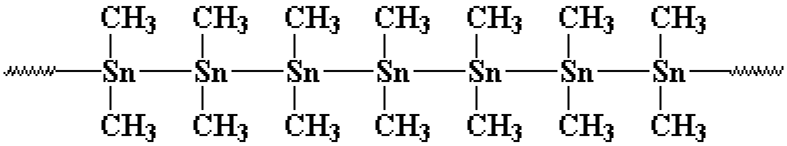
So what are these good for? Polysilanes are interesting because they can conduct electricity. Not as well as copper, mind you, but a lot better than you'd expect for a polymer, and worth investigating. They're also very heat resistant, almost up to 300 ^{o}C, but if you heat them a lot higher you can make silicon carbide out of them, which is a useful abrasive material.

Polygermanes and Polystannanes

Okay, so if silicon can make long polymer chains, what about he other elements in Group IV? Can you make polymers out of germanium? You'd better believe you can! Not only can you make polymer chains out of germanium, but you can even make a polymer chain out of tin atoms. These polymers are called polygermanes and polystannanes, respectively.



polydimethylgermane

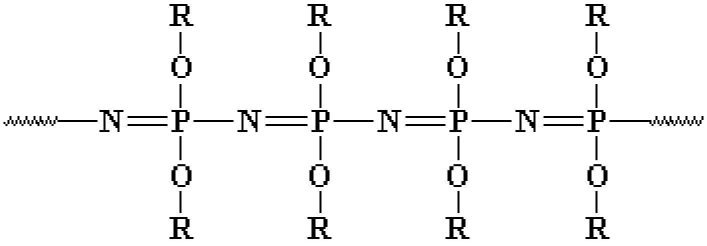


polydimethylstannane

Polystannanes are unique and nifty and wonderful and fabulous because they are the only known polymers with backbones made entirely from metal atoms. Like polysilanes, polygermanes and polystannanes are being studied for use as electrical conductors.

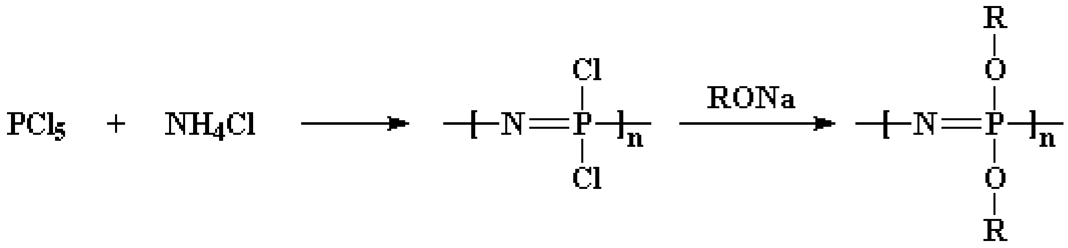
Polyphosphazenes

I hate to break it to you folks, but we're out of Group IV elements. So the last inorganic polymer we're going to look at today is going to have to be made of something else. And that something else is phosphorus and nitrogen. Like the polysiloxanes, polyphosphazes are made of alternating atoms, in this case, the chain is made up of alternating phosphorus and nitrogen atoms, like this:



An ether substituted polyphosphazene. (*R* is a wild card, standing for any hydrocrabon group)

This backbone is very flexible, like the polysiloxane backbone chain, so polyphosphazenes make good elastomers. They're also very good electrical insulators. Polyphosphazenes are made in two steps:

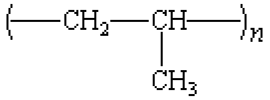
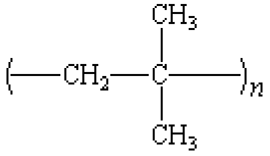
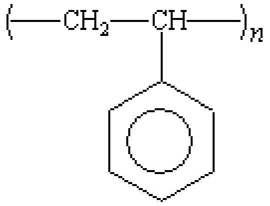


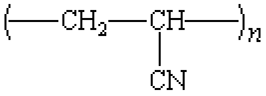
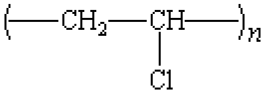
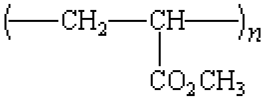
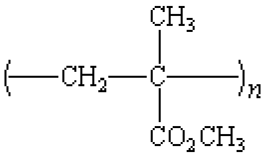
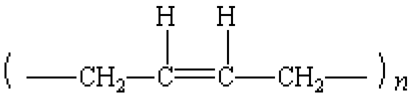
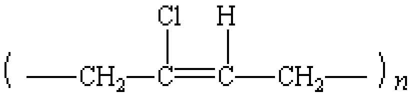
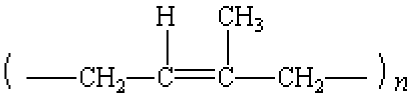
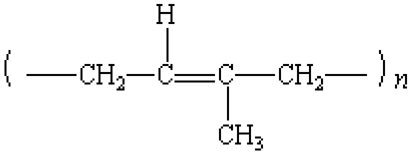
First we take phosphorus pentachloride and react it with ammonium chloride to get a chlorinated polymer. Then we treat it with an alcohol sodium salt, and that gives us an ether-substituted polyphosphazene.

Addition Polymers

Addition polymers such as polyethylene, polypropylene, poly (vinyl chloride), and polystyrene are linear or branched polymers with little or no cross-linking. As a result, they are thermoplastic materials, which flow easily when heated and can be moulded into a variety of shapes. The structures, names, and trade names of some common addition polymers are given in the table below

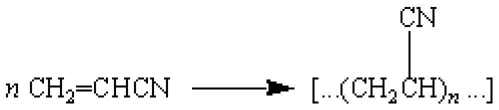
Common Addition Polymers

Structure	*Chemical Name*	*Trade Name or Common Name*
$(-CH_2-CH_2-)_n$	Polyethylene	
$(-CF_2-CF_2-)_n$	Poly(tetrafluoroethylene)	Teflon
 $(-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-)_n$	Polypropylene	Herculon
 $(-CH_2-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-)_n$	Polyisobutylene	butyl rubber
	Polystyrene	

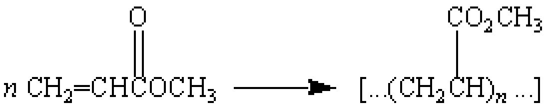
 $(-CH_2-CH(CN)-)_n$	Polyacrylonitrile	Orlon
 $(-CH_2-CH(Cl)-)_n$	Poly(vinyl chloride)	PVC
 $(-CH_2-CH(CO_2CH_3)-)_n$	P oly(methyl acrylate)	
 $(-CH_2-C(CH_3)(CO_2CH_3)-)_n$	poly(methyl methacrylate)	Plexiglas, Lucite
 $(-CH_2-CH{=}CH-CH_2-)_n$	polybutadiene	
 $(-CH_2-C(Cl){=}CH-CH_2-)_n$	polychloroprene	neoprene
 $(-CH_2-CH{=}C(CH_3)-CH_2-)_n$	poly(*cis*-1,4-isoprene)	natural rubber
 $(-CH_2-CH{=}C(CH_3)-CH_2-)_n$	poly(*trans*-1,4-isoprene)	gutta percha

Acrylics **Polymers:**

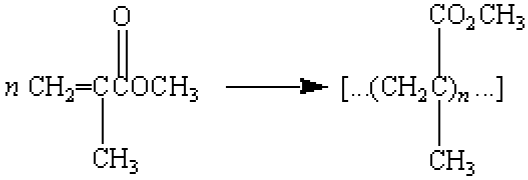
Acrylic acid is the common name for 2-propenoic acid: $CH_2{=}CHCO_2H$. Acrylic fibers such as Orlon are made by polymerizing a derivative of acrylic acid known as acrylonitrile.


$n\,CH_2{=}CHCN \longrightarrow [\ldots(CH_2CH(CN))_n\ldots]$ *Polyacrylonitrile*

Other acrylic polymers are formed by polymerizing an ester of this acid, such as methyl acrylate.


$n\,CH_2{=}CHC(=O)OCH_3 \longrightarrow [\ldots(CH_2CH(CO_2CH_3))_n\ldots]$ *Poly(methyl acrylate)*

One of the most important acrylic polymers is poly (methyl methacrylate), or PMMA, which is sold under the trade names Lucite and Plexiglass.

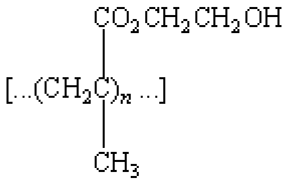


$$n\ \mathrm{CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}OCH_3} \longrightarrow [\ldots(\mathrm{CH_2C(CH_3)(CO_2CH_3)})_n\ldots]$$

Poly(methyl methacrylate), PMMA

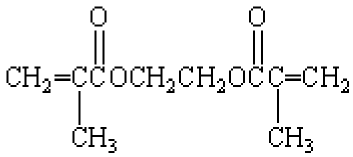
PMMA is a lightweight, crystal-clear, glasslike polymer used in airplane windows, taillight lenses, and light fixtures. Because it is hard, stable to sunlight, and extremely durable, PMMA is also used to make the reflectors embedded between lanes of interstate highways.

The unusual transparency of PMMA makes this polymer ideal for hard contact lenses. Unfortunately, PMMA is impermeable to oxygen and water. Oxygen must therefore be transported to the cornea of the eye in the tears and then passed under the contact lens each time the eye blinks. Soft plastic lenses that pass both oxygen and water are made by using ethylene glycol dimethacrylate to crosslink poly (2-hydroxyethyl methacrylate).



$$[\ldots(\mathrm{CH_2C(CH_3)(CO_2CH_2CH_2OH)})_n\ldots]$$

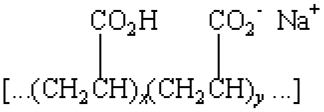
Poly(2-hydroxyethylmethacrylate)



$$\mathrm{CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}OCH_2CH_2O\overset{O}{\overset{\|}{C}}C(CH_3){=}CH_2}$$

Ethylene glycol dimethacrylate

An interesting polymer can be prepared by copolymerizing a mixture of acrylic acid and the sodium salt of acrylic acid. The product of this reaction has the following structure.



$$[\ldots(\mathrm{CH_2CH(CO_2H)})_x(\mathrm{CH_2CH(CO_2^-\,Na^+)})_y\ldots]$$

Sodium polyacrylate

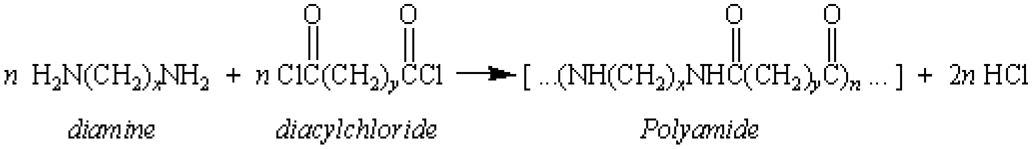
The difference between the Na^+ ion concentration inside the polymer network and in the solution in which the polymer is immersed generates an osmotic pressure that draws water into the polymer. The amount of liquid that can be absorbed depends on the *ionic strength* of the solution — the total concentration of positive and negative ions in the solution. This polymer can absorb 800 times it own weight of distilled water, but only 300 times its weight of tap water. Because the ionic strength of urine is equivalent to an 0.1 *M* NaCl solution, this superabsorbent polymer, which can be found in disposable diapers, can absorb up to 60 times its weight in urine.

Condensation Polymers

The first plastic (Celluloid) and the first artificial fiber (Rayon) were produced from cellulose. The first truly synthetic plastic was bakelite, developed by Leo Baekland between 1905 and

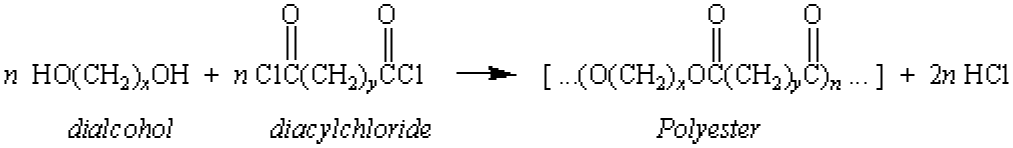
1914. The synthesis of bakelite starts with the reaction between formaldehyde (H_2CO) and phenol (C_6H_5OH) to form a mixture of *ortho-* and *para*-substituted phenols. At temperatures above 100C, these phenols condense to form a polymer in which the aromatic rings are bridged by either $-CH_2OCH_2-$ or $-CH_2-$ linkages. The cross-linking in this polymer is so extensive that it is a thermoset plastic. Once it is formed, any attempt to change the shape of this plastic is doomed to failure.

Research started by Wallace Carothers and co-workers at DuPont in the 1920s and 1930s eventually led to the discovery of the families of condensation polymers known as polyamides and polyesters. The **polyamides** were obtained by reacting a diacyl chloride with a diamine.



$$n\ H_2N(CH_2)_xNH_2 + n\ Cl\overset{\overset{O}{\|}}{C}(CH_2)_y\overset{\overset{O}{\|}}{C}Cl \longrightarrow [\ldots(NH(CH_2)_xNH\overset{\overset{O}{\|}}{C}(CH_2)_y\overset{\overset{O}{\|}}{C})_n\ldots] + 2n\ HCl$$

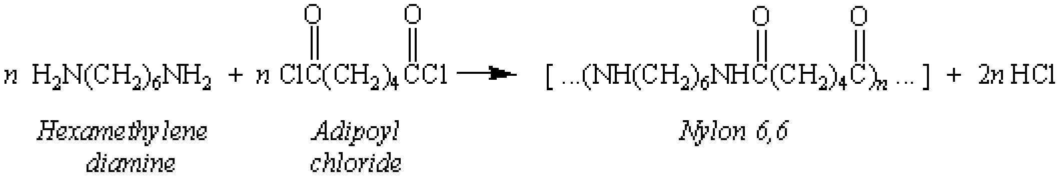
The **polyesters** were made by reacting the diacyl chloride with a dialcohol.



$$n\ HO(CH_2)_xOH + n\ Cl\overset{\overset{O}{\|}}{C}(CH_2)_y\overset{\overset{O}{\|}}{C}Cl \longrightarrow [\ldots(O(CH_2)_xO\overset{\overset{O}{\|}}{C}(CH_2)_y\overset{\overset{O}{\|}}{C})_n\ldots] + 2n\ HCl$$

While studying polyesters, Julian Hill found that he could wind a small amount of this polymer on the end of a stirring rod and draw it slowly out of solution as a silky fiber. One day, when Carothers wasn't in the lab, Hill and his colleagues tried to see how long a fiber they could make by stretching a sample of this polymer as they ran down the hall. They soon realized that this playful exercise had oriented the polymer molecules in two dimensions and produced a new material with superior properties. They then tried the same thing with one of the polyamides and produced a sample of what became the first synthetic fiber: **Nylon**.

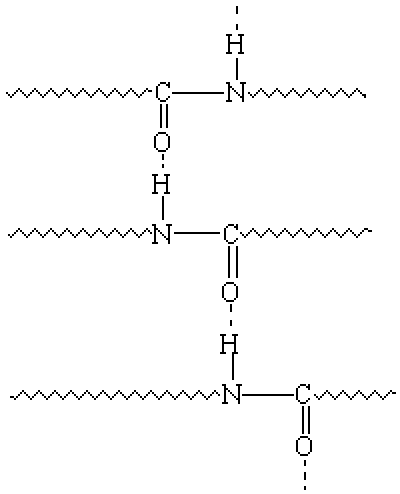
This process can be demonstrated by carefully pouring a solution of hexamethylenediamine in water on top of a solution of adipoyl chloride in CH_2Cl_2.



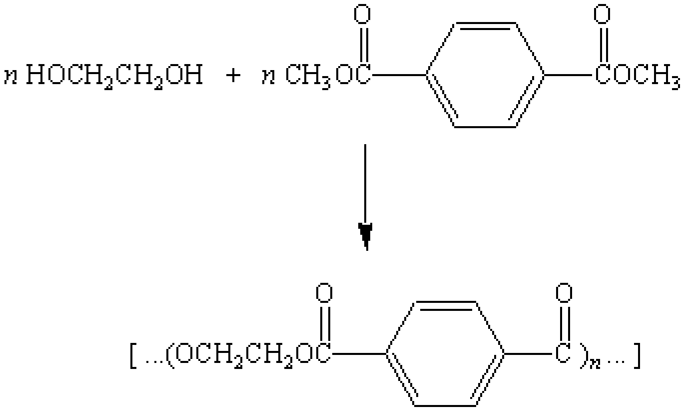
$$n\ H_2N(CH_2)_6NH_2 + n\ Cl\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}Cl \longrightarrow [\ldots(NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C})_n\ldots] + 2n\ HCl$$

A thin film of polymer forms at the interface between these two phases. By grasping this film with a pair of tweezers, we can draw a continuous string of nylon from the solution. The product of this reaction is known as Nylon 6,6 because the polymer is formed from a diamine that has six carbon atoms and a derivative of a dicarboxylic acid that has six carbon atoms.

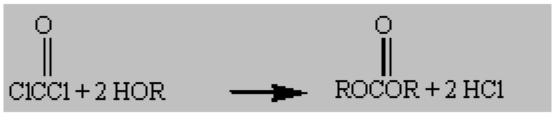
The effect of pulling on the polymer with the tweezers is much like that of stretching an elastomer, the polymer molecules become oriented in two dimensions, suggested that polymers are elastic when there is no strong force of attraction between the polymer chains. Polyamides and polyesters form strong hydrogen bonds between the polymer chains that keep the polymer molecules oriented, as shown in the figure below.



The first polyester fibers were produced by reacting ethylene glycol and either terephthalic acid or one of its esters to give poly (ethylene terephthalate). This polymer is still used to make thin films and textile fibers



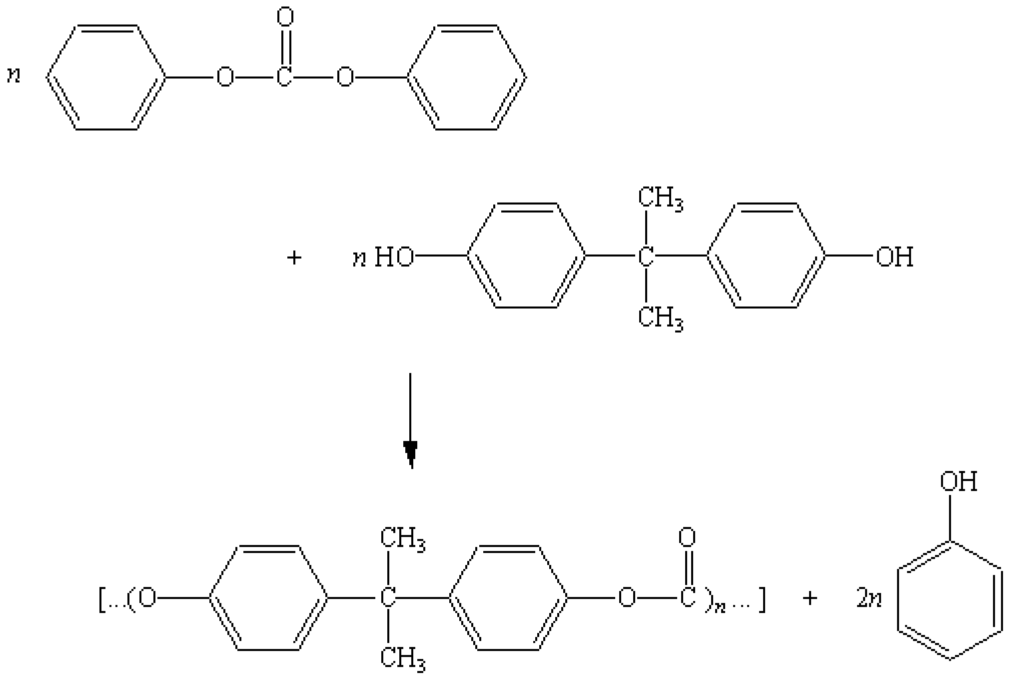
Phosgene ($COCl_2$) reacts with alcohols to form esters that are analogous to those formed when acyl chlorides react with alcohols.



$$\overset{O}{\overset{\|}{ClCCl}} + 2\,HOR \longrightarrow \overset{O}{\overset{\|}{ROCOR}} + 2\,HCl$$

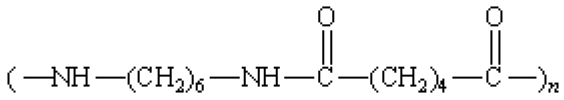
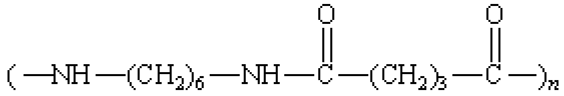
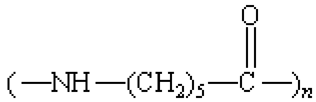
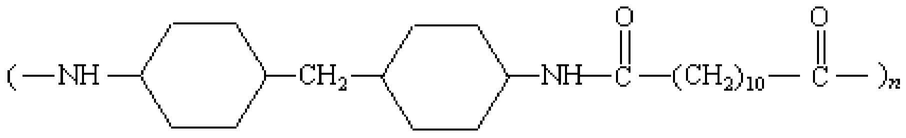
The product of this reaction is called a *carbonate ester* because it is the diester of carbonic acid, H_2CO_3. **Polycarbonates** are produced when one of these esters reacts with an appropriate alcohol, as shown in the figure below. The polycarbonate shown in this figure is known as

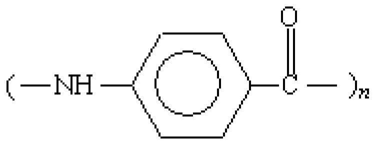
Lexan. It has a very high resistance to impact and is used in safety glass, bullet-proof windows, and motorcycle helmets.



