

# Polymers

Polymers are a part of everyday life and examples can be found almost anywhere. Many people think of polymers simply as plastics used for packaging, in household objects and for making fibers.

The polymers are used in all sorts of applications you might not have thought much about before.

Polymers and composites (materials made by combining two or more materials) are vital to modern dentistry, that mean's these molecules are long chain molecules, consisting of many repeating units containing Hydrogen, Carbon, Oxygen, Nitrogen, Fluorine, Silicon, Sulfur and Chlorine while the monomer is the smallest repeating unit in the polymer chain.

## Polymerization:

is a most important process in which molecules of a low molecular weight compound (**monomer**) react with themselves over and over again to form large, high molecular weight molecules, called **polymers** (long chain molecules with recurring structural units).

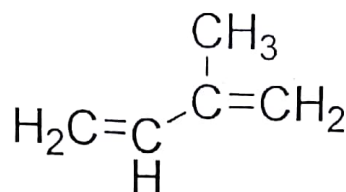
The polymers may be classified depend upon the source into:

### 1. Natural polymers

Natural polymers (from the Greek poly meaning "many" and meros meaning "parts") are found in many forms such as horns of animals, tortoise shell, rosin (from pine trees), asphalt, and tar from distillation of organic materials. One of the most useful of the

natural polymers was rubber, obtained from the sap of the hevea tree. (Rubber was named by the chemist Joseph who found that a piece of solidified latex gum was good for rubbing out pencil marks on paper).

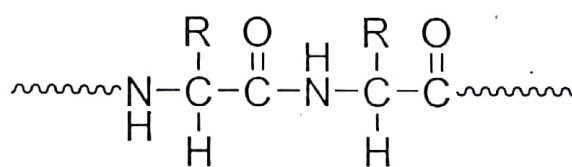
Natural rubber is a polymer of isoprene:



In Great Britain, erasers are still called "rubbers".) Natural rubber had only limited use as it became brittle in the cold and melted when warmed. In 1839, Charles Goodyear discovered, through a lucky accident, that by heating the latex with sulfur, the properties were changed making the rubber more flexible and temperature stable. That process became known as vulcanization.

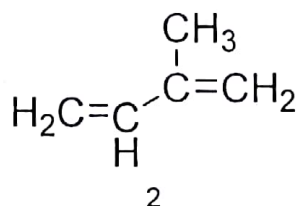
Natural polymers include:

1. Proteins; (or polyamides or polypeptides), containing the chemical group (-CO-NH-) this is known as an amide or peptide link, where as they are naturally occurring polymers with structure:



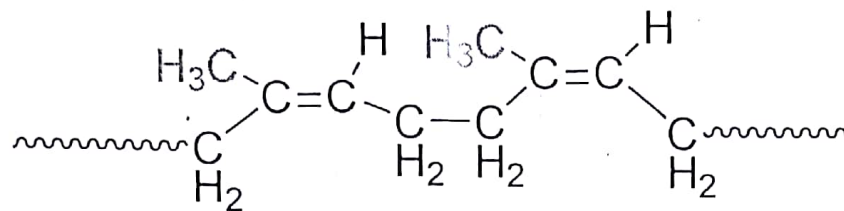
Where R is an organic group.

2. Polyisoprene; 2-methyl-1,3-butadiene as a natural rubber has the formula  $\text{C}_5\text{H}_8$  or :

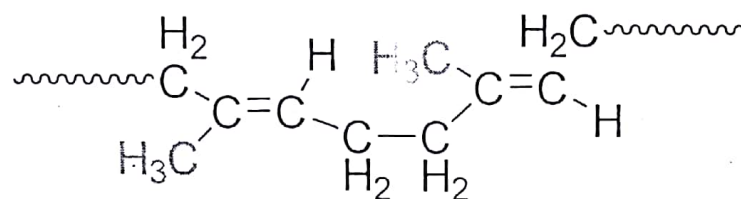


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Poly isoprene occurs in two isomeric forms: (isomers are compounds with the same molecular formula, but the having a different mode of arrangement of atoms):



Natural Rubber(cis-isomer)



Gutta-percha (trans-isomer)

3. polysaccharides are naturally occurring polymers which are carbohydrates, this is, have the general formula  $C_x(H_2O)_y$ .  
e.g. starch, cellulose, agar and alginates.

Agar and alginic acid, both extracted from seaweed, are related to this class of compound. Agar is a sulphuric ester of a polymer of galactose. Alginic acid is a polymer of an hydro- $\beta$ -D-mannuronic acid, Both these materials are linear polymers.

4. polynucleic acids, such as (DNA) and (RNA).

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## 2. Synthetic polymers

The first synthetic polymer, a phenol-formaldehyde polymer, was introduced under the name "Bakelite", by Leo Baekeland in 1909. Its original use was to make billiard balls.

Rayon, the first synthetic fiber was developed as a replacement for silk in 1911.

Synthetic polymers are produced industrially, or in the laboratory, by chemical reactions. Many such materials have become familiar

to everyone, e.g. " Bakelite", "Nylon", "Terylene", "Polythene", "Perspex", "Poly-(vinyl chloride).

Not surprisingly, many of these have been used for dentures, and in other dental applications.

There are two types of chemical reactions they can be used to classify the polymers of dental interest are considered:

(1) Condensation reactions

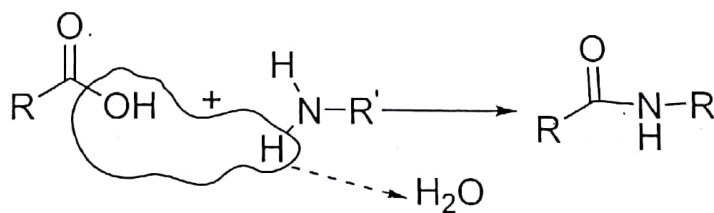
(2) Addition reactions

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(1) Condensation reactions

This is a reaction between two molecules to form a larger molecule, with the elimination of a smaller molecule (this is often, but not always, water), Some examples of interest:

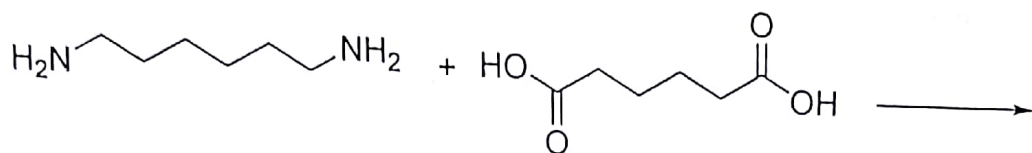
1. "Nylon" An organic acid (with a-COOH group) can react under appropriate conditions with an amine (with a-NH<sub>2</sub> group), to give a material with an amide linkage (as in proteins).



Where R and R' are organic groups.