The structures and names of some common condensation polymers are given in the table below.

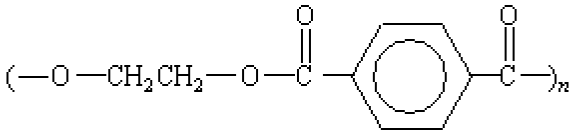
Common Condensation Polymers

Structure	***Trade Name or Common Name***
Polyamides	
 $(-NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-)_n$	Nylon 6,6
 $(-NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_3-\overset{\overset{O}{\|}}{C}-)_n$	Nylon 6,10
 $(-NH-(CH_2)_5-\overset{\overset{O}{\|}}{C}-)_n$	Nylon 6
	Qiana
Polyaramides	

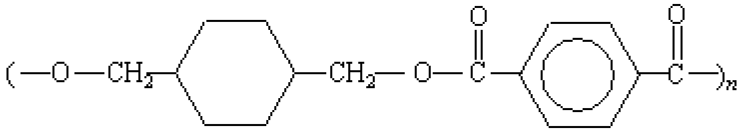


Kevlar

Polyesters

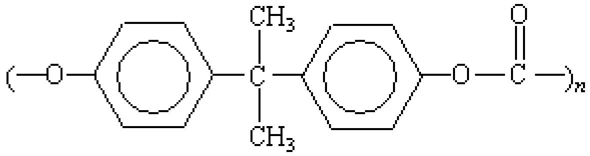


Dacron, Mylar



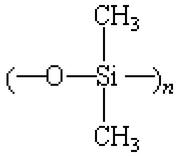
Kodel

Polycarbonates



Lexan

Silicones



$$(-O-\underset{CH_3}{\overset{CH_3}{Si}}-)_n$$

silicone rubber

TACTICITY OF POLYMER: The orientation of monomeric units in a polymer molecule can takes place in an orderly or discordantly fashion with respect to the main chain. This difference in the configuration is known as tactility which affects the physical properties of the polymers.

On the basis of tacticity, the structure of the polymer may be divided into the followingcategories

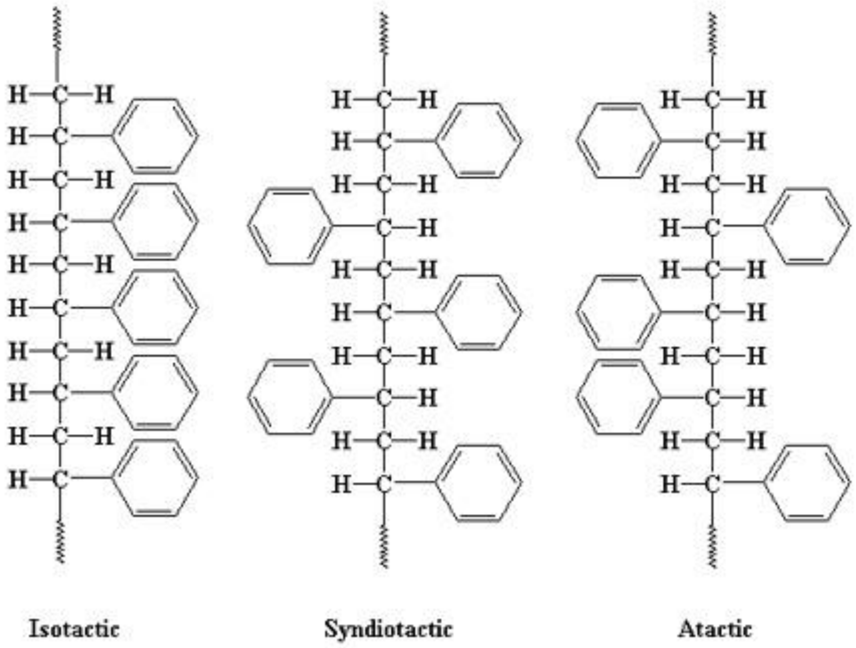
(i) Isotactic (ii) Syndiotactic (iii) Atactic

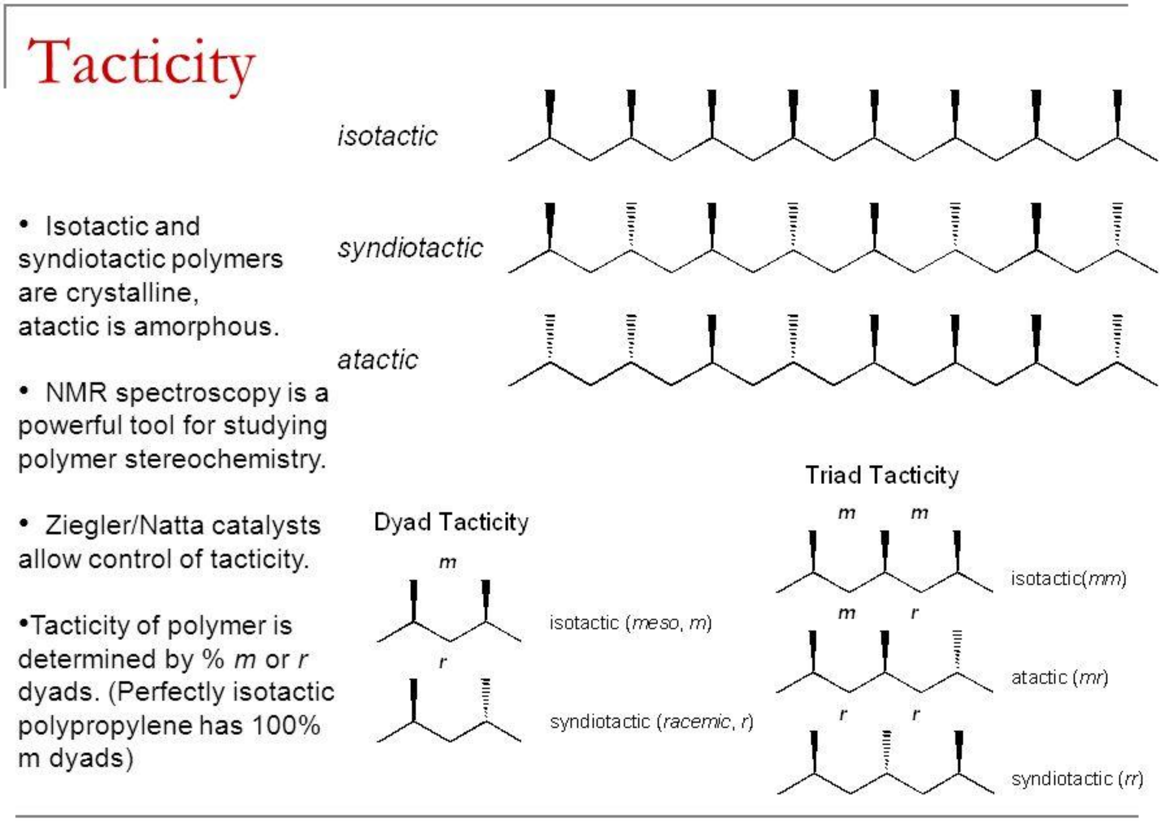
(i) **Isotactic Polymer:** These polymers consist of chain segments which display a regular repetition of the monomer units with teat C atoms of the same satiricconfiguration. In this polymer the substituent group (R) on the polymer lies above or below the plant of the main polymer chain.

(ii) **Syndiotactic polymers:**The chains of these polymers consist of regular species of monomer units in which even second C-atoms of the chain possesses opposed steric configuration. In this polymer the substituent groups (R) lies alternatively above and below the plane of the mam chain

(iii) **Atactic polymers:** The polymeric chain lacks regularity in the distribution of steric configuration of the monomer units.

In these polymersthere is a random arrangementof substituent groups (R) in the polymer chain



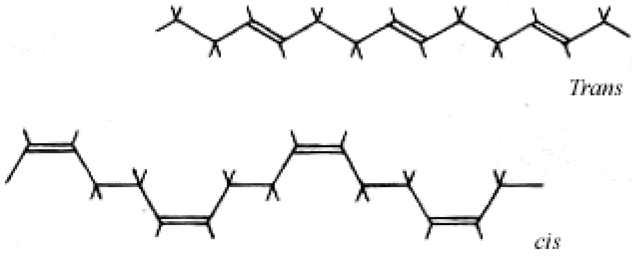


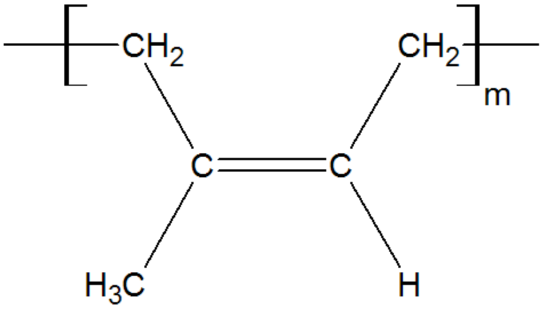
Tacticity

- Isotactic and syndiotactic polymers are crystalline, atactic is amorphous.
- NMR spectroscopy is a powerful tool for studying polymer stereochemistry.
- Ziegler/Natta catalysts allow control of tacticity.
- Tacticity of polymer is determined by % *m* or *r* dyads. (Perfectly isotactic polypropylene has 100% m dyads)

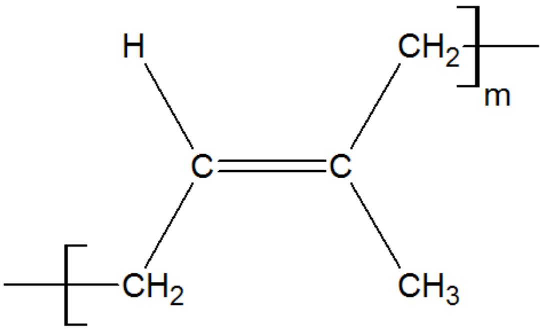
Cis-trans Isomerism in Polymer: Steric arrangement in Cis and Trans Configuration. Polymers with double bonds in the repeat unit give rise to different geometric isomers. These two isomers are called cis and trans poly(1,4-butadiene). The cis-trans isomerism is found in polymers containing double bonds in the main chains. In the cis-isomers the carbon chains are all on the same side of the plane of each double bond, whereas in case of trains-isomers they have alternatively arranged.

Example: Natural rubber and gutta-percha both are poly isoprene's but possesses different physical behaviors i.e. former is elastic whereas latter is hard and rigid.





cis-1,4-polyisoprene



trans-1,4-polyisoprene

Functionality:

Definition: The average number of the reactive groups on the no of bonds produced per monomer molecule will decide the nature of polymerization. Hence the no of bonding sites on the no. of functional groups present in the monomer is said to be the functionality of the polymer. It is classified into the following categories

(a) Mono functional compounds

Methylene alcohol – CH_3-OH

Acetic acid - CH_3-COOH

Methyl amine - CH_3-NH_2

Acetaldehyde - CH_3-CHO

(b) Bi- functional compounds: -

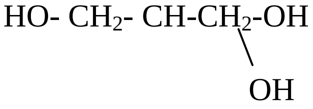
Ethylene glycol – $HO – CH_2- CH_2- OH$

Adipic acid – $HOOC – (CH_2)_4 – COOH$

Hexamethylenediamine. $H_2N- (CH_2)_6- NH_2$

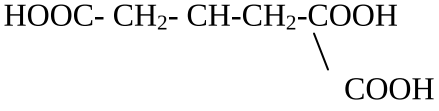
(c) Poly functional compounds: -

Glycerol -



$HO-CH_2-CH(OH)-CH_2-OH$

Tricarbolic acid –



$HOOC-CH_2-CH(COOH)-CH_2-COOH$

(i) Bi-functional monomers containing two functional groups give linear polymers.

(ii) Poly-functional compounds with more than two functional groups per molecule of the monomer give branched or cross-linked polymers.

(iii) Certain trifunctional monomers may react and produces ring or cyclic polymers.

SOME IMPORTANT TERMS:

Plastics: These are the substances of high polymer class which can be molded into articles by heat and pressure. These are mostly synthetic in nature and are called synthetic resins.

They possess highmodulus of elasticity in the range of 10 to 100 kg/ cm^2

Resins: Naturally occurring organic substances which are generally solid or semi-solid polymeric materials are known as resins. It is of natural or synthetic organic substances of relatively high molecular weight which exhibits no sharp M.P and predominantly amorphous in nature. It is insoluble in water and soluble in some organic solvents. These are organic polymers.

Example: Wood, cotton, silk, leather, amber, rubber, shellac, resin etc.

Fibers: If the inter -chain force of attraction in a polymer is very strong, then it must be hard and durable and is known as fiber. In fiber, the chains are oriented along the direction of the pull and the inter- chain forces keep these very strong enough.

Rubber: If the inter- chain forces are very weak, then the polymer is elastic, flexible and soft in nature and is known as rubber. The molecular chains are stretched on pulling but the inter chain forces not being strong enough to keep it in the oriented position, then the chains regain their original position after removal of the deforming forces.

Micelles: They are aggregation of the crystallites of colloidal dimensions that exist in the solid state or in solution as spherical or rod- likes shapes. They represent a reasonably and reproducible dimension as a result of uniform chemical or mechanical treatment such as soaps or colloidal electrolytes in plastic it has been observed that these long chains wonder successively through disordered, random regions, through bundles of organized regions (micelles) amorphous, again ordered regions and so on. The fringed micelles model is very useful in explaining the ordered structure of drawn fibers.

Some Important Polymeric Materials Useful as plastics, Fibers, Rubber, Resins.

Form	**Type**	**Polymeric Materials**
Fibers	Natural Semi synthetic (Cellulosic synthetic)	Cotton, wool, silk and as bestirs Viscos rayon, acetate rayon Polyamides, polyesters, acrylics, policies thanes, polyolefin's, polypropylene PVC, polyvinyl alcohol.
Plastics	Cellulosic plastics Vinyl plastics	Celluloid, cellophane membrane Polyolefines (PE, PP, PTFC) PS, PVC, PVAC,

Rubber	Natural Synthetic	Poly isoprene Poly butadiene, poly chloroprene, (NBR, SBR on BUNA-S and BUNA-N) Badly rubber, polyurethanes polysulfide’s and poly siloxanes, (Silicone rubber)
Resin	Water soluble Water Insoluble	Modified starches, cellulose derivatives polyvinyl alcohol, polycyclic acid and poly acryl amide.

GLASS TRANSITION TEMPERATURE (T_g):

An ordinary rubber ball if cooled below – 70 ^oC, it becomes so hard and brittle that it will break into pieces like a glass ball falling on a hard surface. Why this happens below -70 ^oC. This is because there is a temperature boundary for almost all amorphous polymer and many crystalline polymers only above which the substance remains soft, flexible and rubbery and below which it becomes hard, brittle and glassy.

The temperature below which a polymer is hard and above which it is soft is called the “Glass transition temperature”. The hard, brittle state is known as the glassy state and the soft, flexible state is known as rubbery on Viscoelasticity state. On further heating the polymer (without cross-linked) becomes a highly viscous liquid and starts flowing, which is known as viscous fluid state.

Definition: The temperature at which the internal energy of the molecules of the polymer increases to such an extent that the chain segment of the polymer just gets over its frozen state to a mobile state, capable of leaving the lattice sites is known as glass transition temperature.

One property associated with the glassy state is a low volume coefficient of expansion. This low coefficient occurs as the result of a change in slope of the curve of volume Vs temp. at the point called glass transition temperature (Tg) . This behavior is shown by natural rubber.Another general phenomenon i.e. the amorphous regions of partially crystalline polymers are also assuming a glassy state. i.e. T_g being independent of degree of crystalline to first approximation.

The magnitude of the phenomena associated with Tg decreases with decreasing amorphous content. Hence Tg is sometimes difficult to defect in highly crystalline polymer.

Relation between Glass –transition temp. and Molecular weight of polymer.

The glass transition temperature of a polymer is influenced by its molecular weight and beyond 20,000, the effect of molecular weight is not pronounced.

Following two mathematical relationships have been established.

$Tg = T_g^{\infty} - \frac{K}{M_n}$-------------- (i)

$\frac{1}{T_g} = \frac{1}{T_g^{\infty}} + A/M_n$-------------------(2)

T_g^{∞} - Glass transition temp. at infinite molecular weight ‘K’ and ‘A’ are arbitrary constants.

Glass transition temperature (T_g) and melting point (T_m)

Many attempts have been made to study the relationship between T_g and T_m which are as follows.

$T_g = {}^1/_2 T_m$ ------- (i) (for symmetrical polymers)

$T_g = {}^2/_3 T_m$ ………… (2) (for unsymmetrical polymers)

A combined version of these two equations, irrespective of the molecular symmetry can be.

$1/2 < \frac{T_g}{T_m} < 2/3$…………..(3)

Characteristics of Tg : Tg depends upon the following.

i. Chain length of the polymer

ii. The extent of cross- linking of the polymer

iii. Stannic barrier to internal rotation.

iv. The rate of heating and cooling.

v. T_g of linear polymer is fairly high than cross- linked polymer

vi. Below T_g the polymer is hard and brittle.

vii. Cross-linked polymers almost have no T_g but have a decomposition temperature.

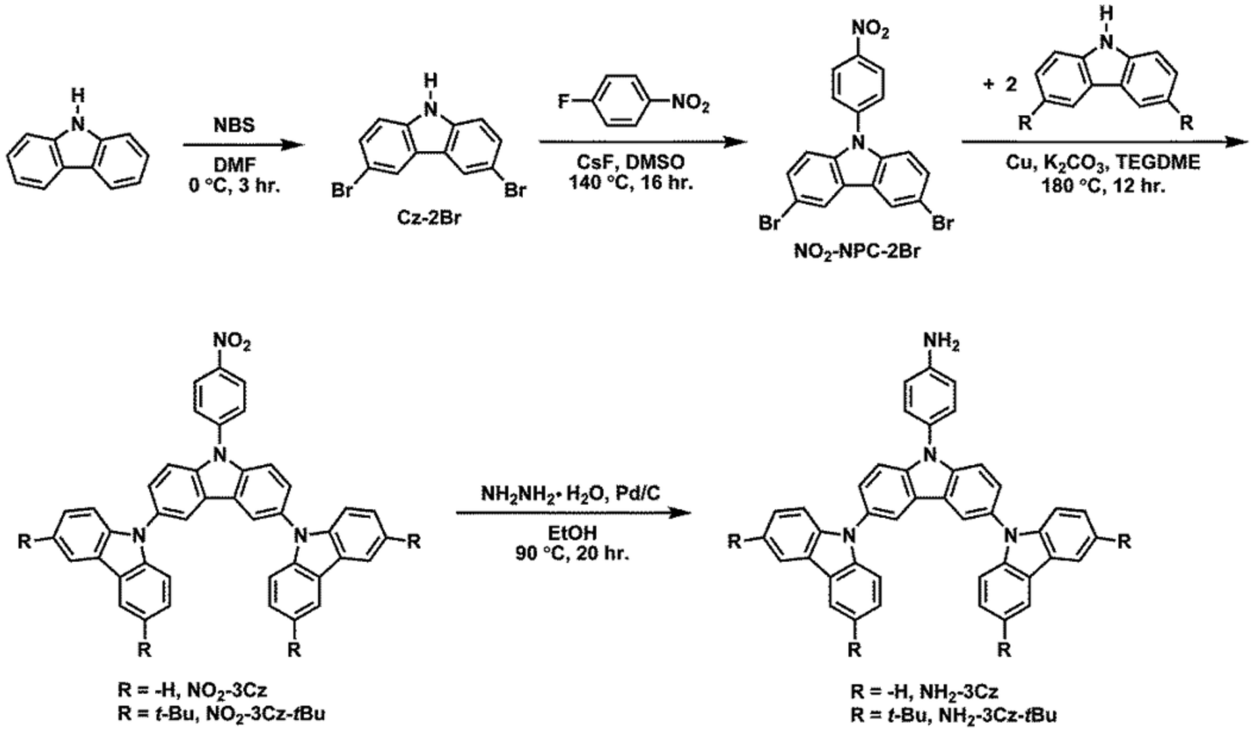
viii. Tg decreases with cross-linking in a particular temperature.

The glass transition temp (T_g) and melting temp (T_m) of a polymer depends on chain geometry , chain flexibility and molecular aggregates.

Examples(i) Polyethylene is made up ethylene repeating unit.

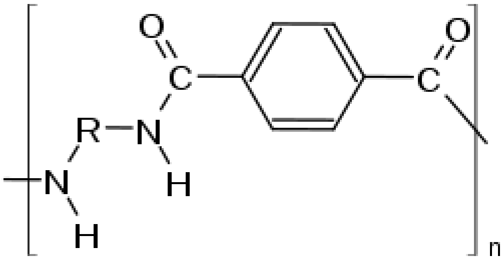
In this case T_g is quite low because strong intermolecular cohesive forces are absent, the substituent groups on the carbon atoms is only hydrogen which is not a bulky group but Nylon-6, a polyamide, has a high T_g (50^0C). It is due to thepresence of a large number of polar groups in the molecules leading to strong intermolecular hydrogen bonding between.>C=o and >N-H groups. The effect of the side group on chain mobility and hence on glass transition temperature can be studied by taking the example of polystyrene and also PMMA.The presence of CH_3--groups in PMMA comes in the way of free rotation around C-C bond of the chain backbone and hence, hinders the chain mobility, resulting in an increase of around 70^oC and 100^oC in their T_g values over poly styrene and PMMA respectively.

Polyvinyl carbazole has a high glass transition temperature (150^oC), because it contains bulky side groups which hinder the freedom of motion.



In the case of polyethylene terephthalates, the presence of the aromatic rings in the chain backbone increate the inflexibility of the chains and the T_g value is high 69^0C

The higher T_g value for the derivatives of cellulose, such as cellulose nitrate is largely due to the rigid ring structure of the chain.



Glass Transition temperature and plasticizers: Plasticizes are low molecular weight non-volatile substances and mostly found in the liquid state, which when added to a polymer improves its flexibility, possibility and hence utility. The plasticizer substantially reduces the brittleness of many amorphous polymers because its addition even in small quantities drastically reduces the T_g of the polymer. This effect is due to the reduction in cohesive forces of attraction between polymer chains. The plasticizer molecules are relatively small in size as compared with polymer molecules, therefore can be penetrated into the polymer matrix and establish polar attractive forces between it and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increased the mobility thereby reducing the T_g value.

Examples of Plasticizers--NS- Naphthyl silicylate, Tri cresyl phosphate

Ms- Methyl salicylate, MA- Methyl acetate.

From the graph although it is seen that t\all plasticizers reduce Tg value considerably but the extent of reduction (Plasticize efficiency) is different and depends on the factors such as solubility parameters, polarity and density.

Many plasticizers such as dibutyl phthalate, dioctyl phthalate and tri-creasyl phosphate are used to decrease the T_g value of PVC.

Glass –Transition Temperature andCopolymers: copolymer is a mixture of two homo polymers. The T_g value of individual homo polymer sand the ratio of the two mono-metric components.

The empirical relation between them is.

$$\frac{I}{T_g(AB)} = \frac{WA}{T_g(A)} + \frac{WB}{T_g(B)} \ldots\ldots\ldots\ldots\ldots\text{(i)}$$

T_g (A), T_g(B)------- Glass transition temperatures of the homo polymers ‘A’ and ‘B’ respectively,

Tg (AB)---- Glass transition temperature of the copolymer.

$W_{A,}$ W_B---- Weight fractions of the respective monomer components of the copolymer.

In this equation it was seen that the glass transition temperature e of a copolymer will be in between these of the respective homo polymers. The glass transition temp. of many homo polymers could thus be lowered by the co-polymerization with small quantities of another suitable monomer.

This process is generally referred to as internal plasticsation.

IMPORTANCE OF T_g:

T_g is an important parameter of any polymeric materials.

(i) It is used as a measure for evaluating the flexibility of a polymer molecule and the type of response the polymeric material would exhibit to mechanical stress. The T_g value of a polymer therefore decides whether a polymer at the “We temp”. Will behave like a rubber or plastic.

(ii) At present it is to know that polymers above their T_g will be soft and flexible and exhibit a delayed elastic response (Viscoelasticity), while those below their T_g will be hard and brittle and will possess dimensional stability.

(iii) The T_g value along with the T_m value gives an indication of the temperature region at which a polymeric material transforms from rigid state to a soft viscous state. This helps in choosing the right processing temperature i.e. the temp. region in which the material can be converted into the finished products through different processing techniques such as moulding calendaring and extrusion.

CRYSTALLINITY OF POLYMERS:

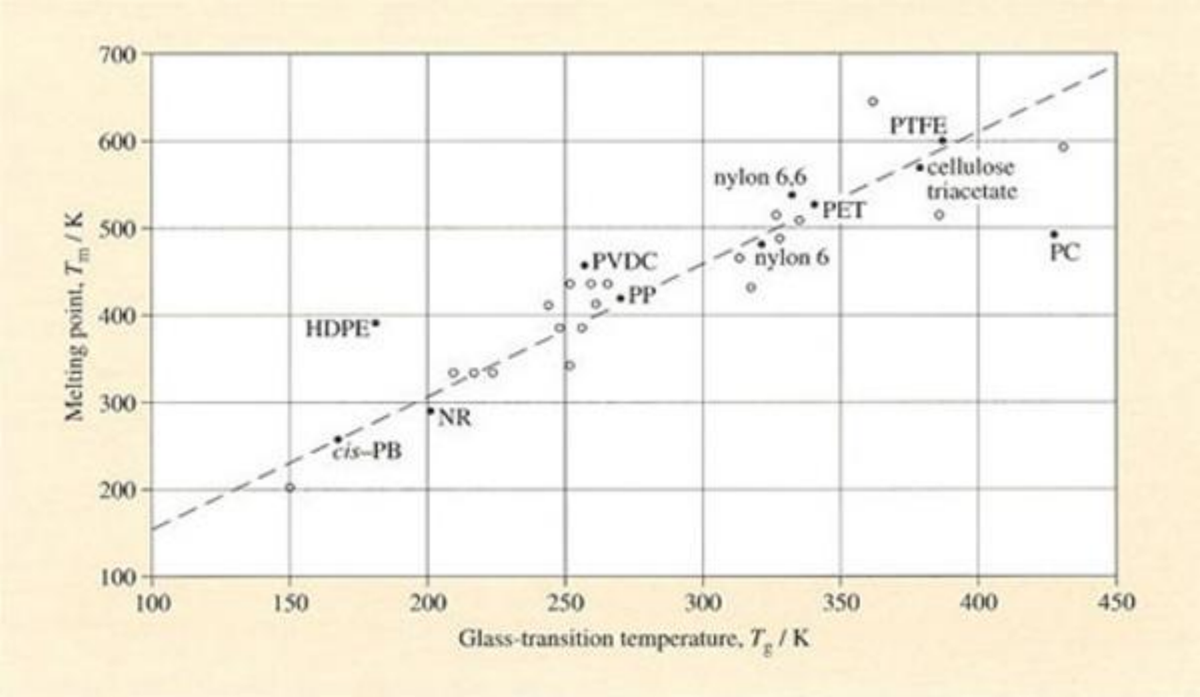
Solid are conventional classified as crystalline or amorphous, depending on whether they possess a “long-range order” or not. The presence or absence of a long-range order makes different solids behave a differently when exposed to X-rays. The crystalline substances give sharp and well-defined X-ray diffraction patterns, when as non-crystalline (amorphous) substances give rather diffuse and broad pattern.

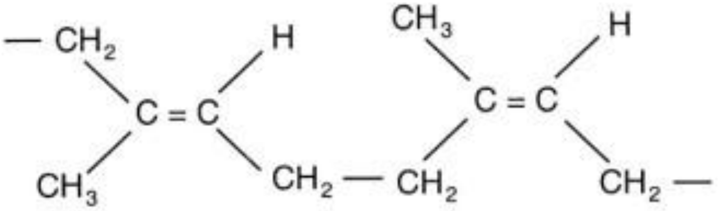
Definition: The degree to which molecules of a polymer are arranged in orderly pattern with respect to each other is a measure of cry-salinity.

(2) There is a close relationship between the regularity of molecular structure and cry-salinity. Typical crystalline polymers are those whose molecules are chemically and geometrically regular in structure. By geometry means the configuration of the chain. Stereo regular polymers polymer i.e. isotopic and syndiotactic are found to be crystallize whereas ataxic ones are unable to do so.

(3) Similar linear polythene has a highly regular configuration, therefore highly crystalline in nature but the crystalline sharply drops when there is branching. Branching imparts irregularity to the molecular structure and reduces the ability of the molecules to get themselves packed closely and hence their ability to crystallize.

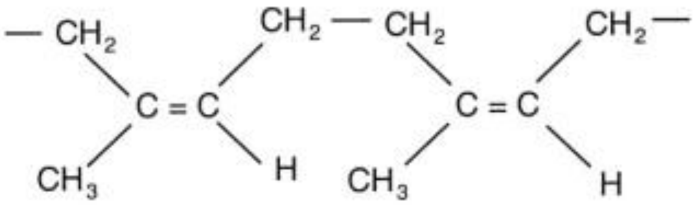
Example: Natural Rubber and gutta- percha both are poly isoprene natural rubber is the cis-icomer, whereas guta- percha is the trans-isomer.





gutta percha (trans-isomer of polyisoprene)

A



natural rubber (cis-isomer of polyisoprene)

B

In natural rubber due to cis- configuration, there is a bending back of the successive isoprene units, giving the molecular a cooled structure. In gutta – percha due to the Trans – configuration there is a straightening out of the successive isoprene units giving a rod like structure to the molecule. A rod like structure enables gutta- percha molecule to orient themselves in an orderly manner and pack up closely as compared to the cooled molecules of the natural rubber. Hence Gutta- percha is more crystalline.

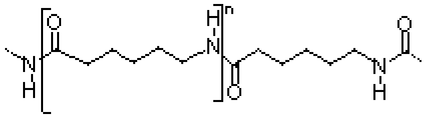
The effect of structural regularity on crystal liability can also be explained by comparing a homo polymer with its copolymer.

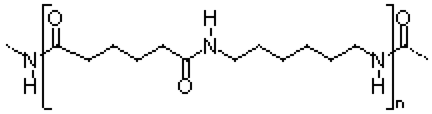
Example: Linearpolyethylene is highly crystalline whereas random copolymer of ethylene and propylene is completely non-crystalline.

The reason is that due to random distribution of the polypropylene repeating units in the copolymer disturbs the structural regularity of the chain molecule and suppress the tendency to cry-stylize. The alternating copolymers where the repeating units are arranged in a regular alternation retain the structural regularity and hence can show a tendency to crystallize.

Factors Affecting Crystallizability: Besides the structural regularity, there are certain other factors which affect the crystallizability of a polymer are as follows: -

Polarity: - Nylon- 6 is highly crystalline in nature. This is due to the presence of polar groups in the molecule leading to hydrogen bonding. In Nylon-6 the carbonyl atoms of one polymer chain forms hydrogen bond with the H-N groups of another polymer chain.This the formation of hydrogen bonding between two adjacent chain increases the inter chain forces of attraction and facilitates tight packing and perfect bonding of the chain with each other.





Effect of bulky groups: Bulky side groups come in the way of a closer molecular packing and hence effect cry stallizability.

Example: Poly vinyl alcohol can be made to crystallize, although it is derived by the hydrolysis of polyvinyl acetate which has never been crystallized.

Example-2: Polyvinyl carbazole which have large bulky groups randomly projecting from the chain backbone is very difficult to crystallize. But in the other hand if the side groups are relatively small i..e in case of poly vinyl alcohol or poly vinyl Fluoride, the polymer can crystallize easily

Smaller groups like CHOH- CH_2, etc. fit into the crystal lattices despite of the stereo chemical irregularity of the polymer on the other hand, the CH_3Cl- group is apparently too large, since chlorinated poly ethylene is non- crystalline. The absence of cry-salinity in polyvinyl and similar polymers is due to the combination of a tactic structure and the relative size of their substituent groups.

Degree ofcrystallinity: -Crystallinity of a polymer sample is expressed in terms of that fraction of the sample which is crystalline in nature. In a polymer sample both crystalline and non-crystalline components coexist. For this reason, the X-ray diffraction patterns of most of the polymer show both sharp as well as broad and diffused bands. The sharp bands are dueto the crystalline regions where as the diffused and broad bonds are due to non-crystalline (amorphous) regions.

Further, amorphous components in a polymer are in the liquid phase whereas the crystalline components are in the crystalline phase. The density of the crystalline component is higher than amorphous component. Hence for a given polymer 100% crystalline polymer will have highest density and 100% amorphous polymers will have lowest density. Since all polymers are partially crystalline therefore density is in between amorphous and crystalline components.

Hence the degree of cry-salinity of the sample can be calculated by the equation.

$$XV = \frac{d-da}{dc-da} \text{ ……………………… (i)}$$

XV- degree ofcrystallinity by volume.

d,da,dc- densities of the sample, fully amorphous and fully crystalline polymers respectively.

The degree of crystallinity of a polymer sample can also be measured in terms of specific volume.

$$Xm = \frac{Va-V}{Va-Vc} \text{ ……………………… (2)}$$

Xm- degree of cry salinity by mass.

V, Va, Vc- specific volume of the sample, fully amorphous and fully crystalline polymers respectively.

Crystalline Melting Point: - The crystallinemelting point in the thermodynamic terms, melting takes place when the free energy of the process is Zero.

$\Delta G = \Delta H_m - T_m \Delta S_m = 0$

Where ΔG- Gibbs free- energy change

ΔS_m= change in entropy of fusion.

ΔH_m= the heat of fusion per mole of repeating units.

$Tm = \frac{\Delta H_m}{\Delta S_m}$ ……………………… (3)

The % of cry salinity can be measured as

% cry salinity = $\frac{dc\ (ds-da)}{ds\ (dc-da)} X\ 100 \ldots\ldots\ldots\ldots\ldots\ldots.(4)$

Note: The degree of cry salinity of a partially cry salinity sample can be experimentally determined by measuring the density or specific volume, the same can also be calculated by using enthalpy (H).

$Xcal = \frac{Ha-H}{Ha-Hc}$ ……………………… (5)

Where Ha, Hc and H are enthalpy of fully amorphous fully crystalline and sample polymers.

CRYSTALLISABILITY: crystallisability is themaximum crystalline that a polymer can achieve at particular temperature, regardless of the other conditions of crystallization. Crystallisability at a particular temperature depends on the chemical nature of the macromolecular chain its geometrical structure, molecular weight and molecular weight distribution.

On the other hand, the actual degree of "order" or the extent of cry-salinity attained at a particular temp. depends very much on such conditions as the rate of cooling, residence time, temperature of the molten polymer and heat dissipation, under which crystallization takes place.

MODULE-II

Polymerization Process: Depending upon the mechanism of polymerization, all the polymerization process mainly divided in to three categories.

(i) Addition polymerization / chain-growth polymerization.

(ii) Poly condensation / step-growth polymerization / step polymerization

(iii) Ring-opening polymerization.

Distinction between Addition and condensation polymerization.

(a) Addition polymerization (chain-growth polymerization.)

- (i) Monomers are unsaturated.
- (ii) Nothing is eliminated as result of this type of polymerization.
- (iii) High molecular weight polymer is attained at once.
- (iv) Only monomers and polymers are present during the course of the polymerization.
- (v) Only monomers add to the growing chain.
- (vi) Chain grows at active centers.
- (vii) Molecular wt. of polymer = DPX Mol. wt. of monomer.
- (viii) Involves opening of double bond by active species like free radical on in.

- (ix) Example: Polyolefins , polygons, vinyl polymers and a cyclic polymers.
- (x) Initiator orcatalyst generate active species that attacks the monomer (free radical, anions, cantons). The process of polymerization is endothermic.
- (xi) Can be done by bulk, solution, suspension and emulsion polymerization technique.
- (xii) Can quickly lead to a polymer with very high molecular weight, cross-linking can be achieved by using monomers with two double bonds i.e. divinely benzene.

Condensationpolymerization (Step-growth polymerization.)

- (i) Monomers contain two or more functions groups.
- (ii) Usually the molecules like H_2O, Alcohols, HX, and NH_3 etc. are eliminated during the process of polymerization.
- (iii) High molecular weight polymer is attained only at very high conversions.
- (iv) All possible molecular weight species i.e.dimmers, trimmers, tetramers and mutineers etc. are present.
- (v) All species are reactive.
- (vi) Stepwise intermolecular conversation.
- (vii) Not so, because some small molecules often get eliminated during the course of polymerization.
- (viii) Involves the reaction between the functional groups.
- (ix) Example: Polyesters, polyamides, and polycarbonates.
- (x) Most of the reaction has higher value of activation energy and hence usually heating is required. Unanalyzed and catalyzed process are possible.
- (xi) Poly condensation can be achieved in melt, solution as well as at the interfacial boundary between two liquids in which the respective monomers are dissolved.
- (xii) Slow stepwise addition process, molecular weight is <1,00,000 highly dependent on monomer stoichiometry, little amount of the on multi-functional monomers develop extensive cross-linking.

STEP POLYMERISATION ORSTEP GROWTH POLYMERISATION OR POLYCONDENSATION.

In step polymerization, the polymer build-up proceeds through a reaction between functional groups of the monomers. The reaction takes place in a step-wise manner and the polymer built-up as generally a slow process. Although many known reactions with organic functional groups can be made use of in step polymerization, condensation, addition, ring-opening, amidation and esterification reactions are the most commonly used ones. Step polymerization reactions are always accompanied by elimination of small groups.

The poly condensation is brought about by monomers containing two or more reactive functional groups such as hydroxyl, carboxyl and amino groups condensing with each other.

In the case of step-growth polymers, the mechanism is simply an extension of the normal organic condensation reactions in which a small molecule i.e. H_2O or HCl are eliminated.

Example: $R\text{-}COOH+H\text{-}OR$ -------- $R\text{-}C\text{-}O\text{-}R\text{-}H_2O$

In step growth polymerization, the poly condensation reaction takes place. The poly condensation reaction is brought about by monomers containing two or more functional groups.When monomers have only are functional group, the following reaction will be possible.

$R\text{-}OH+HOOC\text{-}R$-------------$R\text{-}OOC\text{-}R+H_2O$

Since there is no more reactive functional group left with the product and hence it cannot react further with any other reactant molecules. Let us take two monomers in which are is mono functional and other one is bi -functional Still it contains two reactive groups which can react further. The resultant molecule still contains two active ends and it can also react with both of the monomers if it is available. Hence it is capable of reacting further to form a bigger molecule.

Hence a general reaction may be written as from this illustration the following conclusion can be drawn regarding step polymerization or poly condensation.

(i) The monomers should have two reactive functional groups for polymerization to proceed.

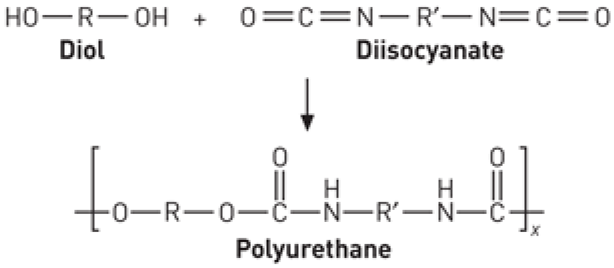
(ii) Polymerization proceeds by step-wise condensation reaction between reactive functional groups.

(iii) Only one type of reaction (i.e. condensation reaction) is evolved between two functional groups in the polymerization.

(iv) The polymer formed still contains both the reactive functional group at its chain ends (as end groups) and hence is “active” and not “dead” as in chain polymerization such type of polymers is known as “active polymers”.

Features orcharacteristics of step-growth polymerization.

1. The group of polymer molecules proceeds by a stepwise intermolecular reaction only and only one reaction type in involved in the polymerization.
2. Monomer units can react with each other or polymers of any size.
3. The functional group at the end of a monomer is usually assumed to have the same reactivity as that on a polymer of any size.
4. A high conversion of functional groups is required in order to produce high-molecular-mass product.
5. Many step-growth polymerization reactions are reversible.
6. Condensation polymerization is usually produced by step-growth polymerization but not all step-growth polymerization are condensation reactions. This there is not elimination product in polyurethane synthesis from a diol and di-isocyanate.



$$\text{HO—R—OH} + \text{O=C=N—R'—N=C=O} \longrightarrow \left[\text{O—R—O—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\text{H}}{\text{N}}\text{—R'—}\overset{\text{H}}{\text{N}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\right]_x$$

Requirements for step growth polymerization:

The step growth Polymerization/polymer can be prepared from bi functional monomers. This reaction may proceed A-A-B-B type poly condensation is di-carboxylic acid and diol.When a single bi-functional molecule undergoes self-condensation the reaction can be depicted as. In both the cases intermolecular condensation occurs in preference to intermolecular condensation. A step-growth polymerization is a stepwise reaction between bi-functional or multifunctional monomers in which a high-molecular-weight polymer is formed after a large number of steps. Many naturally and synthetic polymers are produced by step-growth polymerization including polyesters, polyethers, urethanes, epoxies, and polyamides (see table below). Two well-known examples are the reaction of dicarboxylic acids with diamines to form polyamides (Nylon) and the reaction of organic diacids with alcohols to form polyesters, like polyethylene terephthalate (PET). Due to the nature of the polymerization mechanism, the reaction has to proceed for a long time to achieve high molecular weight polymers. The easiest way to visualize the step-growth mechanism is a crowd of people reaching out to hold their hands to form human chains — each person has two hands (= two reactive sites).