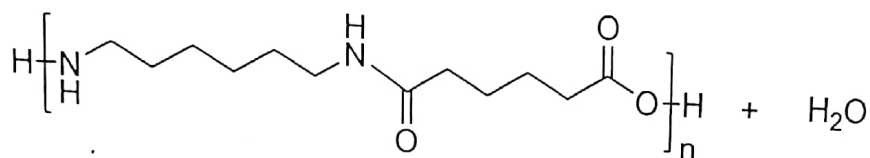
Similarly a **di**-acid (molecule with 2-COOH groups) can react with a **di**-amine (molecule with 2-NH<sub>2</sub> groups) to yield a polymer, called "Nylon", as follows:





Hexamethylene diamine

Adipic acid



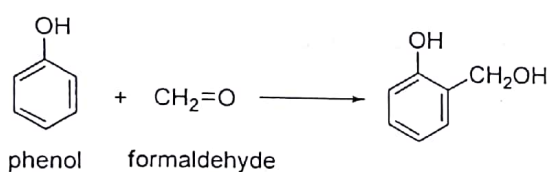
Nylon

N.B.

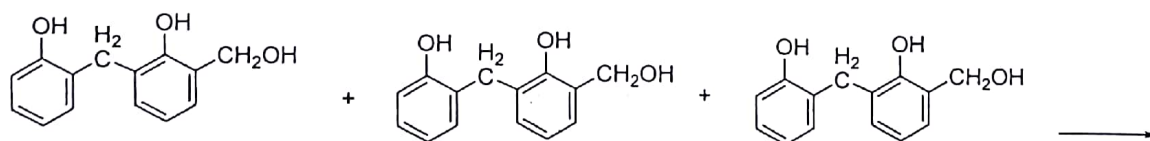
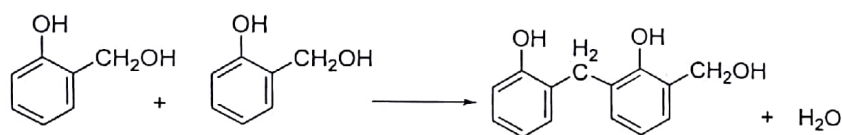
1. Try to react five diamines units with three diacids units and record your notes.

2. Many other nylon polymers are available, using different acid and amine starting materials.

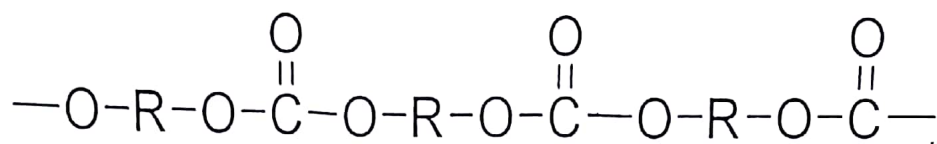
2. "Bakelite." This name is given to condensation polymers, formed by the reaction between phenol and formaldehyde, further condensation reaction can occur between phenol derivatives to yield complex complicated three-dimensional network of molecules.



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### 3. Polycarbonates:

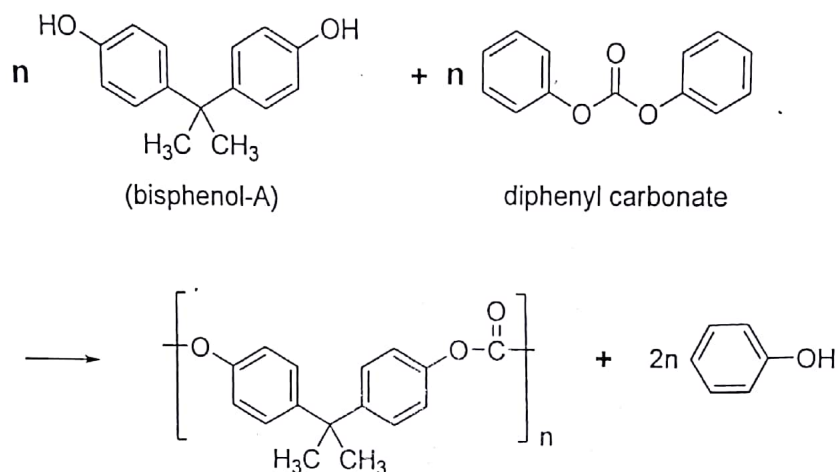


N.B.;

1. Where R is an organic group, such as (CH<sub>2</sub>, phenyl,..., etc)

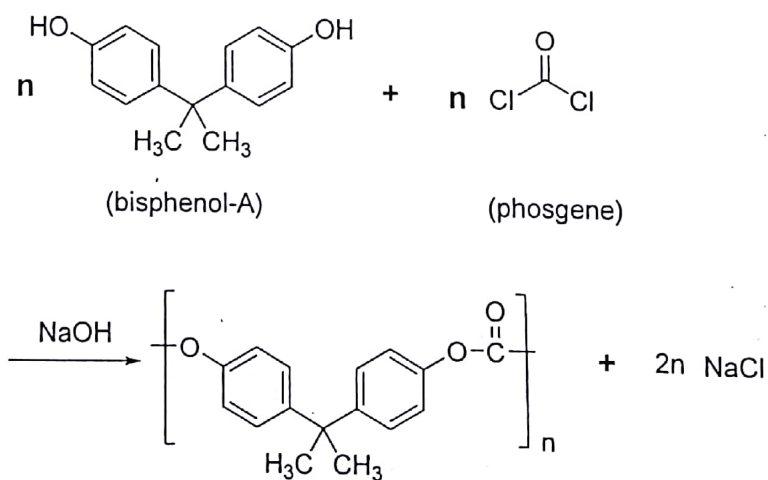
2. They are produced either by:

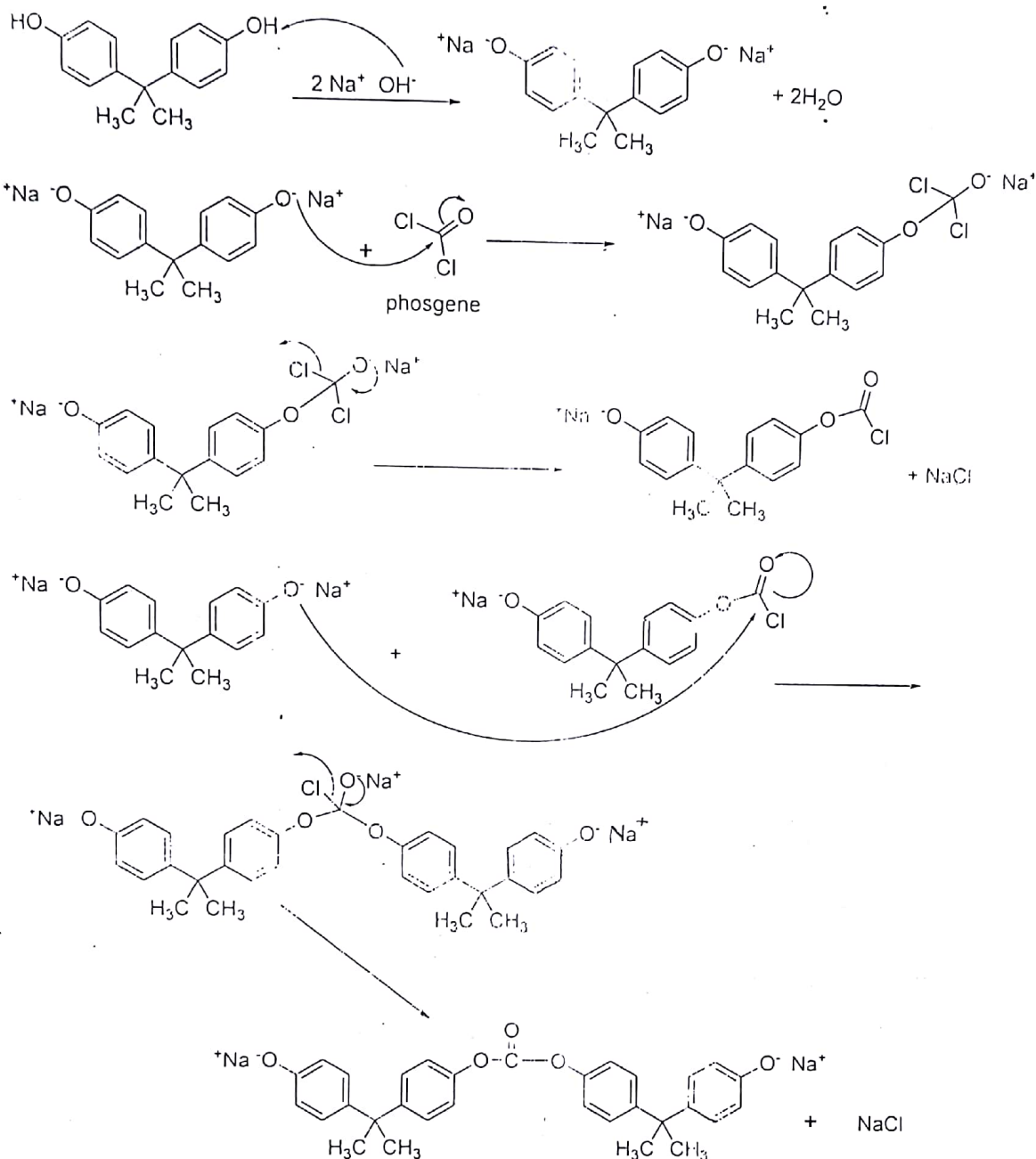
(a) the reaction of bisphenol-A with diphenyl carbonate:



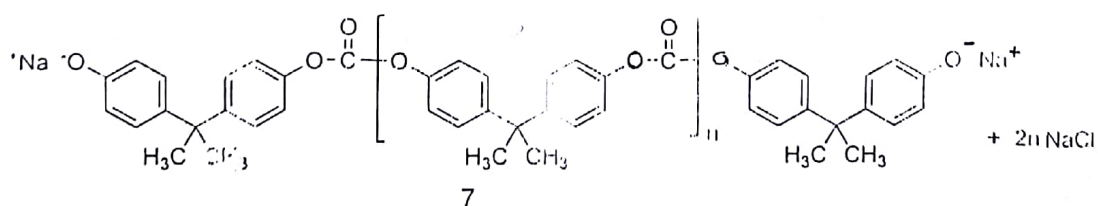
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Or by the reaction of bisphenol-A with phosgene:

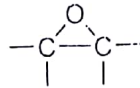




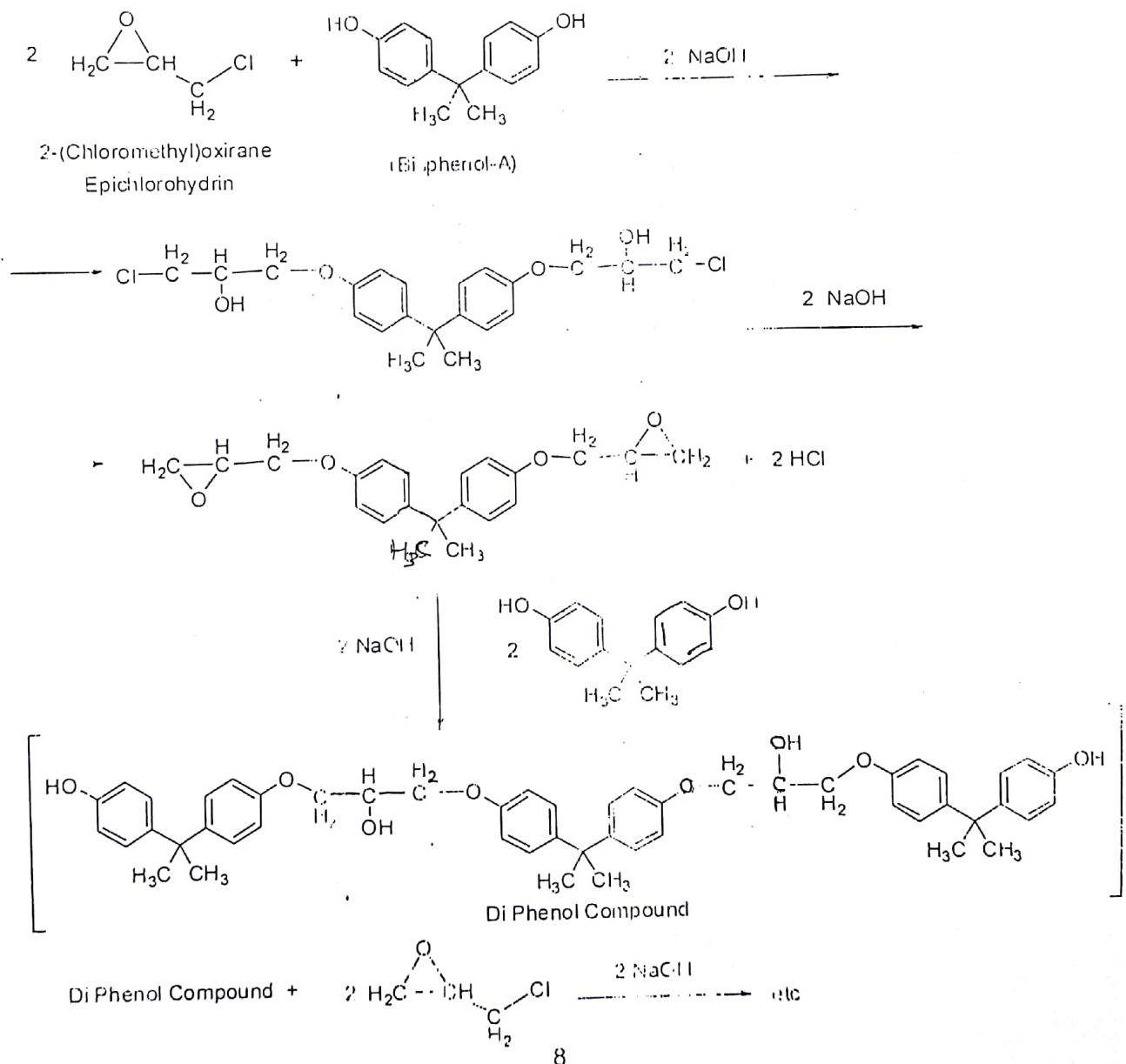
This specific reaction is go on with presence alot of n moles of Bis phenol-A- and n moles of Phosgene, i.e. (Carbonyl compounds) as a general reaction.



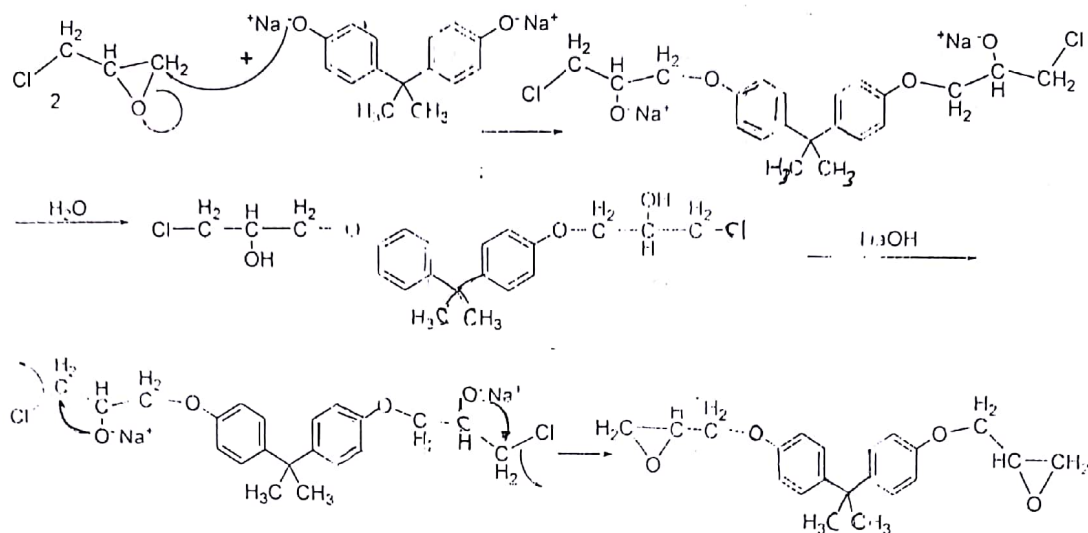
4. "Epoxy compounds", These compounds are very important adhesives, which contains oxygen rings, These rings are very active points due to the ring tension there for there are favorite compounds in wide world applications.



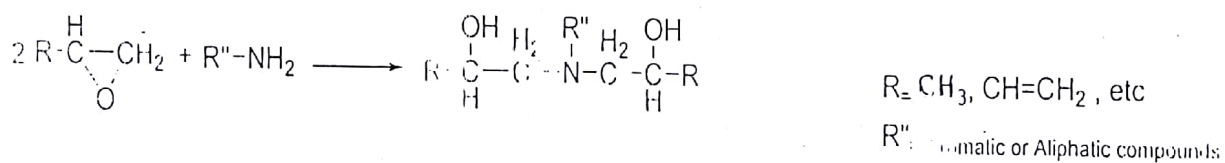
Some of their chemical reactions are: such compounds can react with Bisphenol-A, The latter compound (or polymer of it) are frequently used as **starting products** in the preparation of other polymers;





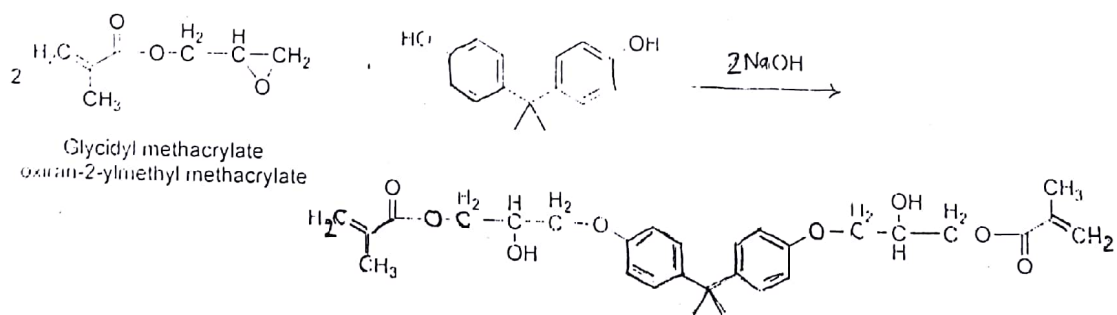


Such epoxides can react with amines. Thus amines can be used to link two epoxy containing molecules together;



Glycidyl methacrylate is another important epoxy compound,

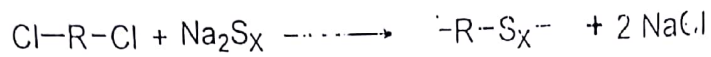
Try to complete the reaction below:



W.H.

Draw the mechanism of the reaction above.

5. "Poly sulphides" the basic constituents of some synthetic rubber materials are formed as follow:

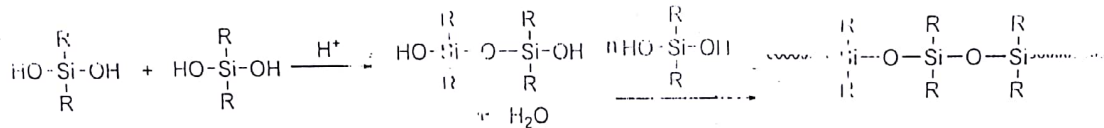


Where  $x > 2$

For example:



6. "Silicones" are inorganic polymers formed by the condensation of silanols, also with presence a lot of silanols Leading to the formation of a polymer chain;



## (2) Addition reactions

An addition reaction occurs between two molecules (either the same or dissimilar) to give a larger molecule without the elimination of a smaller molecule such as water. This type of reaction takes place for vinyl compounds, these are reactive organic compounds containing carbon-carbon double bonds. Some examples are listed in below:

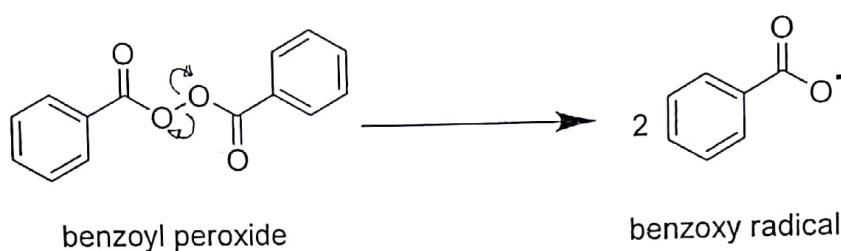
Few common polymers prepared via addition polymerization

Name(s)	Formula	Monomer	Properties
Polyethylene low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	soft, waxy solid
Polyethylene high density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	rigid, translucent solid
Polypropylene (PP) different grades	$-[CH_2-CH(CH_3)]_n-$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid
Poly(vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$	strong rigid solid
Polystyrene (PS)	$-[CH_2-CH(C_6H_5)]_n-$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents
Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2-CF_2)_n-$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[CH_2-C(CH_3)(CO_2CH_3)]_n-$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid
cis-Polyisoprene natural rubber	$-[CH_2-CH=C(CH_3)-CH_2]_n-$	isoprene $CH_2=CH-C(CH_3)=CH_2$	soft, sticky solid