The two most important step-growth polymerizations are condensation and addition polymerization. In the case of a condensation reaction, two monomers combine with the loss of a small molecule, usually an alcohol, a water molecule or an acid, whereas an addition reaction involves only the rearrangement of the electrons of a double bond to form a single bond with another molecule

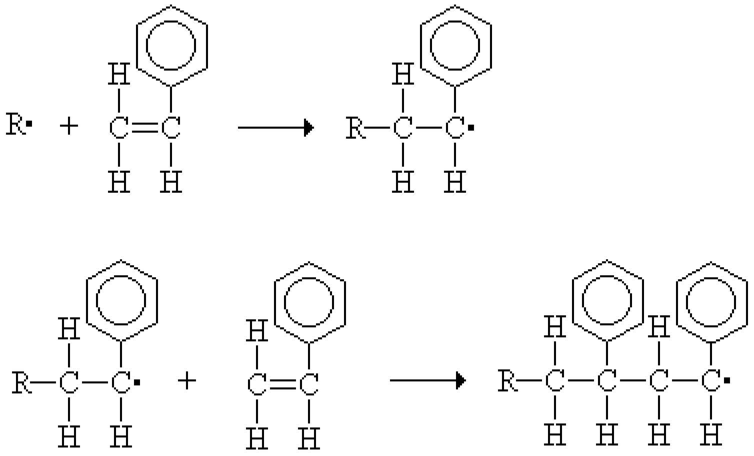
EXAMPLES OF STEP-GROWTH POLYMERIZATIONS

Functional Groups	Linkage	Polymer Type
-OH + -COOH	-C(=O)-O-	Polyester
-OH + -NCO	-O-C(=O)-NH-	Polyurethane
$-NH_2$ + -NCO	-NH-C(=O)-NH-	Polyurea
$-NH_2$ + -COOH	-NH-C(=O)-	Polyamide
-OH + -OH	-O-	Polyether

.

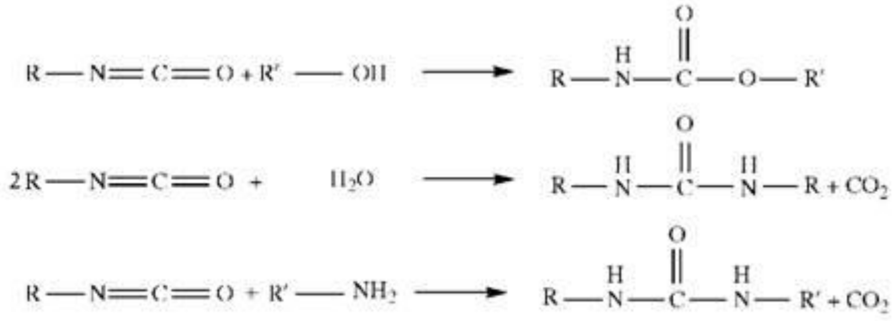
Polyaddition polymerization: - The poly addition polymerization reaction is brought about by the migration of atoms from one monomer molecule to another monomer molecule on to the intermediate product. Vinyl monomers as well as monomer pairs with reactive functional groups can undergo poly addition polymerization.

Example: Styrene can be polymerized in the presence of the perchloric acid by this method and the mechanism involves are as follows:



It is an interesting manner in which the polymer is formed by a simple addition at the double bond, without the formation of any free radical, harmonium in or car anion in. However, like in chain polymerization monomer units are simply added one after another to form a polymer without eliminating any small molecules. Since the polymer is formed by the migration of hydrogen atom from the monomer and its addition at the double bond-a process involving a higher activation energy as compared to the free radical or ionic process- the polymer growth is rather gradual and is brought about step by step as against the rapid chain growth in chain polymerization.

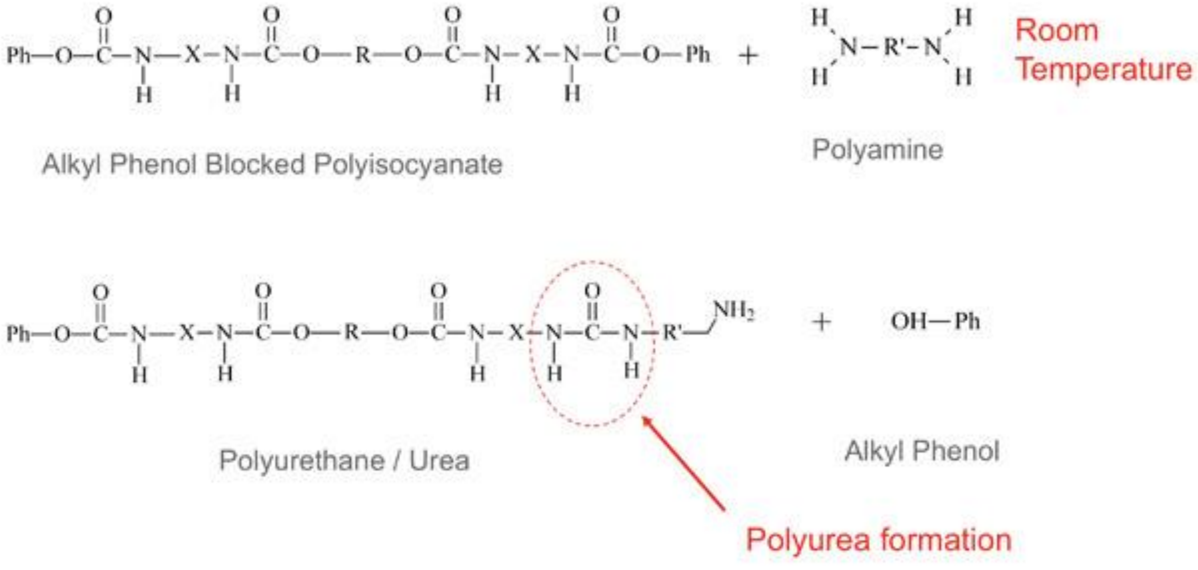
Oligomers (i.e. liquid polymers of M.W of the order of 2,00, or so) of vinyl monomers are, raven theless made by this technique. On the other hand, in a hydroxyl on in an among group is highly mobile and hence monomers such as polyhydric alcohols and polyamines can easily undergoes poly addition with poly Isocyanides, yielding poly urethanes



$$R-N=C=O + R'-OH \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-R'$$

$$2R-N=C=O + H_2O \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R + CO_2$$

$$R-N=C=O + R'-NH_2 \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R' + CO_2$$



R = Polyether X = Moiety from Poly isocyanate

Kinetics of stepwise polymerization: With the concept of functional group reactivity independent of molecular weight, the kinetic of step wise polymerization becomes quite simple. The formation of polyester from glycerol and a dibasic acid may be taken as an example. This reaction is catalyzed by acid and in the absence of the added strong acid, the second molecule of the acid being esterifies and act as catalyst. The reaction of i.e. and may be represented by a general chemical equation as follows.

-A+B+calyst ---------------------   -AB- + catalyst.

Rate=[A] [B] [catalyst] ……………..(3)

In etherification reaction acid (H+) is the catalyst and if the stoichiometry of the functional group ‘A’ and ‘B’ is assumed.

[A] =[B]

Eq ----(3) canbe written as rate= $\frac{-d(A)}{dt} = k[A]^2[H+]$……..(4)

In self-catalysis polymerization poly etherification reaction.

$[H^+] = [A] = [B]$

eq (4) can be written as

$\frac{-d[A]}{dt} = k\ [A]^3$……………………… (5)

On integration of equation------ (5)

$\int \frac{-dc}{C^3} = \int kdt.$

2kt=$\frac{1}{C^2} - \frac{-1}{C^2}$………………………… (6)

It is convenient to introduce the extent of reaction (P), which is defined as the fraction of the functional groups that has reacted at time ‘t’

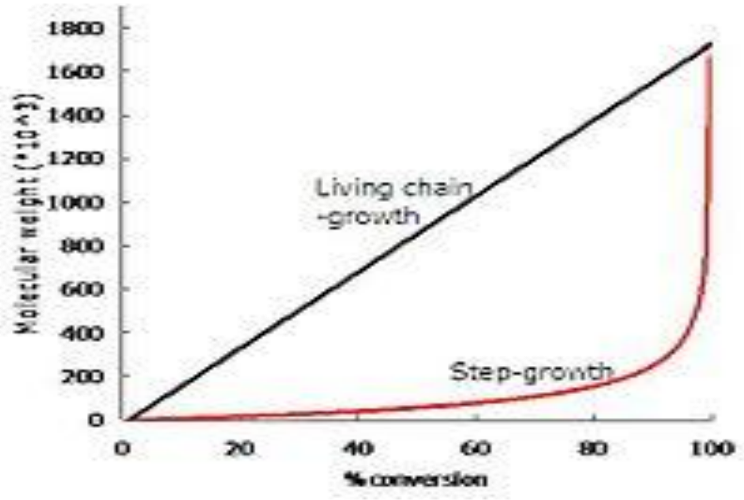
$C=C_o$ (1-P) ………………….. (7)

Putting the value of equation (7) in eq (6)

2kt = $\frac{1}{[C_o(1-p)]}$ - $\frac{1}{C_o^2}$

2kt C_o^2 = $\frac{1}{(1-p)^2} - 1 \ldots\ldots\ldots\ldots\ldots.(8)$

Eq (8) implies that a graphical plot of $\frac{1}{(1-p)^2} \sim time$ must be linear. Experomally it is found to be true.



$$C_oK_t = \frac{1}{(1-P)} - 1$$

$$\frac{1}{(1-P)} = CoK^{'}t + 1.$$

$$(Xn)2 = CoK^{'}t + 1.$$

$$\frac{\overline{Mn}}{Mo})2 = CoK^{'}t + 1 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(3)$$

The above equation can be verified experimentally by plotting 1/1-p) versus t' for the reaction of decamethylene glycol with acidic acid using Para-toluene sulphonic acidas catalyst.

KINETICS OFPOLYMERIZATION WITHOUT STRONG CATALYST

A classic example of a step-growth polymerization is the esterification reaction between an alcohol and a carboxylic acid. The progress of the polyester-forming reaction can be easily followed by titration of the unreacted acids in the samples removed from the batch at different times. Simple esterification reactions are known to be catalyzed by acids. In the absence of a strong acid, a second acid molecule functions as catalyst. The rate of the polymerization reaction can therefore be written

$$-d[COOH] / dt = k \cdot [COOH]^2 \cdot [OH]$$

where k is the rate constant of the step-growth reaction and [X] are the mole concentrations of the monomers.

The concentrations are usually defined as mole equivalents of functional groups per unit volume. By this convention, we avoid having to write separate equations for each condensation product (dimer, trimmers etc.). However, this simplification is only valid if we assume that all reaction species have the same rate constants k regardless of size (molecular weight). If we choose equal concentrations of hydroxyl and carboxyl groups, the equation above can be rewritten as

$$-dc / dt = k \cdot c^3$$

On integration, we get an expression for a third-order reaction:

$$2kt = 1 / c^2 - 1 / c_0^2$$

where c_0 is the initial concentration of the functional groups. The extend of the reaction is often written as the fraction of functional groups that has reacted at time t,

$$p = (c_0 - c) / c_0$$

Then $C = C_0 \cdot (1 - p)$ and after substitution of c with this expression the rate of the polymerization equation reads

$$2C_0^2 \cdot kt = 1 / (1 - p)^2 - 1$$

In the esterification reaction, p can be directly calculated from the carboxyl group titer. If we plot $1/(1-p)^2$ against time, t, we find a linear relationship, which is the case for many esterification reactions of glycols and organic acids. This is usually considered proof that all monomer units have similar rate constants k.

CASE 2: POLYMERIZATION WITH STRONG CATALYST

If the polymerization is carried out in the presence of a strong acid (sulfonic acids) and if the catalyst concentration is kept constant throughout the process, the polymerization follows the kinetics of a second-order reaction:

$$-dc / dt = k' c^2$$

where k’ = k [catalyst]. Integration of this expression yields

$$k' t = 1 / c - 1 / c_0$$

And after replacing the concentration with the extend of the reaction, p, this expression reads

$$c_0 k' t = 1 / (1 - p) - 1$$

In this case, the average degree of polymerization, defined as

X_n = No. of monomers / No. of monomer units = $1 / (1 - p) = c_0 / c$,

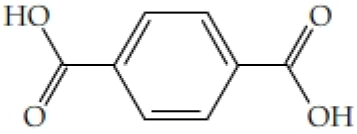
increases linearly with the reaction time, which is a much more favorable situation for obtaining high average molecular weight polymers than the weak-acid catalyzed third-order reaction.

MOLECULAR WEIGHT CONTROL OF LINEAR POLYMERISATION: -

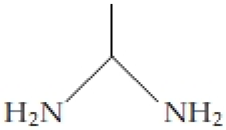
In the synthesis of polymer one is usually interested in obtaining a product of very specific molecular weight. Since the properties of the polymer will be highly dependent on molecular weight. The molecular weight higher on lower than the desired weight are equally desirable. Since the DP is a function of the reaction time, the desired molecular weight can be obtained by quenching the reaction (i.e cooling) at appropriate time.However, the polymer obtained in this manner is unstable but again on subsequent heating it may leads to change in molecular weight because the ends of the polymer molecules portion functional groups that can react further with each other.

This situation can be avoided by adjusting the conc. Of two monomers (diol and dibasic acid) so that they are slightly non-stoichiometric. One of the monomer present in slight excess. The polymerization then proceeds to a point at which are reactant is completely used up and all the chain ends possess same functional group i.e the group which is in excess. Further polymerization is not possible and the polymer is stable to subsequent molecular-weight changes.

Example: The use of excess in the polymerization of a di-amine in the polymerization reaction yields a polyamide with amine end groups.

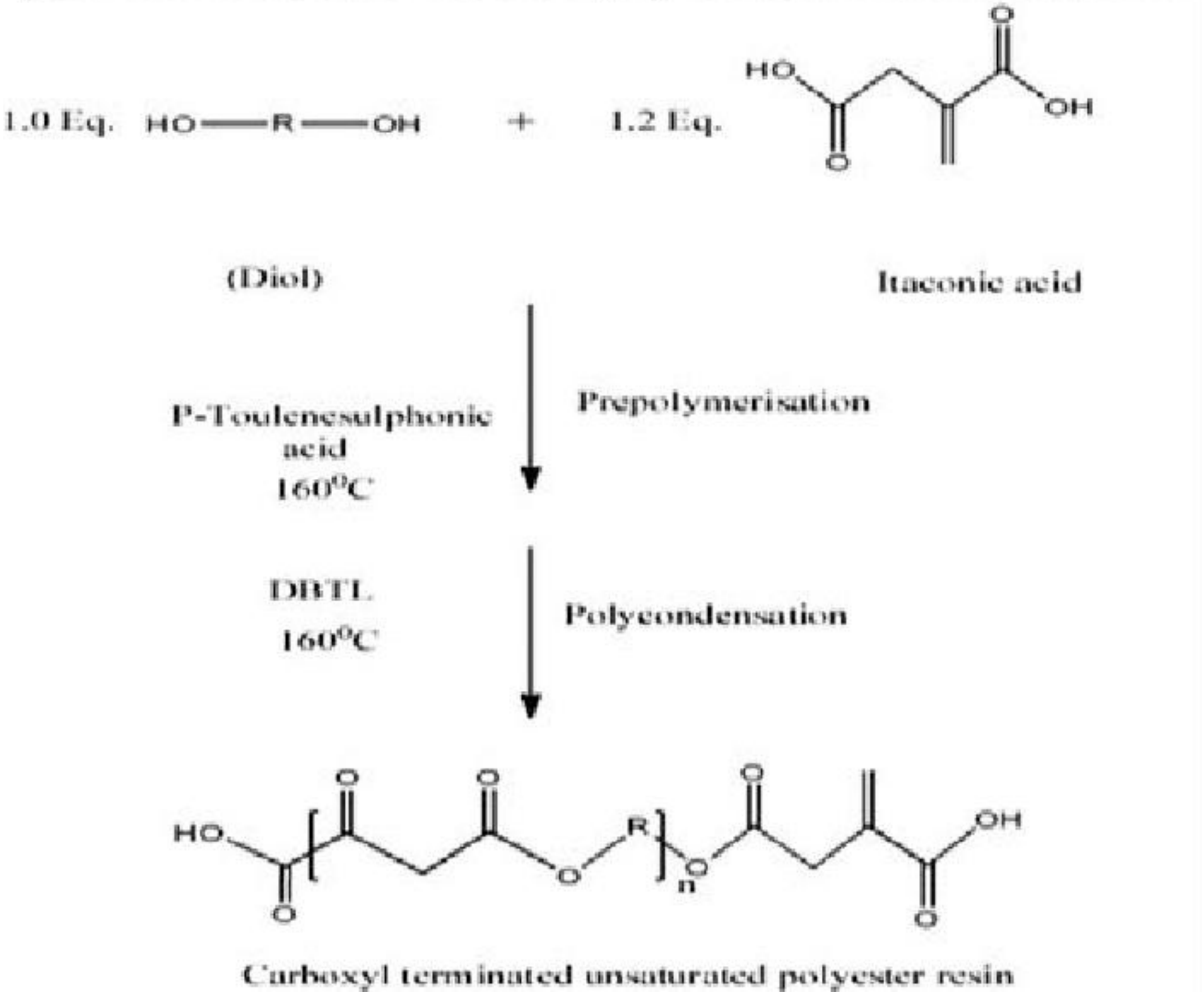


Terephthalic Acid



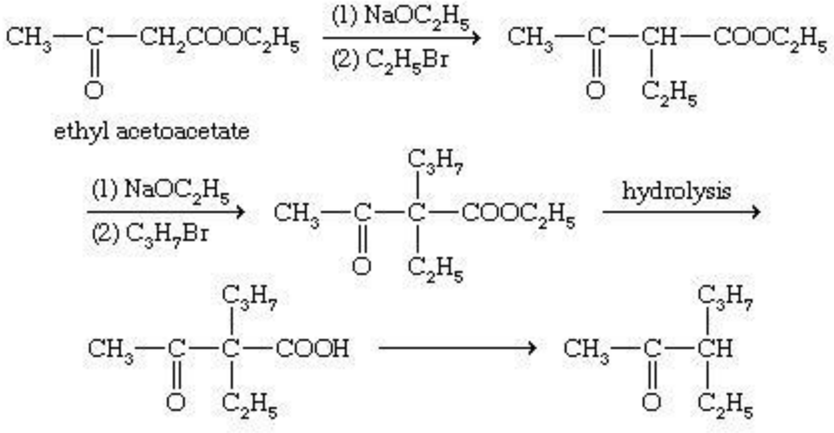
1,1-Diaminoethane

Synthesis of biobased unsaturated polyester resin from Itaconic acid -



Which are incapable of further reaction, since diamine has completely reacted.

Another method of achieving the desired molecular weight is the addition of small amount of nonfunctional monomers Example- Acetic acid or lauric acid are often used to achieve molecular weight stabilization of polyamide.



The nonfunctional monomer controls and limits the bi-functional monomer in the polymerization process because its reaction with the growing polymer yields chain ends devoid of a functional group and therefore incapable of further reaction.

Thus the use of benzoic acid yields a polyamide with phenyl end groups.

H_2N – R- NH_2+ HO_2C-R'- CO_2H + ΦCO_2H-----------

Φ-CO(- NH-R-NHCO-R'-CO)$_n$- NHRNGΦCOΦ

Which is unreactive towards polymerization reaction.

MOLECULAR-WEIGHT DISTRIBUTION IN LINEAR POLYMERISATION.

A typical synthetic polymer sample contains chains with a wide distribution of chain lengths. This distribution is seldom symmetric and contains some molecules of very high molecular weight. The exact breadth of the molecular-weight distribution depends upon the specific conditions of polymerization,for example, the polymerization of some olefins can result in molecular-weight distributions that are extremely broad. In other polymerizations, polymers with very narrow molecular-weight distributions can be obtained. As will be shown in subsequent chapters, many polymer properties, such as melt viscosity, are dependent on molecular weight and molecular-weight distribution. Therefore, it is useful to define molecular-weight averages associated with a given molecular-weight distribution as detailed in this section.

The molecular-weight distribution (MWD) has been derived by Flory by a statistical approach based on the concept of equal reactivity of functional groups. At every stage of polymerization all the un reacted functional groups possess equal opportunity to take part in the reaction irrespective of the size of the molecule to which it is attached. At the end of the reaction, the probability that a given functional group has reacted is equal to the function of all the functional groups which have reacted.

The derivation which follows is essentially that applied equally to A-B and stanchion metric A-A Plus B-B types of step polymerization.

Let as consider the poly condensation of us hydroxyl acid

In a polymer containing ‘n’ repeat units, there would be (x-1) ester linkages.

The extent of reaction which also gives the probability of reaction occurring between two functional groups.

- The probability that the carboxyl group of the first unit as esterifies =p^2.
- The probability of the formation of second ester linkage rent to the first=P^2.
- The probability of the formation of (x-1) ester linkages rent to (x-2) = P^{x-1}.