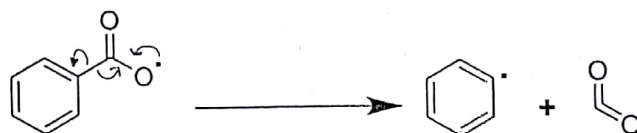
## (2-i) Free radical

### 1. Activation and initiation

The polymerization of a vinyl compound requires the presence of *free radicals*, these are very reactive chemical species having an odd (unpaired) electron. Such free radicals are formed, for example, in the decomposition of a peroxide. Thus under appropriate conditions, a molecule of benzoyl peroxide can yield two free radicals:



These in turn can decompose to give other free radicals:



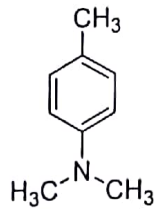
Such chemical species are able to initiate vinyl polymerization; they will be designated  $R^\cdot$

Before initiation occurs, however, the initiator requires to be activated. Activation is achieved by decomposition of the peroxide,

Either by:

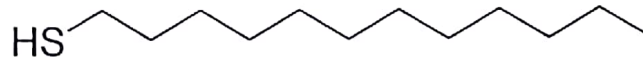
- (a) ultra-violet light, visible light or other electromagnetic radiation such as  $\gamma$ -rays.
- (b) heat.
- (c) other chemicals, such as tertiary amines: (e.g. N,N-dimethyl-p-toluidine,





N,N-dimethyl-p-toluidine

or mercaptans (e.g. lauryl mercaptan " 1-dodecanethiol" )



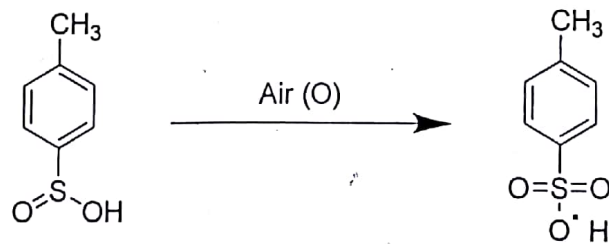
lauryl mercaptan

In practice, methods (b) and (c) above are widely used for dental acrylic polymers, thus these are "heat-cured" and "self-cured" acrylics.

Instead of using a two-component system for activation and initiation, such as peroxide and amine, as in (c) above, a chemical such as p-toluene sulphonic acid May be employed. This produces free radicals which can initiate the polymerization.

### N.B.

p-toluene sulphonic acid can provide free radicals to initiate the polymerization of methyl methacrylate, however, an unstable compound, being readily oxidized in air to p-toluene sulphonic. the latter compound cannot initiate polymerization.

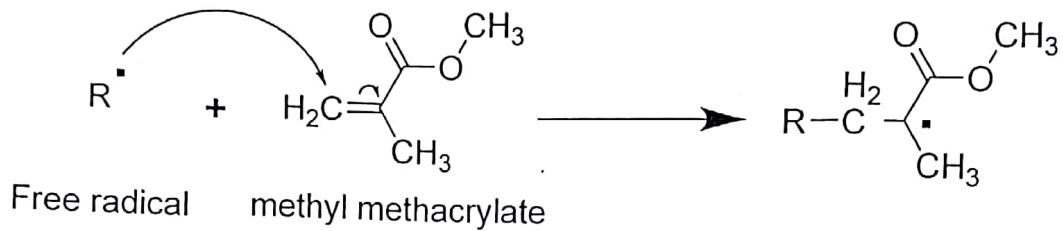


Para toluene sulphonic acid

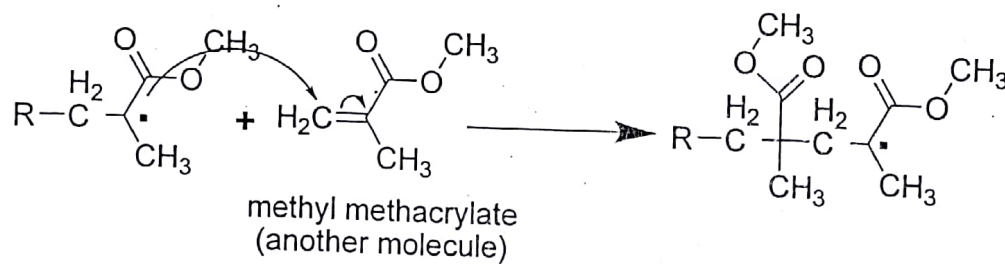
Para toluene sulphonic acid

## 2. Propagation

Free radicals can react with monomer as follows:

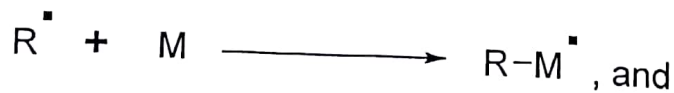


This free radical in turn react with another molecule of monomer:



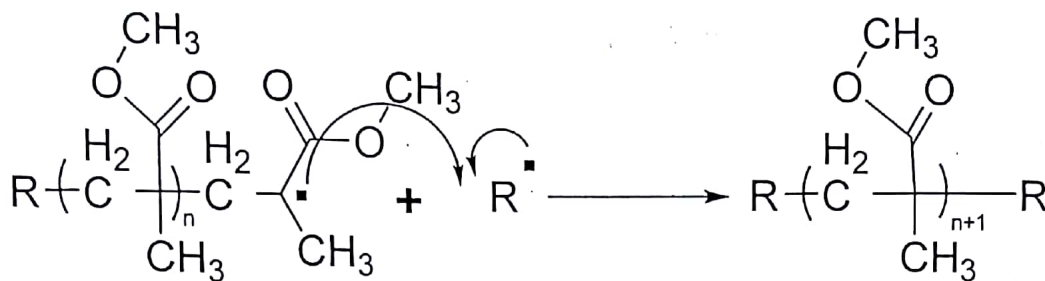
Thus the reaction proceeds, leading to the formation of a polymer chain.

These equations may be written in a simplified form, where M represents a molecule of monomer:

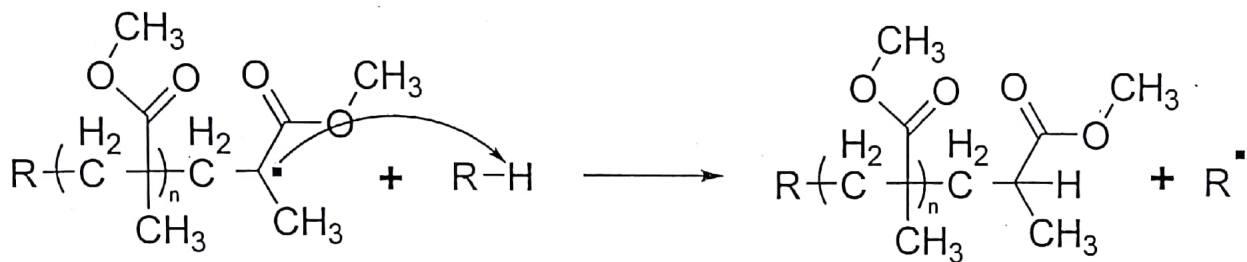


### 3. Termination

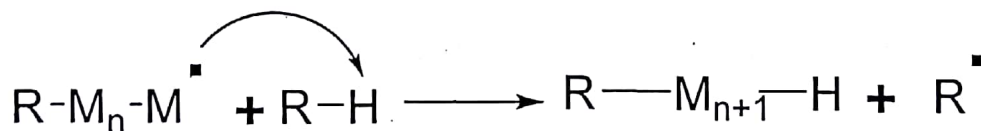
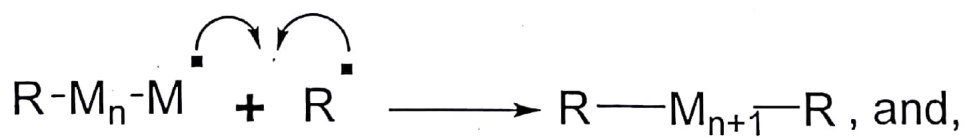
This occurs when two free radicals react to form a stable molecule:



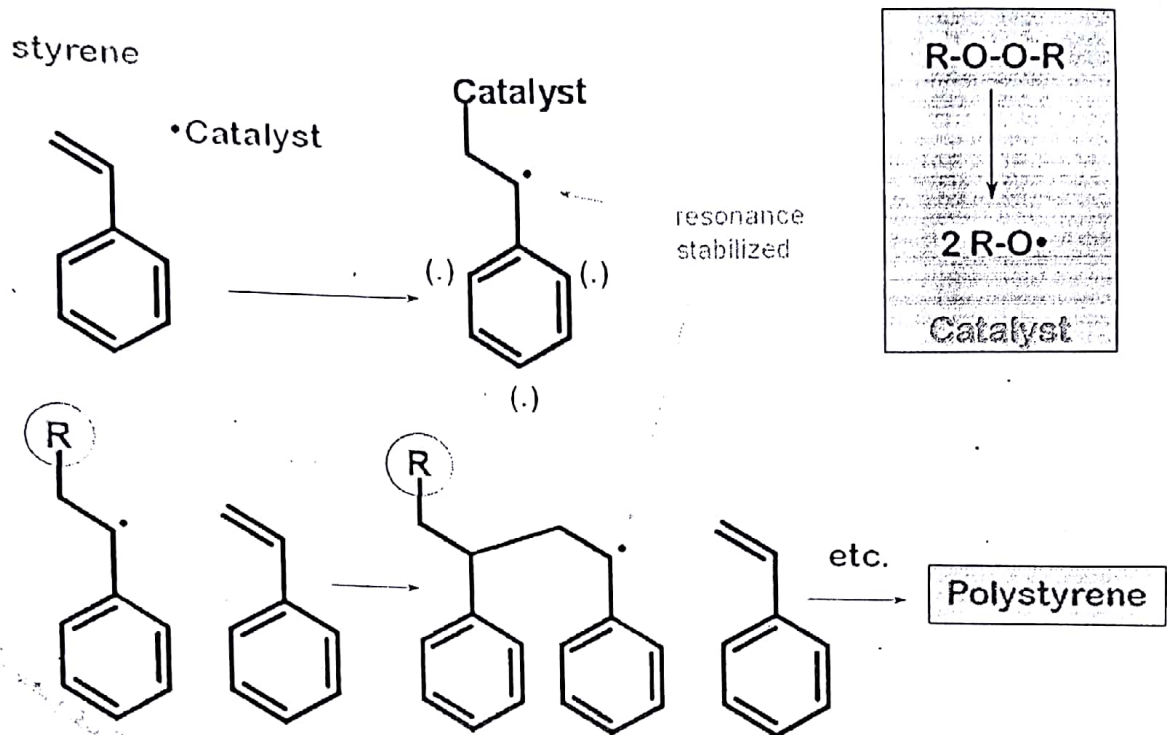
Or by a transfer process:



In simplified form:



# RADICAL MECHANISM



## Polymerization Processes

Addition Polymerization •

No Byproducts –

Usually heat driven –

Condensation Polymerization •

Byproducts produced –

Removal of byproduct controls rate –

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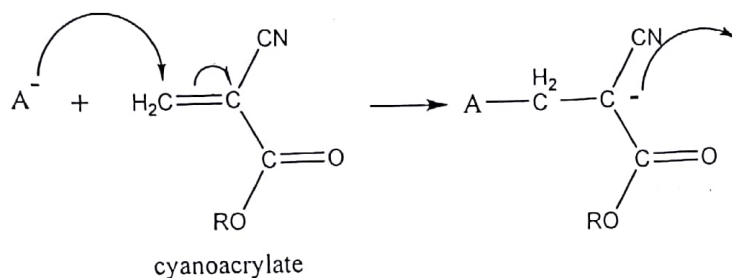


## (2-ii) Ionic polymerization

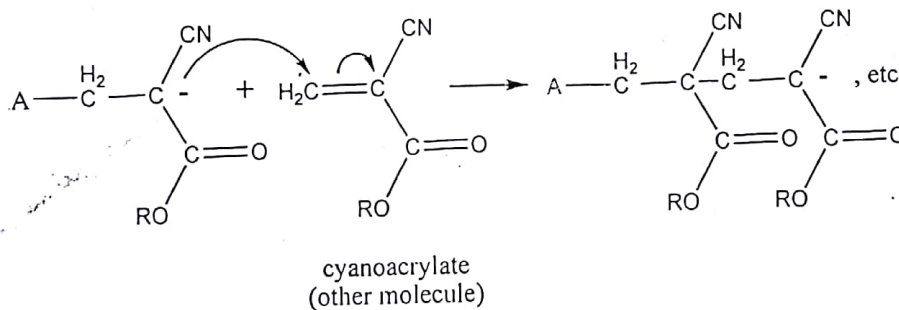
Addition polymerization can occur by ionic as well as by free-radical mechanisms.

### (2-ii)-1 Anionic polymerization

For example the polymerization of cyanoacrylates:



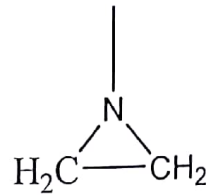
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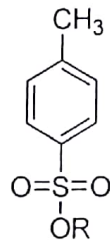
where R may be methyl, ethyl, propyl or butyl group, and  $A^-$  may be, for example,  $OH^-$

## (2-ii)-2 Cationic polymerization

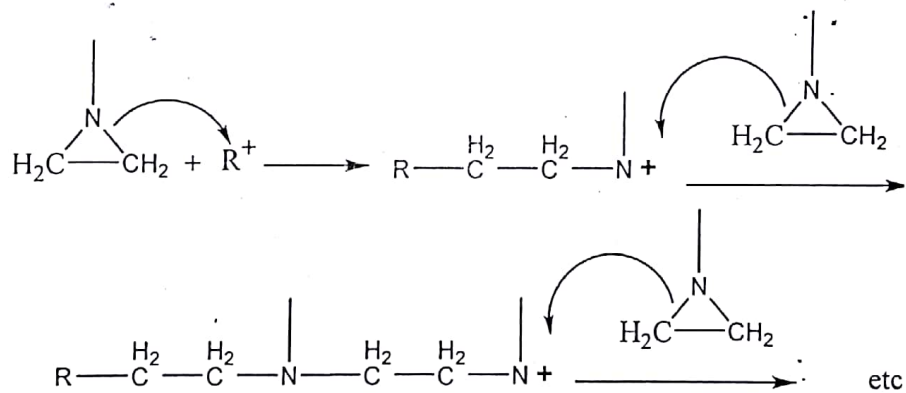
For example Epimine compounds contain the group:



A material such as benzene sulphonate ester:

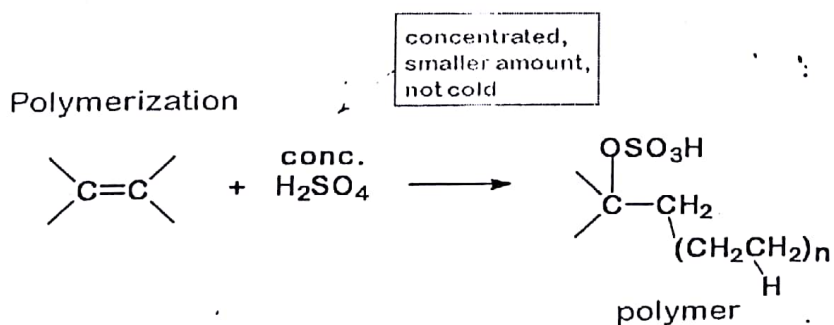


Can supply cations,  $R^+$  which can add to an epimine group causing ring opening:

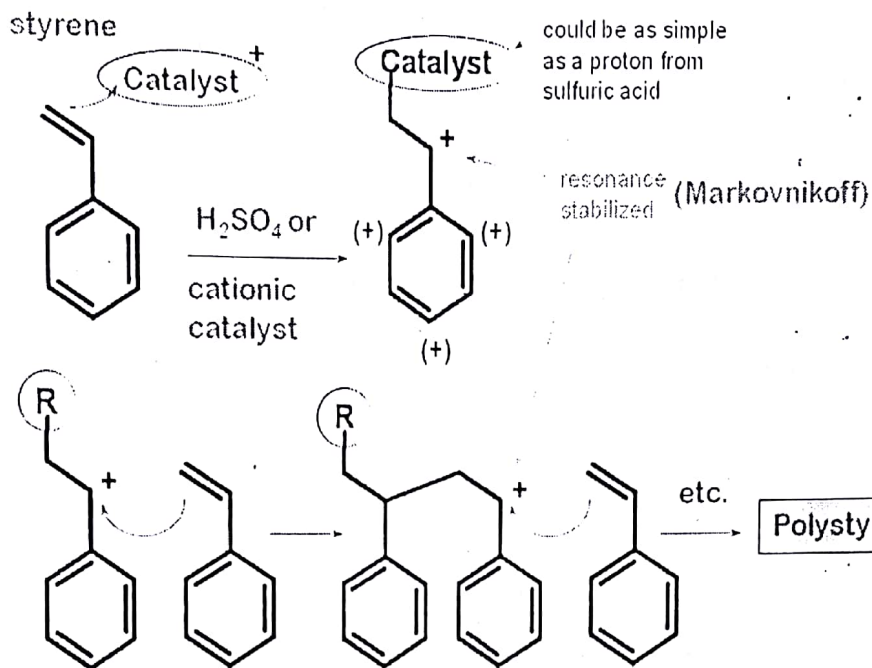


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## POLYMERIZATION

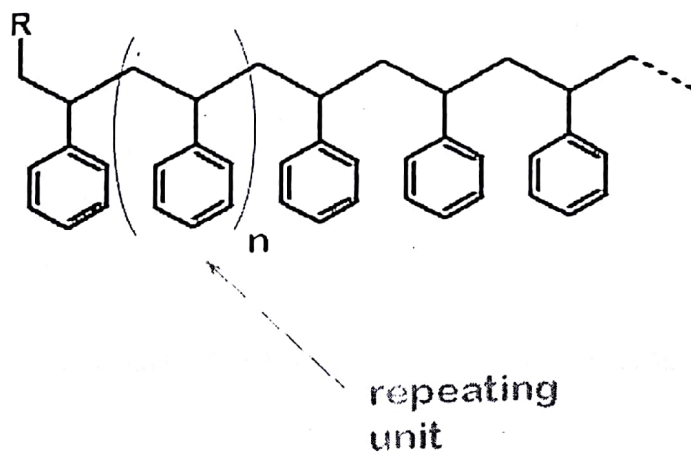


# CATIONIC MECHANISM



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## POLYSTYRENE



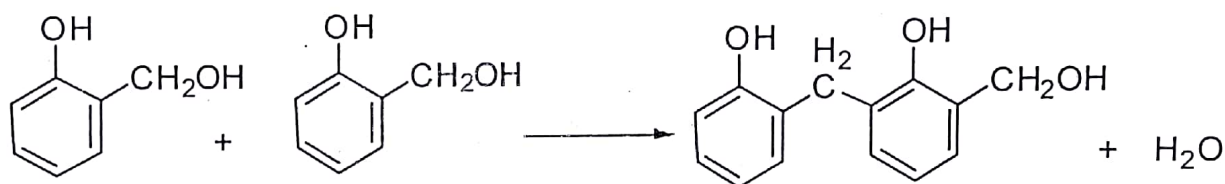
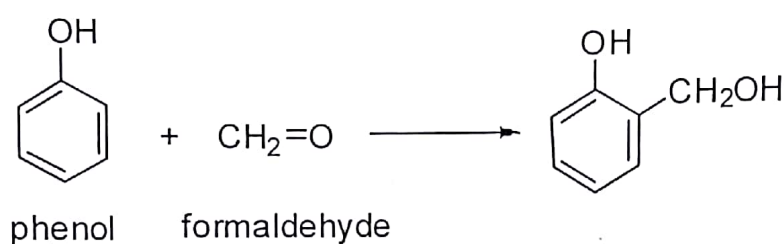
### (2-iii) Cross-Linking

Many reactions can be used to prepare polymers with chemical bonds between different chains. These materials are called cross-linked.

For example:

(a) Some condensation polymers. such as

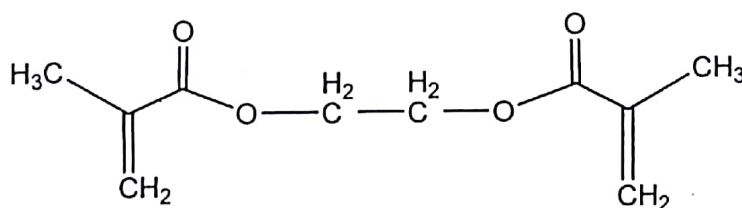
Phenol-formaldehyde.



(b) Dimethacrylate compounds can undergo similar free-radical addition reactions to methyl methacrylate.