Hence the probability that all the ester linkages have been formed = P^{x-1}. The polyester should also possess unreached ester linkages at the end.

The probability that a group has not reacted = (1-P)

The probability that the molecule is composed of ‘x’ units is represented by $P_x = P^{(x-1)}(1 - p) \dots \dots \dots \dots \dots \dots (1)$

If the total number of molecule present at time ‘t’ is ‘N’ then that total number of x-mers (i.e. that contain x structural unit) is given by.

$N_x = N P^{(x-1)} (1-P)$………………….. (2)

If No – Total no. of molecules / structural units present initially

N=No (1-P)…………………….. (3)

Hence N_x-No $(1-P)^2$ $P^{(x-1)}$………….. (4)

N_x is synonymous with the mole on number fraction of the molecules in the polymer mixture that are x-mars.

NOTE: N_x is the number fraction of n-mars in the total no of polymer molecules 'N' present.

Eq (4) represents the expression for the number of molecules of length 'x' in terms of the mitral number of molecules No and the extent of reaction 'P'.

The weight fraction Wx for a particular length of the polymer can be written as.

$$Wx = \frac{Mass\ of\ molecule\ \ of\ lengt\,h\ 'x'}{Total\ \ mass\ \ of\ \ all\ \ the\ molecules\ \ .}.$$

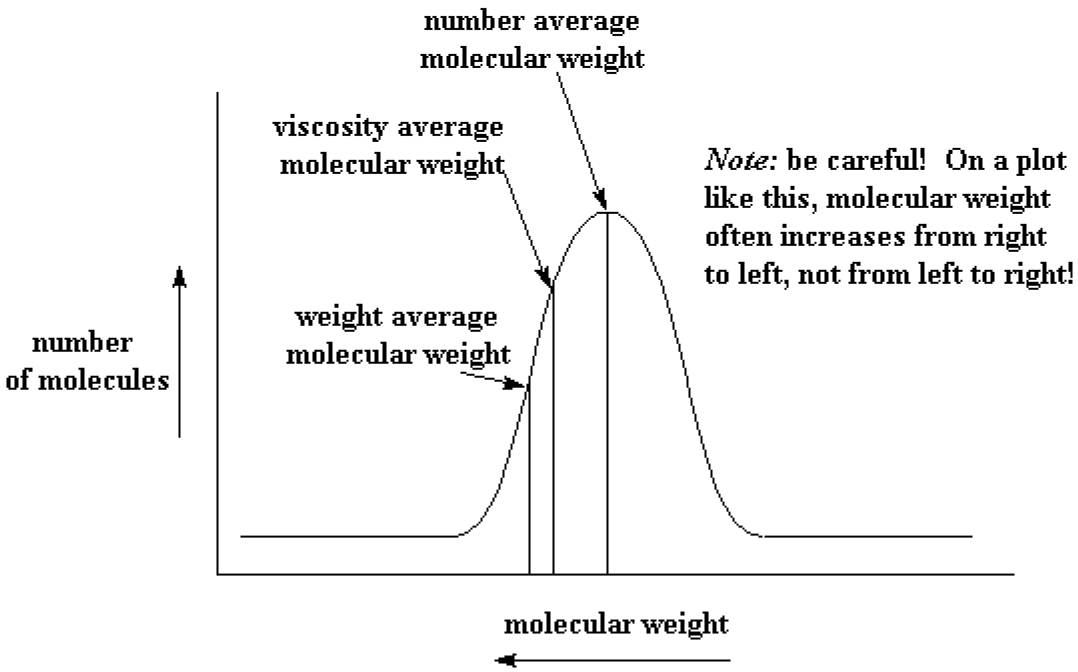
$$= \frac{N_x\ X\ (xXMo\ )}{No\ X\ Mo} = \frac{X\ Nx}{No} \ldots \ldots \ldots \ldots (5)$$

Where Mo= Molar molar mass of the repeat unit or monomer molecule.

Now ignoring the end-groups and the difference in mass between repeat units and monomer molecules, and combining eq --(4) and (5) we get.

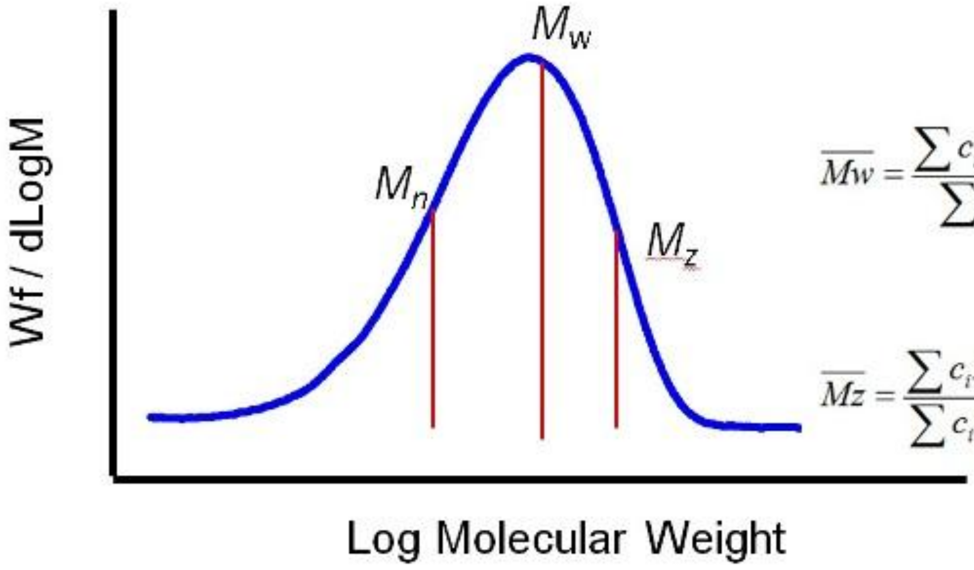
$Wx=xp^{(x-1)}(1-p)^2$

$$Wx = \frac{xN}{No} = xp^{(x-1)}(1-p)^2 \ldots\ldots\ldots\ldots\ldots (6)$$



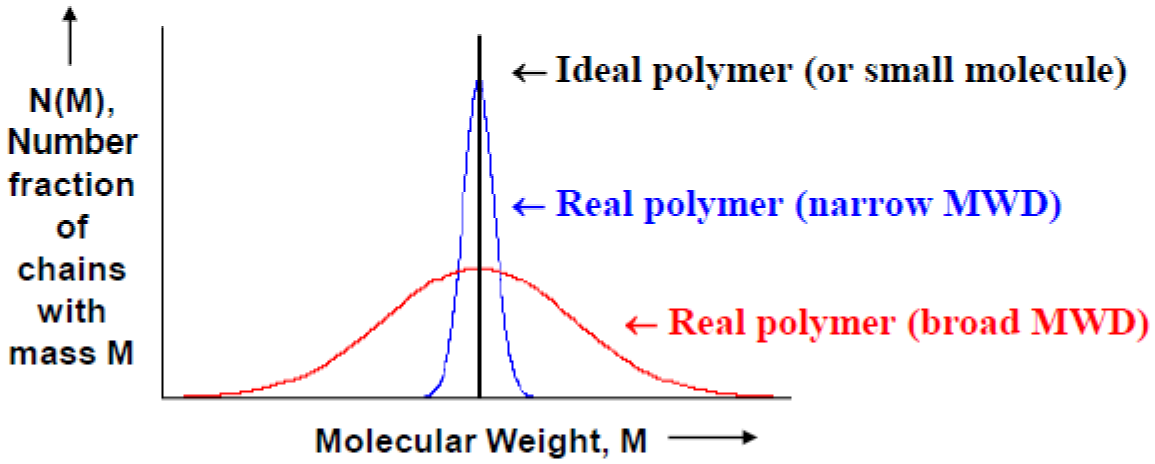
Note: be careful! On a plot like this, molecular weight often increases from right to left, not from left to right!

$$\overline{Mn} = \frac{\sum c_i}{\sum c_i / M_i} = \frac{\sum N_i M_i}{\sum N_i}$$



$$\overline{Mw} = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\overline{Mz} = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$



Carothers Equation: Carothers for the first time proposed the relationship between the number average degree of polymerization Xn and the extent of reaction 'P'.

Let No = Number of molecules initially present.

N= Number of molecules remaining at time 't'.

$$P = \frac{Number\ \ of\ groups\ \ that\ have\ reacted}{Number\ \ of\ groups\ \ initially\ \ present}$$

$$P = \frac{No - N}{NO}$$

$$\frac{No}{N} = \frac{1}{1-p} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

$$\text{Now } xn = \frac{Number\ \ of\ molecules\ \ preent\ \ initially}{Number\ \ of\ molecules\ \ reactin\ g\ after\ \ time\ 't'}$$

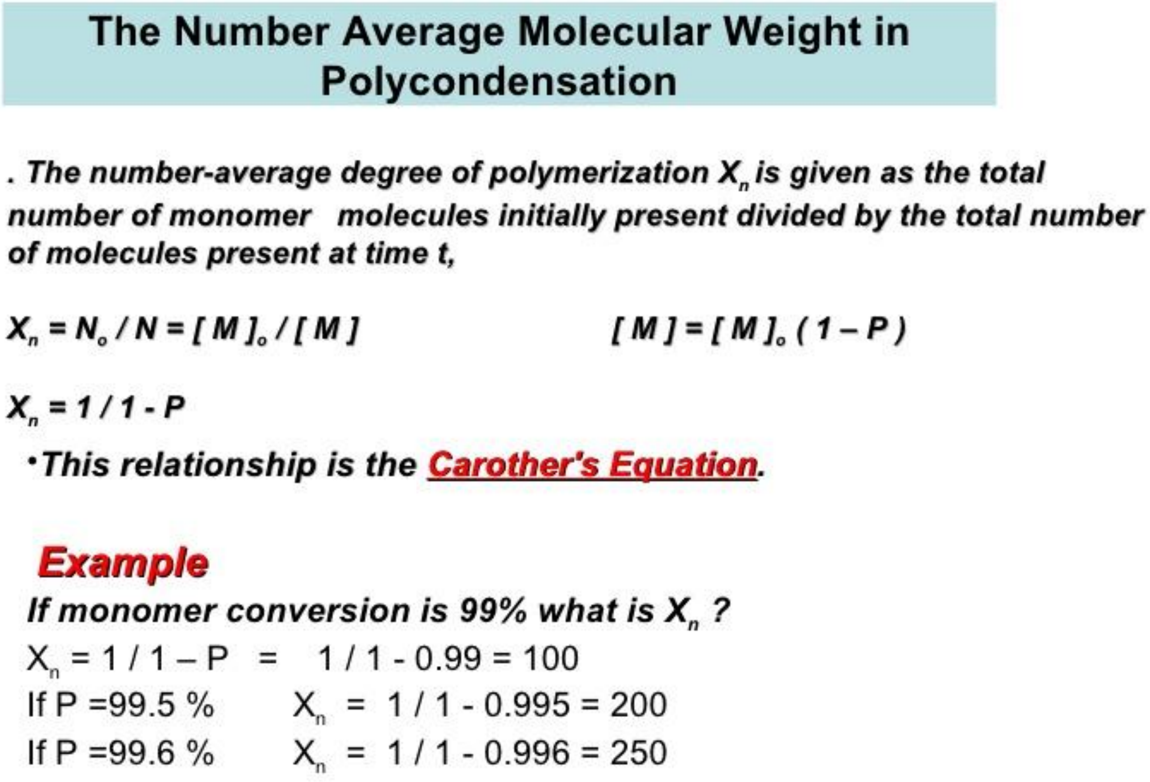
$$Xn = \frac{No}{N} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (2)$$

Combining eq (1) and (2)

$$Xn = \frac{1}{1-p} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

This equation is known as Carothers equation.

In step-growth polymerization, the Carothers equation (or Carothers' equation) gives the degree of polymerization, Xn, for a given fractional monomer conversion, p.



The Number Average Molecular Weight in Polycondensation

. The number-average degree of polymerization X_n is given as the total number of monomer molecules initially present divided by the total number of molecules present at time t,

$X_n = N_o / N = [M]_o / [M]$ $[M] = [M]_o (1 - P)$

$X_n = 1 / 1 - P$

- ***This relationship is the Carother's Equation.***

Example

If monomer conversion is 99% what is X_n ?

$X_n = 1 / 1 - P = 1 / 1 - 0.99 = 100$

If P =99.5 % $X_n = 1 / 1 - 0.995 = 200$

If P =99.6 % $X_n = 1 / 1 - 0.996 = 250$

Poly functional Step-Reaction Polymerization: -

- Three dimensional step-reaction polymers are produced from the polymerization of the reactants with more than two functional groups per molecule. The structures of these polymers are more complex than those of linear Step-reaction polymers.
- Three dimensional polymerization is complicated experimentally by the occurrence of gelatin on the formation of infinitely large polymer networks in the reaction mixture. The sudden onset of gelatin marks the division of the mixture in two parts.
- The ‘gel’ which is insoluble in all non-degrading solvents.
- The ‘Sol’ which remains soluble and can be extracted from ‘gel’.

- Since the polymerization proceeds beyond the gel point the amount of gel increases at the expense of sol and the mixture rapidly transforms from a viscous liquid to on elastic material of infinite viscosity.
- In the statistical consideration of three- dimensional step polymerization, it is assumed that all functional groups are equally reactive and independent of molecular weight on viscosity. This assumption is however is not correct i.e. for glycerol where the secondary hydroxyl group is known to be less reactive than two primary hydroxyl group but this complication does not affect the general conclusions of the theory.
- It is also assumed that all the reactions occur between functional groups on different molecules. This is known to be somewhat in error, for it can be shown that the number of interknit ticks formed is always greater that the corresponding decrease in the number of molecules present.
- Prediction of the gel point:- In order to calculate the point in the reaction at which relation takes place, a branching coefficient ‘α’ is defined as the probability that a given functional group on a branch unit is connected to another branch unit.

The value of ‘α’ at which relation becomes possible can be deduced as follows.

Consider the case where bi functional A-A, B-B units along with poly functional Af with functionality ‘f’ are present. The structures resulting in this system consist of chain segments of the type.

$A_{(f-1)}$ – A [B-BA-A] B-BA-A $_{f-1}$

Where € may have any value.

The criteria for gel formation is that at least one of the (f-1) segments radiating from the end of a segment of the type shown is in turn connected to another branch unit.

The probability of this occurring = $\frac{1}{(f-1)}$

Hence the critical value of 'α' for relation is

$\propto c = \frac{1}{f-1}$..............(1)

Here 'f' is the functionality of the branch units. If more than one type of branch unit is present an average 'f' over all types of branch unit is present an average over all types of branch units may be used.

If the extents of reaction for A and B group are Pa and Pb and the ratio of A groups on branch units to all 'A' groups in the mixture is P. The probability

That a 'B' group has reacted with a branch unit is P_BP, with a bi-functional A.P_B (1-P) . The probability that a segment of the type shown is obtained is given by.

$P_A\ [P_B\ (1-P)\ P_A]\ {}^{2}P_BP$

Sunning over all values of I gives.

$\propto \frac{P_A P_B p}{1-P_A P_B\ (1-p)}$ ... ... (2).

Either P_A on P_B can be eliminated from this equation by defining $r={}^{NA}/_{NB}$ where $P_B=rP_A$

$\propto = \frac{rP_A^2 P}{1-rP_A^2(1-P)} = \frac{P_B^2 p}{r-p_B^2(1-p)}$............. (3)

Simple relations can be derived for several cases, when equal number of A and B groups are present, r=1 and $P_A=P_B=P$

(r-1$\propto = \frac{P^2+}{1-P^2\ (1-p)}$........................... (4)

When there are no A-A Units X=1 and

(x=1) $\propto = rP_A{}^2 = \frac{P_B^2}{r}$ .... (5)

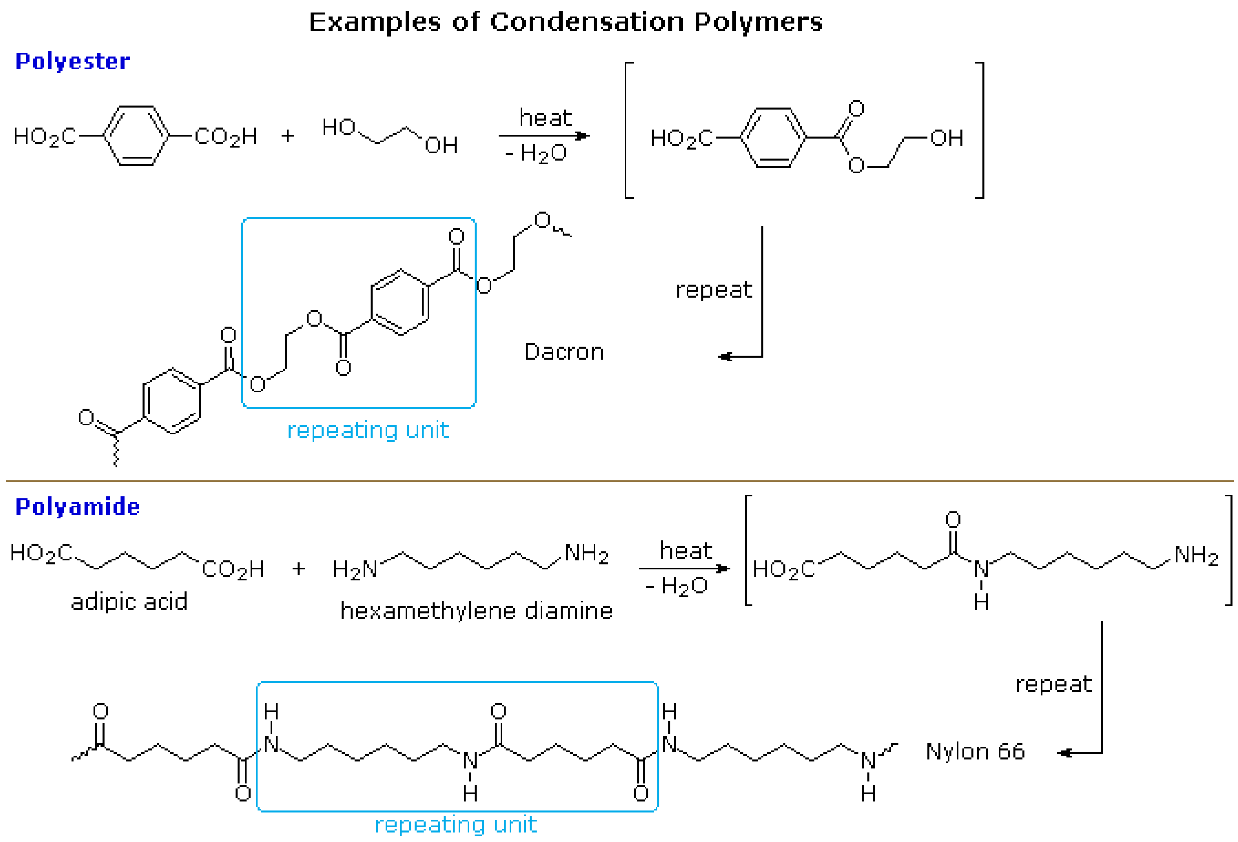
Finally, with only one branch unit present the probability that a functional group on a branch unit leads to another branch unit is just the probability that it has reacted.

(Branch unit only) $\alpha = p$……………………. (6)

Module-III

CODENSATION POLYMERIZATION:

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but precede instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as step-growth polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

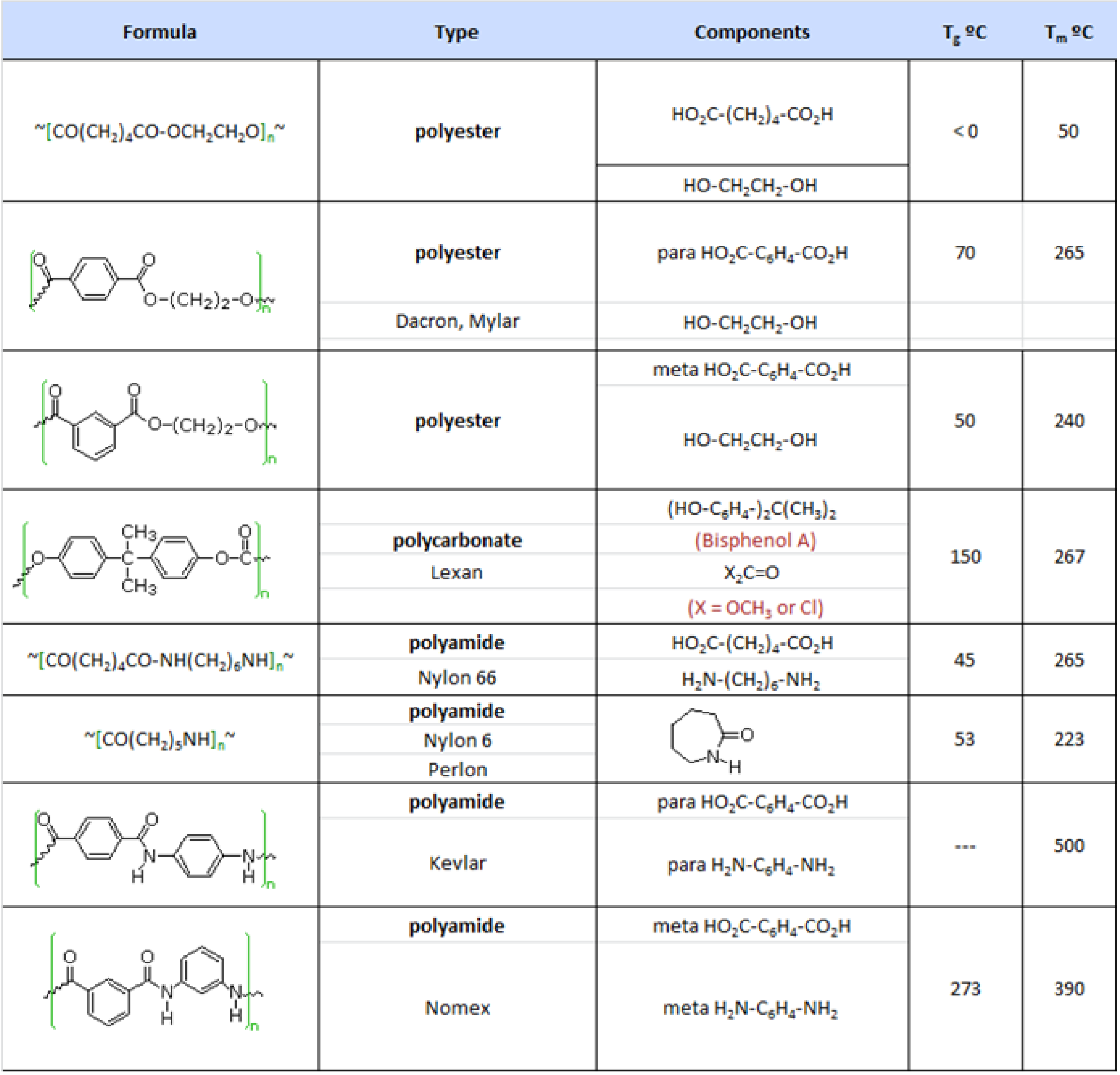


Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly (β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. Formulas for these will be displayed below by clicking on the diagram.

Characteristics of Condensation Polymers: Condensation polymers form more slowly than addition polymers, often requiring heat, and they are generally lower in molecular weight. The terminal functional groups on a chain remain active, so that groups of shorter chains combine into longer chains in the late stages of polymerization. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if these involve hydrogen bonding, and thereby crystallinity and tensile strength. The following examples of condensation polymers are illustrative.

Note that for commercial synthesis the carboxylic acid components may actually be employed in the form of derivatives such as simple esters. Also, the polymerization reactions for Nylon 6 and Spandex do not proceed by elimination of water or other small molecules. Nevertheless, the polymer clearly forms by a step-growth process.

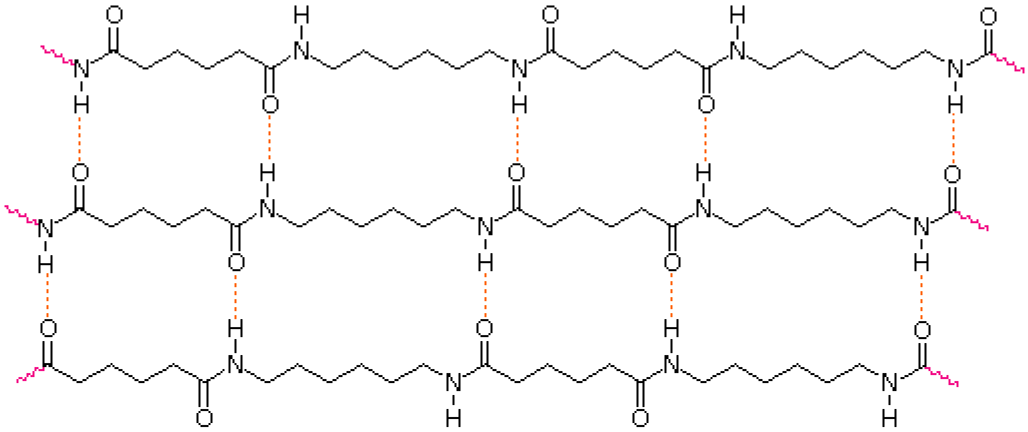
SomeCondensation Polymers



Formula	Type	Components	T_g ºC	T_m ºC
~$[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n$~	**polyester**	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	< 0	50
	polyester Dacron, Mylar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	70	265
	polyester	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	50	240
	polycarbonate Lexan	$(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$ (Bisphenol A) $X_2C{=}O$ ($X = OCH_3$ or Cl)	150	267
~$[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n$~	**polyamide** Nylon 66	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $H_2N\text{-}(CH_2)_6\text{-}NH_2$	45	265
~$[CO(CH_2)_5NH]_n$~	**polyamide** Nylon 6 Perlon		53	223
	polyamide Kevlar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ para $H_2N\text{-}C_6H_4\text{-}NH_2$	---	500
	polyamide Nomex	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ meta $H_2N\text{-}C_6H_4\text{-}NH_2$	273	390

- The difference in Tg and Tm between the first polyester (completely aliphatic) and the two nylon polyamides (5th & 6th entries) shows the effect of intra-chain hydrogen bonding on crystallinity.
- The replacement of flexible alkylidene links with rigid benzene rings also stiffens the polymer chain, leading to increased crystalline character, as demonstrated for polyesters (entries 1, 2 &3) and polyamides (entries 5, 6, 7 & 8). The high Tg and Tm values for the amorphous polymer Lexan are consistent with its brilliant transparency and glass-like rigidity. Kevlar and Nomex are extremely tough and resistant materials, which find use in bullet-proof vests and fire resistant clothing.

Interchain Hydrogen Bonding Enhances Crystallinity



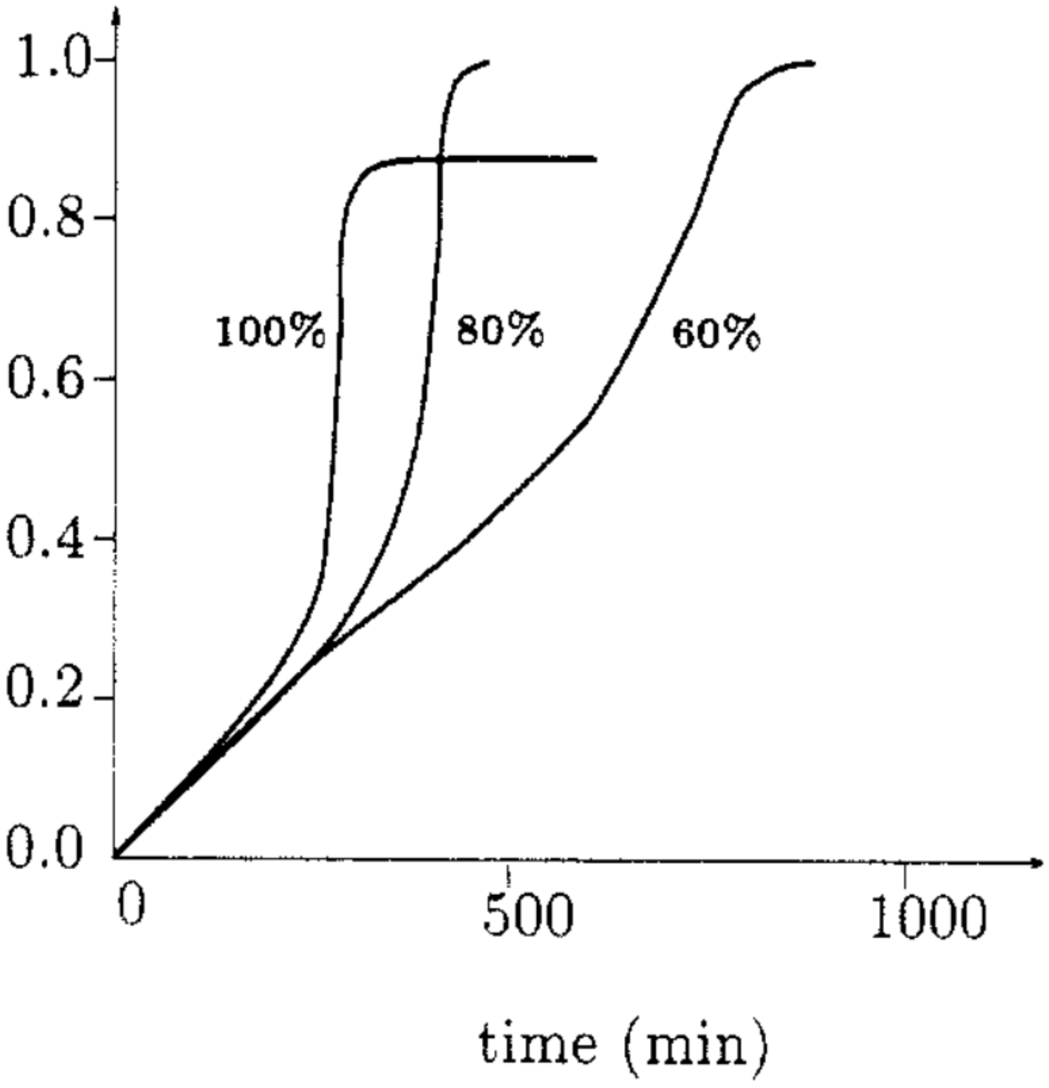
- Many polymers, both addition and condensation, are used as fibers The chief methods of spinning synthetic polymers into fibers are from melts or viscous solutions. Polyesters, polyamides and polyolefins are usually spun from melts, provided the Tm is not too high. Polyacrylates suffer thermal degradation and are therefore spun from solution in a volatile solvent.
- Cold-drawing is an important physical treatment that improves the strength and appearance of these polymer fibers. At temperatures above Tg, a thicker than desired fiber can be forcibly stretched to many times its length; and in so doing the polymer chains become untangled, and tend to align in a parallel fashion.
- This cold-drawing procedure organizes randomly oriented crystalline domains, and also aligns amorphous domains so they become more crystalline. In these cases, the physically oriented morphology is stabilized and retained in the final product. This contrasts with elastomeric polymers, for which the stretched or aligned morphology is unstable relative to the amorphous random coil morphology.

Auto-acceleration (gel effect, Trommsdorff–Norrish effect

It is a dangerous reaction behavior that can occur in free-radical polymerization systems. It is due to the localized increases in viscosity of the polymerizing system that slow termination reaction.**Autoacceleration** (**gel effect**, **Trommsdorff–Norrish effect**) is a dangerous reaction behavior that can occur in free-radical polymerizationsystems. It is due to the localized increases in viscosity of the polymerizing system that slow termination reactions. The removal of reaction obstacles therefore causes a rapid increase in the overall rate of reaction, leading to possible reaction runaway and altering the characteristics of the polymers produced

Autoacceleration of polymerization rates during free radical polymerization is known as the Trommsdorff or "gel" effect. For free-radical polymerization one expects a first-order kinetic with respect to the monomer concentration. This is indeed observed for most vinyl polymers over a wide extent of polymerization. However, the polymerization of some monomers, both undiluted and diluted, shows a marked deviation from first-order

kinetics at a certain conversion. One observes a considerable increase in both the polymerization rate and the molecular weight which is known as the gel or Trommsdorff effect. The effect is particularly pronounced with methyl methacrylate, methyl acrylate, and acrylic acid at various concentrations. It occurs also with other monomers, such as styrene and vinyl acetate, but for these monomers the effect is less pronounced.
Auto -acceleration is independent of the initiator and can be observed even under isothermal conditions. In fact, if the reaction is exotherm, autoacceleration results in in a noticeable increase in temperature. An example is shown below for the polymerization of methyl methacrylate at 50 °C in the presence of benzoyl peroxide initiator (BPO) at various initial concentrations of monomer in benzene



According to the kinetics of free radical polymerization, the rate of polymerization depends on the rate constants of initiation, propagation and termination: Rp ∝ kp (f Kd / Kt)1/2

Since the effect is not a function of the initiator, it must depend on the rate constant ratio Kp/Kt1/2, which has to increase by as much as a hundredfold to explain the effect shown in the figure above.

Norrish and Smith, Trommsdorff, and Schulz and Harborth postulated that the drastic increase in the rate of polymerization and the simultaneous increase in the average molecular weight is caused by a noticeable decrease in the termination rate when the system reaches a certain concentration and molecular weight. They attributed the decrease in the termination rate kt to the high viscosity of the medium at high(er) conversion rates (around 20 %). According to Trommsdorff et al., the overall diffusion rate of the growing polymer chains depends on the viscosity of the medium. If the viscosity is high, the termination rate, that is, the combination of two free chain radicals, becomes diffusion controlled.

Although the intrinsic reactivity of the free radicals does not change much, the probability that two radicals will approach and annihilate each other will be rather small since the kinetics of the termination will be dominated by entanglement and (chain-end) diffusion. In fact, the reaction rate between two polymers of very different length will be entirely determined by the shorter chain and the rate of termination is given by a power law

kt ~N-α φ-β

Where φ is the volume fraction of polymer and N is the average chain length.

The consequence on termination reactions is dramatic; since N is large, the net rate of termination in the auto-acceleration regime will dramatically decrease, whereas the reactivity of the monomers will not change much due to the small size of the monomers. In fact, the concentration of active radicals will rise to a much higher level, and consequently, the consumption of monomer will increase proportionately. Another important consequence is, that the addition of a polymer, like a rubber toughened, will shift the Trommsdorff effect to lower polymer concentrations.

Coordination polymerization or Zieglar-Natta polymerization

The polymerization catalyzed by transition metal complex such as Zieglar-Natta catalysts or metallocene catalysts is also known as coordination polymerization. The Ziegler –Natta catalysts system may be heterogeneous (some titanium based system) or soluble (most vanadium containing species). The best known are derived from $TiCl_4$ or $TiCl_3$ and aluminium trialkyl. These catalysts are highly stereospecific and can orient the monomer in specific direction before addition to the chain. The Ziegler-Natta and metallocene initiators are considered as coordination initiators that perform stereoselectivity by co-ordination. The olefin polymerization is carried out in presence of Ziegler–Natta catalyst ($TiCl_4$ supported on $MgCl_2$).

(a) **Heterogeneous Ziegler–Natta Polymerization:**The Ziegler–Natta initiators are the only initiators that polymerize α–olefins such as propene and 1-butene which cannot be polymerized by either radical or ionic initiators. Thousands of different combinations of transition and Group I-III metal components, often together with other compounds such as electron donors, studied for use in alkene polymerizations.

(b) Catalysts are prepared by mixing the compounds in a dry, inert solvent in the absence of oxygen usually at a low temperature. The mixture of aluminum compound with titanium compound is to form radical, the first of this kind catalyst being used as shown below.

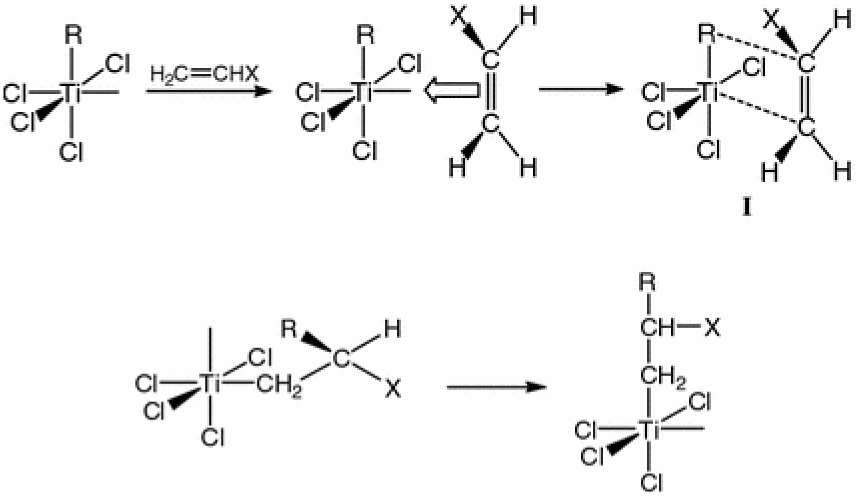
$AlR_3+TiCl_4 \rightarrow AlR_2Cl+TiRCl_3$-------------------------------------1

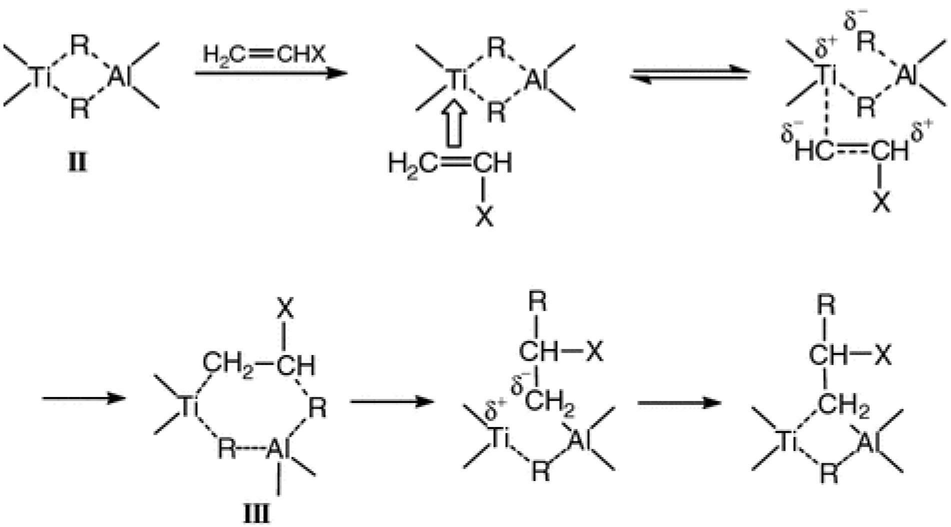
$AlR_2Cl+TiCl_4 \rightarrow AlRCl_2+TiRCl_3$------------------------------------2

$AlR_3+TiRCl_3 \rightarrow AlR_2Cl+TiR_2Cl_2$---3
$TiRCl_3 \rightarrow TiCl_3+R\cdot$ --4
$TiR_2Cl_2 \rightarrow TiRCl_2+R\cdot$ --5
Further reduction may also occur:
$TiRCl_2 \rightarrow TiCl_2+R\cdot$
$TiRCl_3 \rightarrow TiCl_2+RCl$
In addition, $TiCl_3$ may be formed by the equilibrium
$TiCl_4+TiCl_2 \rightleftharpoons 2TiCl_3$
With the appropriate choice of catalyst, specific stereo- chemical arrangements of polymerization of diene monomer can be obtained

Reaction Mechanisms

The coordination polymerization of alkene can be preceded either by monometallic mechanism or bimetallic mechanism depending on the catalyst. ,the reaction mechanism of substituted alkene being polymerized by using titanium compound catalyst. The double bond of alkene will undergo cis addition and coordinate with the empty orbital of titanium compound to form four membered ring coordinate intermediate -I. The stereo specificity of substituted alkene is preserved via intermediate- I. Then the bond is formed on the Ti compound catalyst. If the catalyst is made from aluminum compound and titanium compound, the polymerization will proceed through bimetallic mechanism as shown in figA bridge structure II is formed between two metal compounds first. Then the substituted alkene is coordinated with Ti compound to form six-membered ring coordination III. The stereo specificity of substituted alkene is preserved via intermediate III.

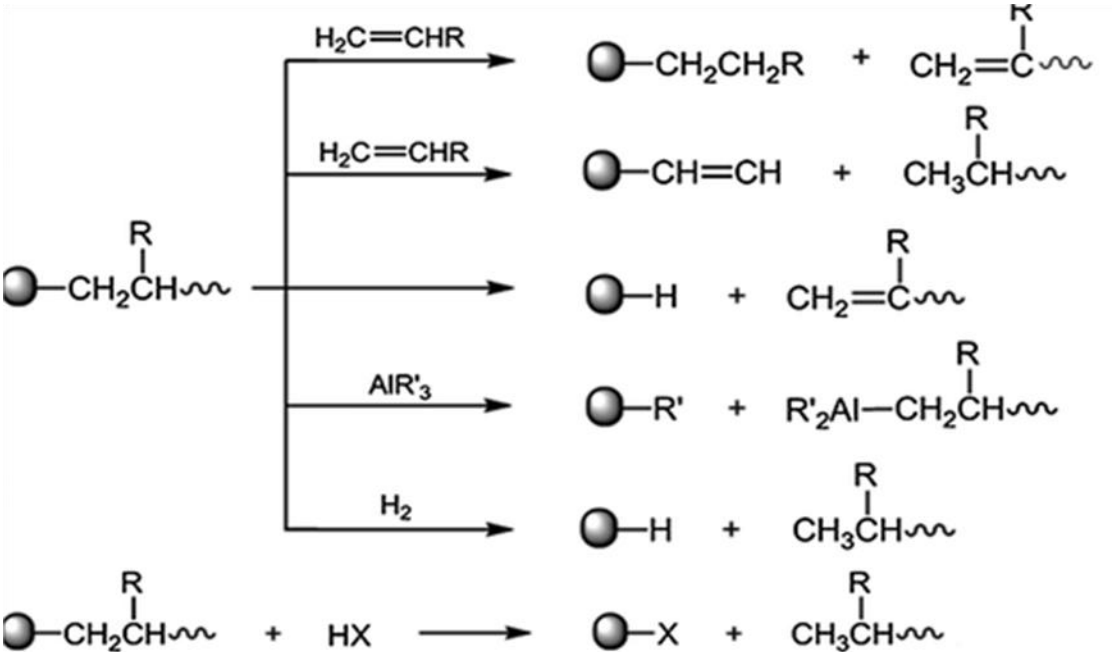




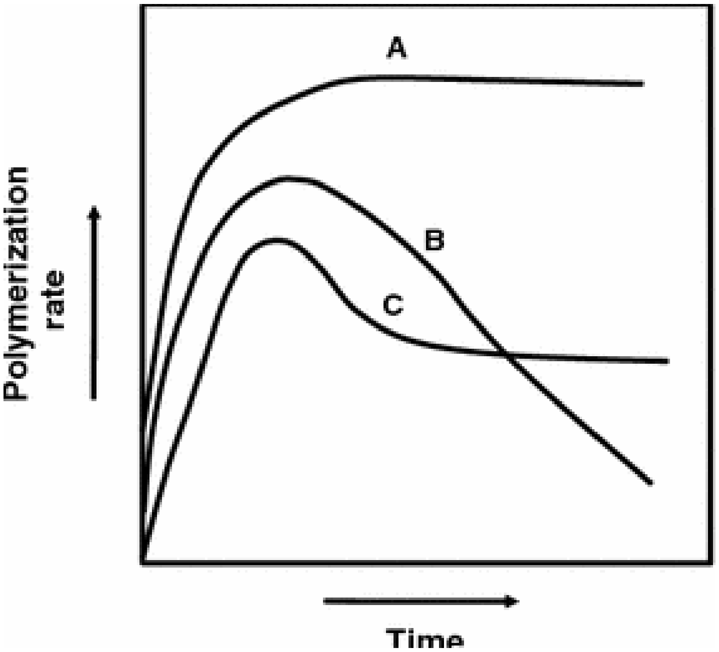
The polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer and the R group originally present in the organometallic cocatalyst ends up as the terminal group of the chain. Monomer activity decreases with increasing steric hindrance about the double bond as shown below:

$CH_2{=}CH_2 > CH_2{=}CHCH_3 > CH_2{=}CHCH_2CH_3 > CH_2{=}CHCH_2CH(CH_3)_2 > CH_2{=}CHCH(CH_3)_2 > CH_2{=}CHCH(CH_2CH_3)_2 > CH_2{=}CH{-}C(CH_3)_3$

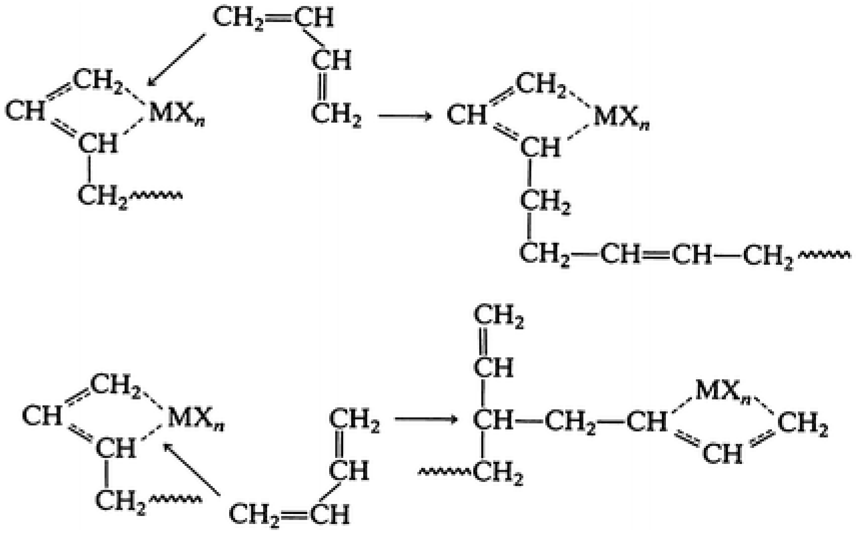
The reaction has the characteristic of living anionic polymerization. The reaction is usually terminated by active hydrogen as shown in the following equations. Hydrogen is the preferred transfer agent for controlling molecular weight due to low cost and clean reaction but the termination reaction is usually carried out by hydrogen containing compounds



The relationship between the polymerization rate and time is shown in Fig. The decaying rate type is most common. That is due to structural changes from the reducing the number or activity of active centers. It is also due to the encapsulation of active centers by polymer which prevents approach by monomer



There are two theories to explain the reaction mechanisms of coordination of dienes. One theory is based on whether the catalyst coordinates one or both double bonds of the diene. Coordination of one would thus lead to 1,2-polymerization and coordination of both to 1,4-polymerization. Another theory is based on the coordination of a π-allylic structure that directs the monomer approaching direction and determines the polymer structure (Scheme 9.3). If the monomer approaches the CH2-metal (M) bond of the complex, 1,4-polymerization forms (Eq. 9.16). If it approaches the CH-metal bond, 1,2-polymerization results (Eq. 9.17). This mechanism provides no information on the geometric arrangement of the double bond or the tacticity at a stereogenic carbon.

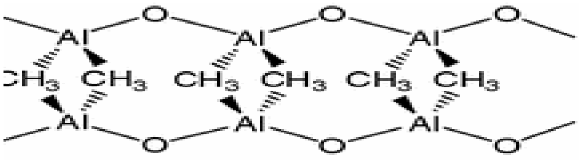


Homogeneous Ziegler–Natta Polymerization:

The homogeneous Ziegler–Natta polymerization using metallocene catalysts such as bis(cyclopentadienyl)titanium dichloride1, and dialkylaluminum chlorid 2. Their structures are shown below.

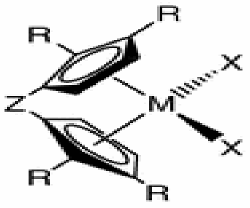
Cp_2TiCl_2 R_2AlCl

Compounds 1 and 2 exhibit low catalytic activity towards ethylene and are generally unreactive toward propylene. The addition of water increases the activity substantially. The increase is the result of a reaction between the water and the alkylaluminum cocatalyst to form complex alkylalumoxanes such as methyl alumoxanes (MAO). The MAO is used in conjunction with metallocene catalysts exhibit especially high activities. MAO formed by controlled hydrolysis of trimethylaluminum that has a complex oligomeric structure with molecular weights of 1000–1500, most likely consisting of methyl-bridged aluminum atoms alternating with oxygen as shown in structures 3 and 4. MAO is now used with a wide variety of metallocenes having the general structure 5. Examples of catalysts are 6 and 7 which form isotactic and syndiotactic polypropylene, respectively.



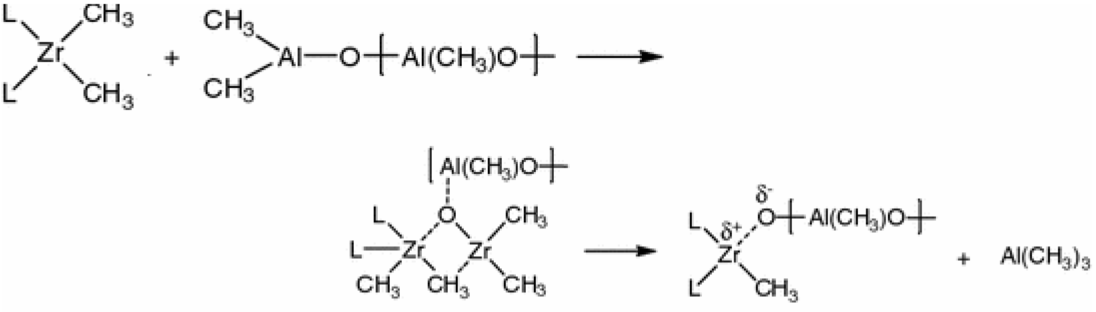
3

4



5

Metallocene has well-defined molecular structure and polymerization occurs at one position in the molecule, the transition metal atoms. Thus, the metallocene is also called single-site catalyst in contrast to the multi active site of heterogeneous catalyst. Scheme 9.4 shows an example of the formation of active site in a zirconium catalyst, L2ZrCl2 (where L represents the π ligands) which involves initial complexation between MAO and the catalyst, is followed by Cl-CH_3 exchange to form L2Zr(CH3)$_2$. The methylated zirconocene reacts further with MAO to form the active species of 8.



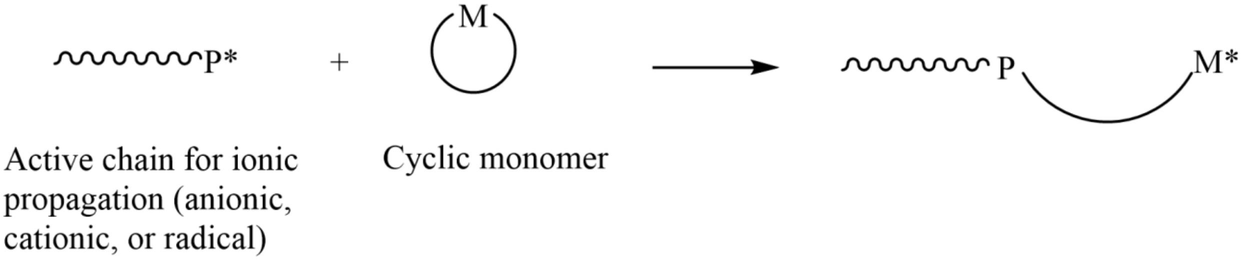
8

Ziegler-Natta Catalysts

Ziegler-Natta catalysts have been defined as the products of reaction between Compounds of transition metal elements of groups IV to VIII (titanium, vanadium or zirconium etc.halides) and compounds such as the hydrides or alkyls of groups I-III such as $LiEt_3$, $BeEt_3$, $AlEt_3$ or $AlEt_2Cl$. In common practice, the transition element component is called the catalyst while the hydride or alkyls are referred to as co-catalyst

Ring opening polymerization:

In polymer chemistry, ring-opening polymerization is a form of chain-growth polymerization, in which the terminal end of a polymer chain acts as a reactive center where further cyclic monomers can react by opening its ring system and form a longer polymer chain.



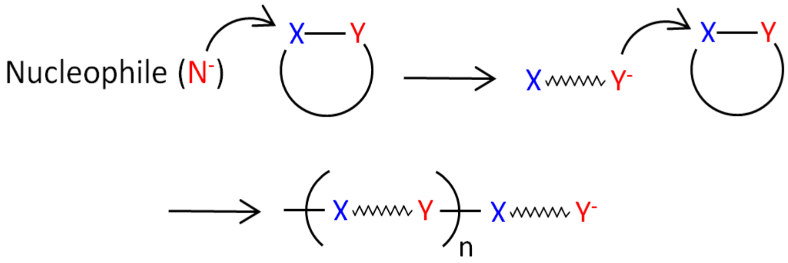
In polymer chemistry, ring-opening polymerization (ROP) is a form of chain-growth polymerization, in which the terminal end of a polymer chain acts as a reactive center where further cyclic monomers can react by opening its ring system and form a longer polymer chain The propagating center can be radical, anionic or cationic. Some cyclic monomers such as norbornene or cyclooctadiene can be polymerized to high molecular weight polymers by using metal catalysts. ROP continues to be the most versatile method of synthesis of major groups of biopolymers, particularly when they are required in quantity.

The driving force for the ring-opening of cyclic monomers is via the relief of bond-angle strain or steric repulsions between atoms at the center of a ring. Thus, as is the case for other types of polymerization, the enthalpy change in ring-opening is negative

Mechanisms of ring opening polymerization:

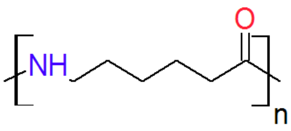
A ring-opening polymerization (ROP) is another form of chain-growth polymerization in which the terminal end group of a polymer chain acts as a reactive center where further cyclic monomers can be added by ring-opening and addition of the broken bond. Typical cyclic monomers that can be polymerized via ROP are di-functional monomers that carry two different reactive groups like one amine or alcohol and one carboxylic acid that have undergone a cyclization reaction. Two examples are caprolactam and caprolactone:

To polymerize these moieties, one of the rings has to open prior polymerization. This can be achieved, for example, by adding a small amount of a nucleophilic reagent (Lewis base) as an initiator. This reaction is called *anionic ring-opening polymerization* (AROP):

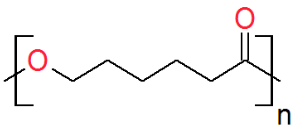


Two well-known thermoplastic polymers that can be synthesized via anionic ring-opening polymerization are polycaprolactam (Nylon 6) and polycaprolactone (PCL):

Polycaprolactam



Polycaprolactone



Most monomers that undergo AROP contain polar bonds like ester, amide, carbonate, urethane, epoxide, and phosphate which polymerize to the corresponding polyester, polyamide, polycarbonate, polyurethane, polyepoxide, and polyphosphate. The ring opening polymerization is classified into the following categories

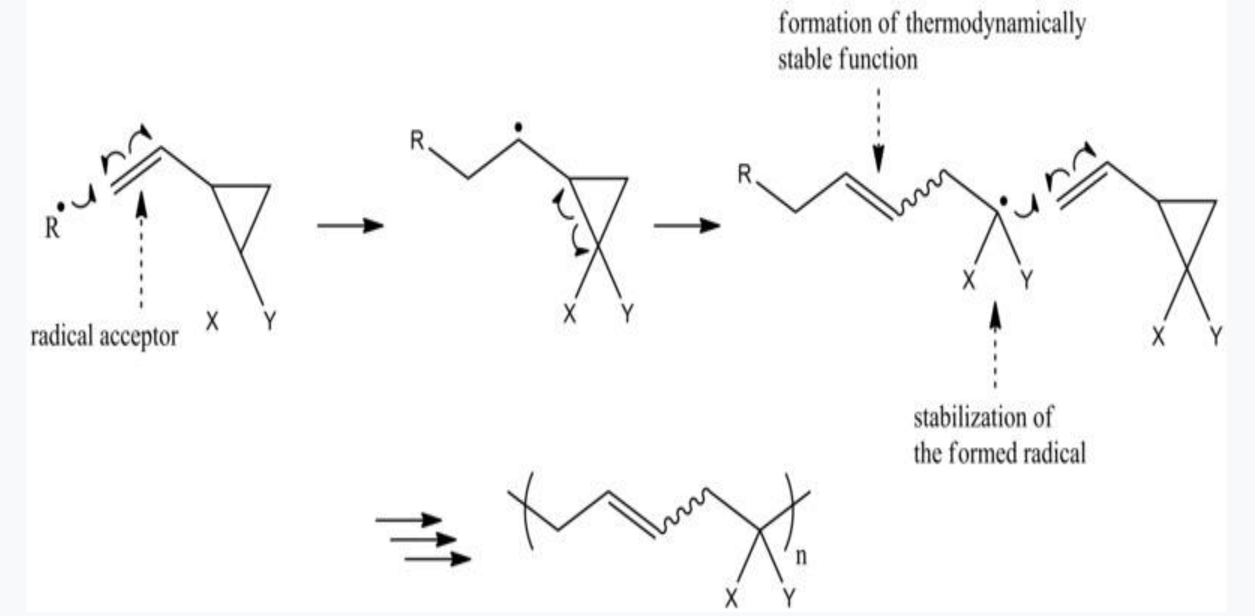
1. ***Cationic ring-opening polymerization*** **(CROP**) is also possible. In this case, a small amount of an electrophilic reagent (Lewis acid) is added to the monomer to initiate polymerization. However, not all cyclic monomers containing an heteroatom undergo CROP. Whether and how readily a cyclic monomer undergoes CROP depends on the ring size, to be more specific, on the ring strain. Cyclic monomers with small or no ring strain will not polymerize whereas small rings with greater ring strain like 4, 6, and 7-membered rings of cyclic esters, polymerize readily through CROP.

Some examples of cyclic monomers that polymerize through anionic or cationic ring-opening polymerization include cyclic ethers, lactones, lactams, and epoxides.

Ring-opening polymerization can also proceed via *free radical polymerization*. The introduction of an oxygen into the ring will usually promote free radical ring-opening polymerization, because the resulting carbon–oxygen double bond is much more stable than a carbon-carbon double bond. Thus, cyclic hetero monomers that carry a vinyl side group like cyclic ketene acetals, cyclic ketene aminals, cyclic vinyl ethers, and unsaturated spiro ortho esters will readily undergo free radical ring-opening polymerization. Copolymerization of these monomers with a wide variety of vinyl monomers will introduce ester, amide, keto or carbonate groups into the backbone, which results in functionally terminated oligomers.

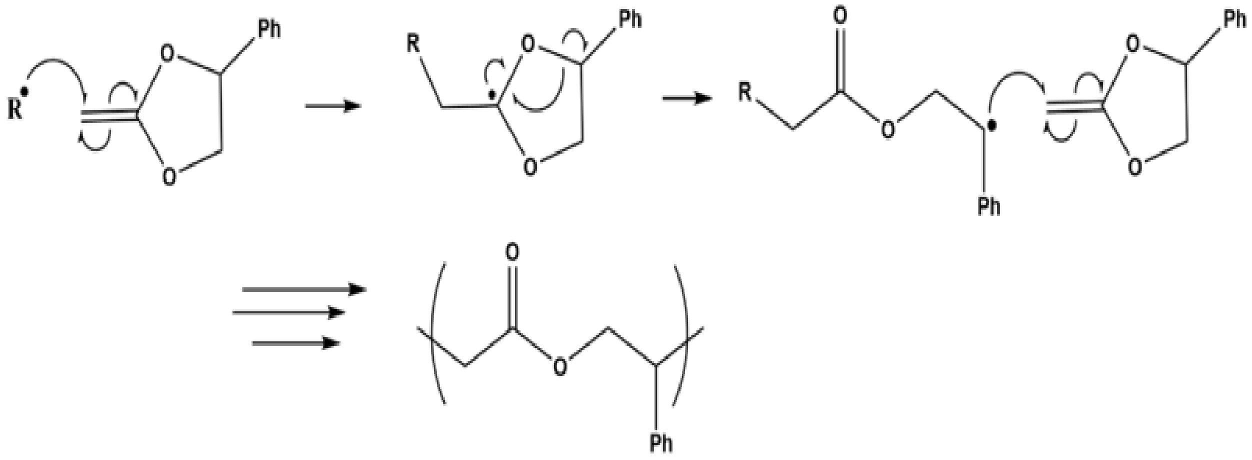
1.Radical ring opening polymerization

Scheme 1: The terminal vinyl group accepts a radical. The radical will be transformed into a carbon radical stabilized by functional groups (i.e. halogen, aromatic, or ester groups). This will lead to the generation of an internal olefin.



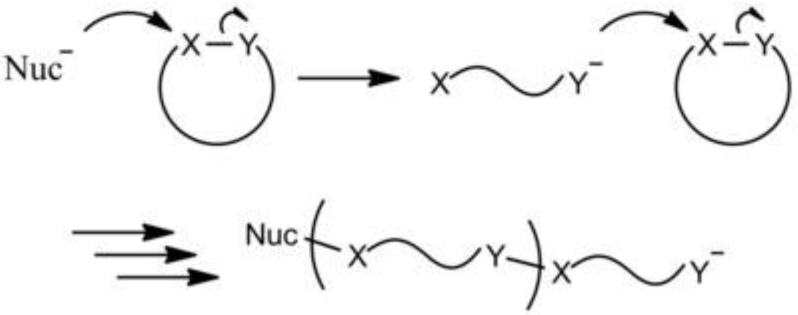
Radical ring-opening polymerization of vinyl cyclopropane

Scheme 2: In this case, the exo-methylene group is the radical acceptor. The ring-opening reaction will form an ester bond, and the radical produced is stabilized by a phenyl group.



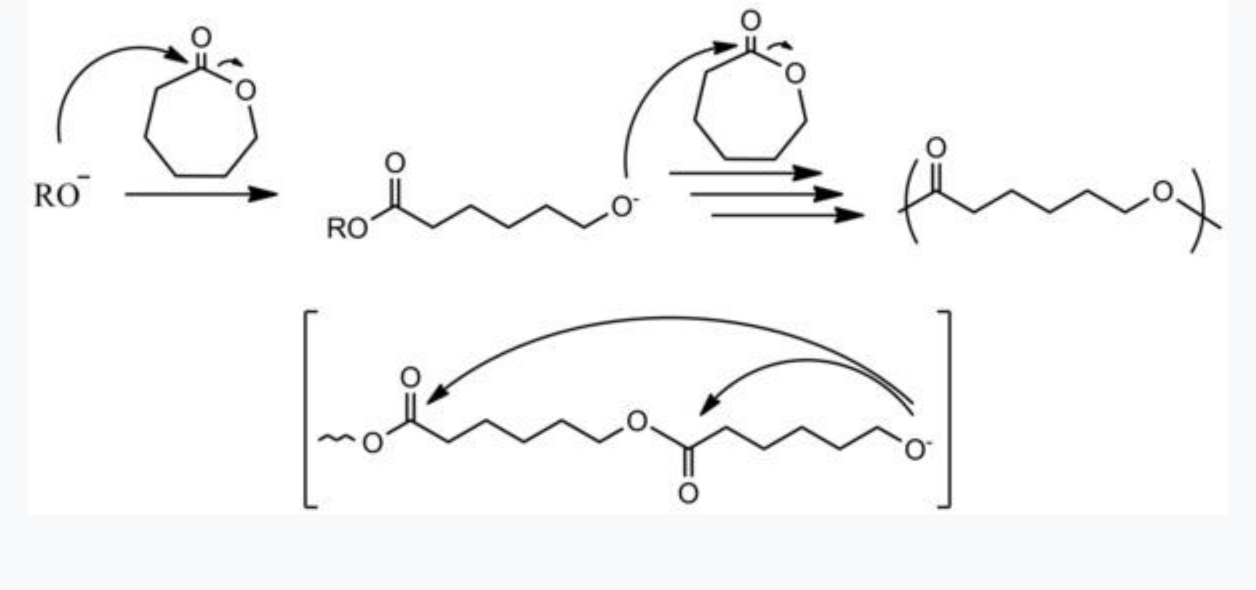
2. Anionic ring-opening polymerization

[



The general mechanism for anionic ring-opening polymerization. Polarized functional group is represented by X-Y, where the atom X (usually a carbon atom) becomes electron deficient due to the highly electron-withdrawing nature of Y (usually an oxygen, nitrogen, sulfur, etc.). The nucleophile will attack atom X, thus releasing Y-. The newly formed nucleophile will then attack the atom X in another monomer molecule, and the sequence would repeat until the polymer is formed.[13]

A typical example of anionic ROP is that of ε-caprolactone, initiated by an alkoxide functional group.

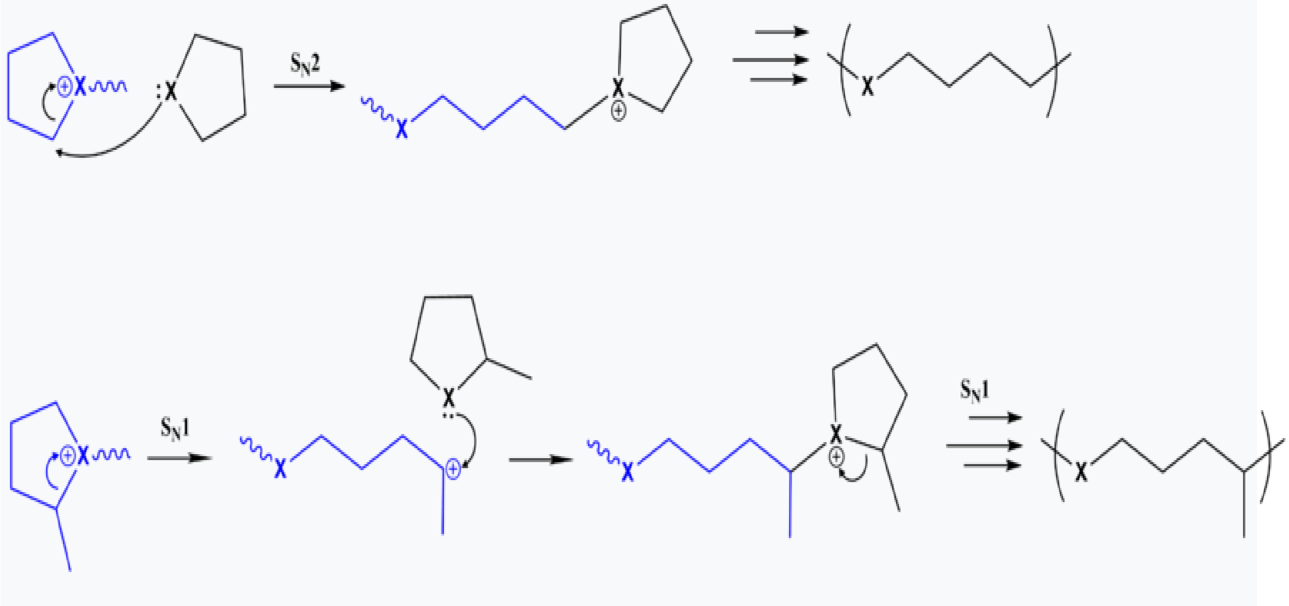


3.Cationic ring-opening polymerization

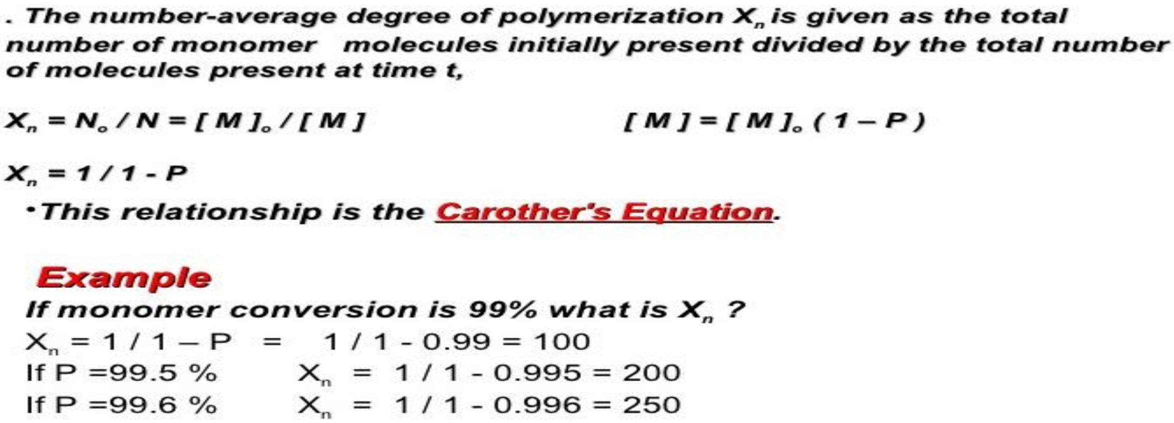
is also possible. In this case, a small amount of an electrophilic reagent (Lewis acid) is added to the monomer to initiate polymerization. However, not all cyclic monomers containing an heteroatom undergo CROP. Whether and how readily a cyclic monomer undergoes CROP depends on the ring size, to be more specific, on the ring strain. Cyclic monomers with small or no ring strain will not polymerize whereas small rings with greater ring strain like 4, 6, and 7-membered rings of cyclic esters, polymerize readily through CROP.

Some examples of cyclic monomers that polymerize through anionic or cationic ring-opening polymerization include cyclic ethers, lactones, lactams, and epoxides.

Ring-opening polymerization can also proceed via *free radical polymerization*. The introduction of an oxygen into the ring will usually promote free radical ring-opening polymerization, because the resulting carbon–oxygen double bond is much more stable than a carbon-carbon double bond. Thus, cyclic hetero monomers that carry a vinyl side group like cyclic ketene acetals, cyclic ketene aminals, cyclic vinyl ethers, and unsaturated spiro ortho esters will readily undergo free radical ring-opening polymerization. Copolymerization of these monomers with a wide variety of vinyl monomers will introduce ester, amide, keto or carbonate groups into the backbone, which results in functionally terminated oligomers.



Carother Equation:In step-growth polymerization, the Carothers equation (or Carothers' equation) gives the degree of polymerization, X_n, for a given fractional monomer conversion, p. There are several versions of this equation, proposed by Wallace Carothers who invented nylon in 1935



. The number-average degree of polymerization X_n is given as the total number of monomer molecules initially present divided by the total number of molecules present at time t,

$X_n = N_o / N = [M]_o / [M]$ $\qquad$ $[M] = [M]_o (1 - P)$

$X_n = 1 / 1 - P$

- ***This relationship is the Carother's Equation.***

Example

If monomer conversion is 99% what is X_n ?

$X_n = 1 / 1 - P = 1 / 1 - 0.99 = 100$

If P =99.5 % $\quad X_n = 1 / 1 - 0.995 = 200$

If P =99.6 % $\quad X_n = 1 / 1 - 0.996 = 250$

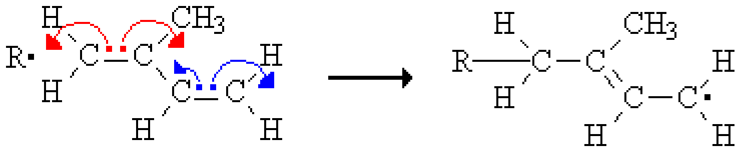
ISOMERISM OF POLYMERIC MATERIALS

It is a general rule that for a polymer to crystallize, it must have highly regular polymer chains11. Highly irregular polymers are almost inevitably amorphous. Polymer chains can have isomeric forms that decrease the regularity of the chains.

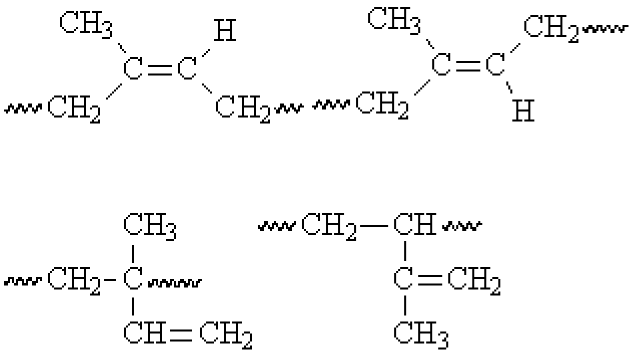
There are three important forms of isomerism in polymers**.**

1.Structural Isomerism

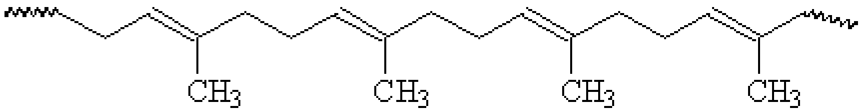
Double bonds in the polymer chain can show cis- or trans-isomerism. When a monomer with two conjugated double bonds, such as isoprene, undergoes chain polymerization one double bond can remain in the chain.



This segment of the poly-isoprene chain can have four different isomers.

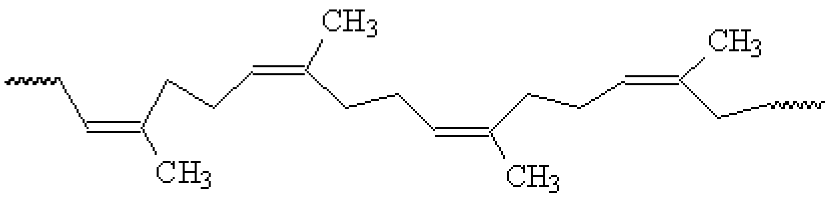


The difference between the properties of the cis- and trans-isomers is apparent for naturally-occurring polyisoprenes13. Gutta percha is predominantly trans-1,4-polyisoprene, which has a regular structure that allows crystallization. As a result, gutta percha is hard and rigid. Natural rubber is cis-1,4-polyisoprene, which has a less symmetrical structure that does not allow easy crystallization. Natural rubber is an amorphous rubbery material



.

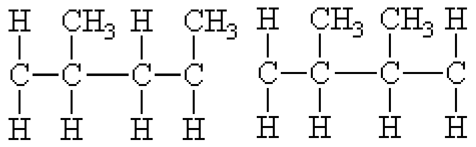
Gutta Percha (trans-1,4-polyisoprene)



Natural Rubber (cis-1,4-polyisoprene)

2.Sequence Isomerism (Head-to-Tail or Head-to-Head)

In chain polymerization monomers with pendant groups can attach in two ways.

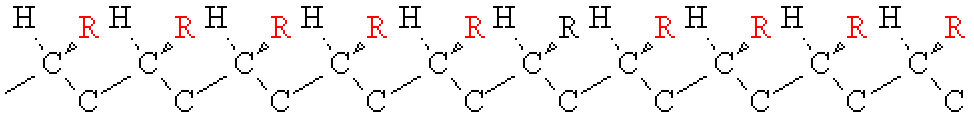


Head to tail arrangement Head to head arrangement

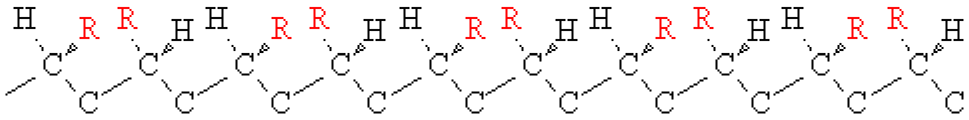
The usual arrangement is head-to-tail with the pendant groups on every other carbon atom in the chain

3.Stereoisomerism (Tacticity)

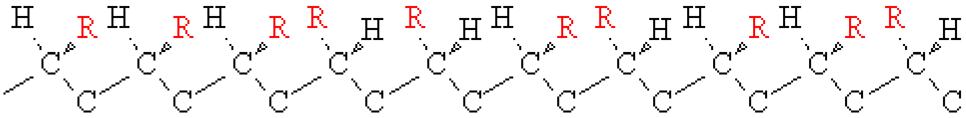
When a chiral center is present in a polymer molecule, different configurations or optical isomers are possible23. Three of them are shown below for a monosubstituted vinyl polymer.



Isotactic



Syndiotactic



Atactic

Stereochemistry can have an important effect on chain packing. Isotactic polypropylene (PP), for instance, is highly crystalline because the regular chains can pack closely together. Isotactic PP has a melting point of 160^{o}C. Atactic PP, on the other hand is a soft noncrystalline polymer with a melting point of only 75^{o}C.

Monomer Reactivity Ratio and Copolymerization

Block copolymers consist of two or more strands (blocks) of different polymers chemically attached to each other. The properties of these polymers depend on the copolymer sequence distribution, the chemical nature of the blocks, the average molecular weight and the molecular weight distribution of the blocks and the copolymer.

Block copolymers, particularly those of type A-B-A can exhibit properties that are very different from those of random copolymers.

In the case of copolymerization of vinyl polymers, block copolymers are often prepared by controlled sequential monomer addition. In this case, one of the two monomers is polymerized first. When polymerization of the first component is complete, a second (suitable) monomer is added to the "living" radical bearing polymers which then copolymerizes with the first component.

Another method involves monomers that have a strong tendency to homopolymerize but still copolymerize. This is the case, if the reactivity ratios, defined by

$r_1 = k_{11} / k_{12}$

$r_2 = k_{22} / k_{21}$
are (much) larger than unity:

$r_1 \approx r_2 > 1$,
or

$k_{11} > k_{12}$, $k_{22} > k_{21}$

where K_{xy} are the reaction constants of the four different types of polymerization reactions:

$M_1^* + M_1 \rightarrow M_1M_1^* \quad R_{11} = k_{11} [M_1^*] [M_1]$

$M_1^* + M_2 \rightarrow M_2M_1^* \quad R_{12} = k_{12} [M_1^*] [M_2]$

$M_2^* + M_2 \rightarrow M_2M_2^* \quad R_{22} = k_{22} [M_2^*] [M_2]$

$M_2^* + M_1 \rightarrow M_1M_2^* \quad R_{21} = k_{21} [M_2^*\cdot] [M_1]$

M1* and M2* represent reactive chain ends of type 1 and 2.
For $r_1 > 1$ and $r_2 > 1$, each radical has a strong preference to add monomers of its kind to the growing polymer chain. The addition of the same type of monomer will continue until there is a chance of addition of the other kind of monomer, and then polymerization of the other monomer will continue. In the case of a very low probability of cross- polymerization ($r >> 1$), large M1 and M2 blocks will form and in the extreme case of both reactivity ratios very large, $r1 \approx r2 \rightarrow \infty$, the two monomers only react with themselves, leading to a mixture of two photopolymers. However, complete free radical homopolymerization in the presence of another monomer has not been observed yet.

Azeotropic copolymerization:
Azeotropic Copolymerization. Copolymers constitute a large portion of commercial polymers. In analogy to vapor-liquid equilibira, the composition of an azeotropic blend will be constant

throughout the polymerization, that is, both the feed and the copolymer composition will not change.
Copolymers constitute a large portion of commercial polymers. The monomers can have similar of very different physical properties, which results in a large variety of copolymers with very different properties and end uses.
The incremental composition of the copolymers (i.e. the composition along the backbone) will usually vary, because the monomers have different reactivites; to be more specific, the composition of the copolymer will depend on the reactivity ratios:
The condition for azeotropic monomer blends can be calculated with the Mayo-Lewis equation:

$d[M_1]/d[M_2] = (|M_1|/|M_2|) \cdot (r_1[M_1]/[M_2] + 1) / ([M_1]/[M_2] + r_2)$
With $d[M_1]/d[M_2] = (|M_1|/|M_2|)$ this equation reads

$[M_1] / [M_2] = (1 - r_2) / (1 - r_1)$

$f_1,c = (1 - r_2) / (2 - r_1 - r_2)$

If both reactivity ratios are smaller or greater than unity, then f_1. c has non-negative solution and an azeotropic blend exist. However, if $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, then no critical blend exists.

Ideal copolymerization:
In the ideal random vinyl copolymerization, each radical bearing chain has no preference for adding monomers of type M_1 or M_2. Furthermore, both types of radical bearing end groups have the same rate of addition. This means, the probability of the addition of a M_1 monomer to a $M_2\cdot$ radical is the same as the addition of a M_2 monomer to same radical. The same is true for the addition of monomers to a $M_1\cdot$ radical. Therefore, the sequence of repeat units in an ideal copolymer is completely random. These polymers are called random or statistical copolymers
If r_1 and r_2 are monomer reactivity ratios defined by

$r_1 = k_{11} / k_{12}$

$r_2 = k_{22} / k_{21}$

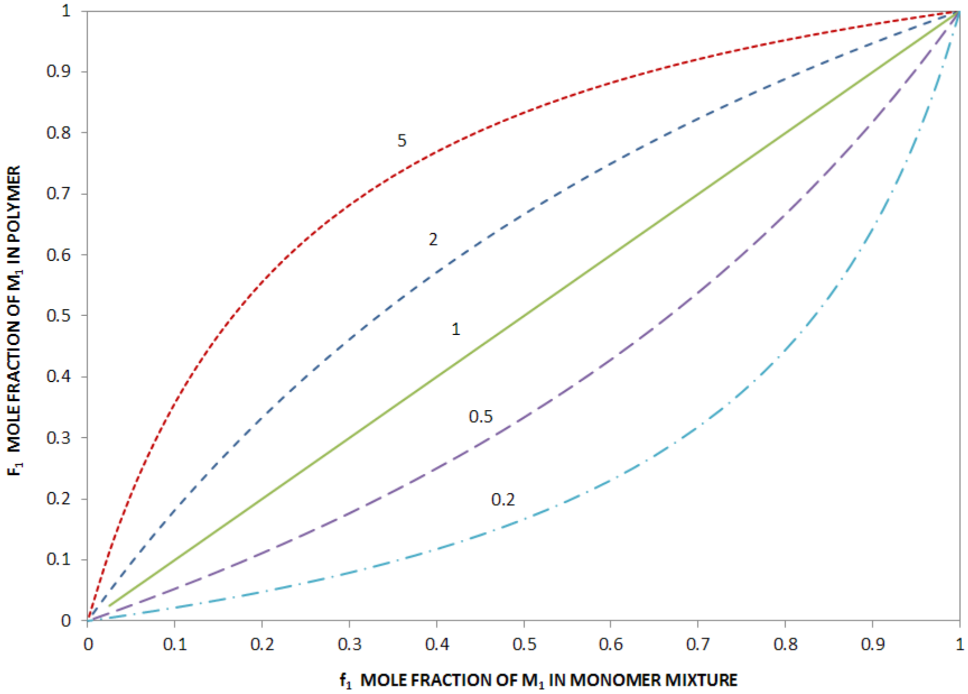
then the condition for random copolymerization is

$r_1 = 1 / r_2$

$k_{21} / k_{22} = k_{11} / k_{12}$
Case 1: $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, $r_1 r_2 = 1$
Each radical has no preference and the copolymer has a completely random sequence of monomers. However, one monomer is more reactive than the other. Consequently, the copolymer will consist of a greater portion of the more reactive specimen in the random sequence of repeat units.

Case 2: $r_1 = r_2 = 1$

The sequence is not only random, but the composition is identical with the composition of the monomer blend throughout the range. However, the reactivity of the two radicals might differ, that is, k_{11} need not be equal to k_{22}



The figure above shows the incremental polymer composition as a function of monomer composition for different reactivity ratios r_1/r_2 of an ideal copolymerization. The ordinate (F_1) represents the composition of the copolymer increment formed from the monomer blend of composition f_1 shown on the abscissa. The straight line $r_1 = 1$ is the trivial case in which $r_1 = r_2 = 1$, $\Rightarrow k_{12} = k_{11}$ and $k_{21} = k_{22}$.

This means the two radicals are equally reactive towards each monomer. The radicals sequence is then not only random, but the incremental composition is identical with the mole fractions of the unreacted monomer blend.