These dimethacrylates may be:

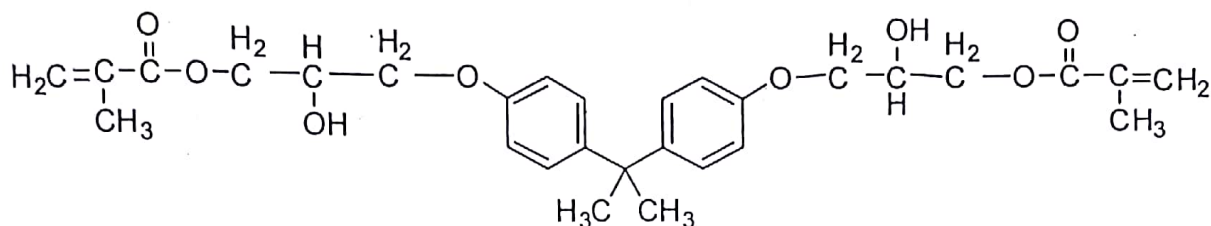
**-Aliphatic**, such as ethylene glycol dimethacrylate:



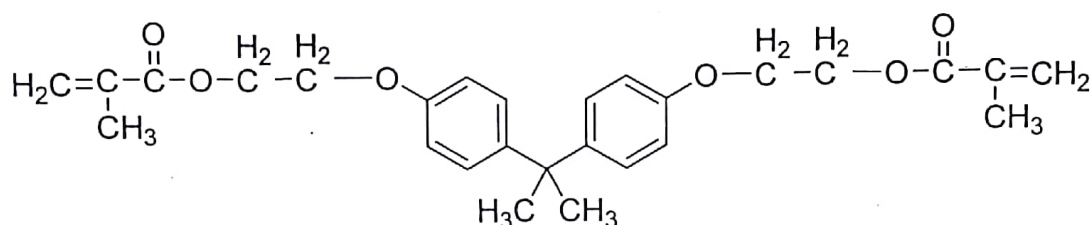
ethane-1,2-diyl bis(2-methylacrylate)



-**Aromatic**, such as **BIS-GMA** "Bowen's resin", an aromatic dimethacrylate used in many composite restorative materials:



A similar dimethacrylate, but without hydroxyl groups has been used also:



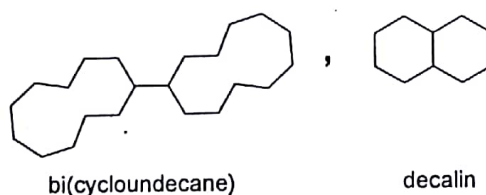
### -Alicyclic

An alicyclic is an organic compound that is both aliphatic and cyclic with one or more rings which may be either saturated or unsaturated and may or may not have aliphatic side chains attached, but **do not** have aromatic character.

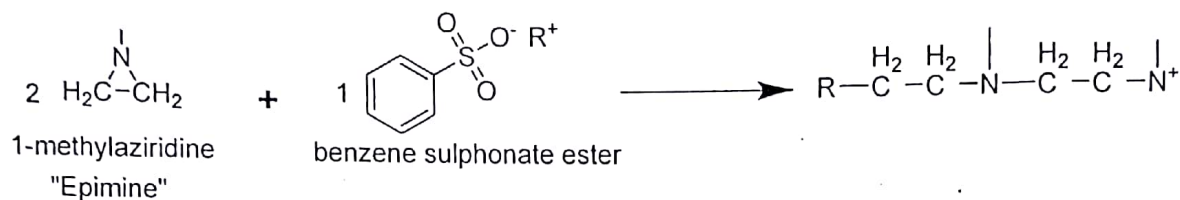
The simplest alicyclic compounds are the monocyclic: cyclopropane, cyclobutane, cyclopentane, and so on.



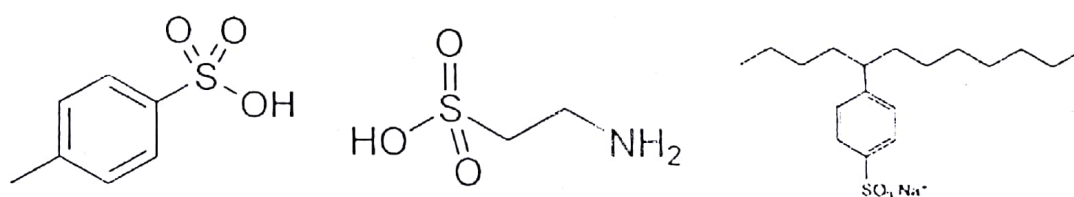
Bicyclic alkanes include bicycloundecane and decalin.



(c) Compounds with two epimine groups can be cross-linked by a benzene sulphonate ester:

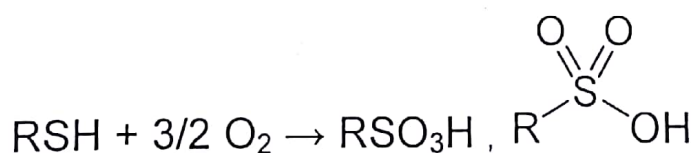


A sulfonic acid refers to the class of organosulfur compounds with the general formula  $\text{RS}(=\text{O})_2\text{-OH}$ , where R is an organic alkyl or aryl group such as:



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The  $\text{S}(=\text{O})_2\text{-OH}$  group is a sulfonyl hydroxide. Antibacterial drugs sulfa drugs are produced from sulfonic acids. Thiols can be oxidized to sulfonic acids:



(d) Elastomers are also cross-linked.

The elasticity property which is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibilities, it's generally having low viscous elasticity compared with other materials.

Temperature effects are also present in the demonstrated elasticity of a polymer. Elastomers that have cooled to a glassy or crystalline phase will have less mobile chains, and consequentially less elasticity, than those manipulated at temperatures higher than the glass transition temperature of the polymer.

## Polymer structure and properties

### 1-Degree of Polymerization and Molecular Weight

the smallest repeatable unit in a polymer molecule is the mer unit (monomer). The size of a molecule is determined by dividing the molecular weight by the mer weight, this number is called chain length or the degree of polymerization (DP).

$$DP = (\text{molecular weight}) / (\text{mer weight})$$

As the (IUPAC), DP is defined as the number of monomeric units in a macromolecule or polymer or oligomer molecule.

For a homopolymer, there is only one type of monomeric unit and the number-average degree of polymerization is given by:

$$DP_n = M_n / M_0$$

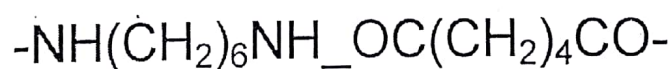
where  $M_n$  is the number-average molecular weight (molecular weight) and  $M_0$  is the molecular weight of the monomer unit.

As an example, a polyvinyl chloride molecule may have a molecular weight of (35,000 g/mol). Since the unit weight for  $C_2H_3Cl$  is  $2*(12) + 3*(1) + 1*(35.5) = 62.5$  g/mol, the DP is  $(35,000 \text{ g/mol}) / (62.5 \text{ g/mol}) = 560$  mers/molecule. In commercial plastics the DP normally falls in the range of 75 to 750 mers per molecule.

For most industrial purposes, DP in the thousands or tens of thousands are desired.

Sometimes, DP is defined as the number of repeat units which joined together in the back bone of the polymers chains where for copolymers the repeat unit may not be identical to the monomeric unit.

For example, in Nylon<sub>66</sub> the repeat unit contains the two monomeric units:



So that a chain length contains of 1000 monomeric units,

The DP equal 1000 by (IUPAC) definition,

while corresponds to 500 repeat units by the second.



## Average molecular weight

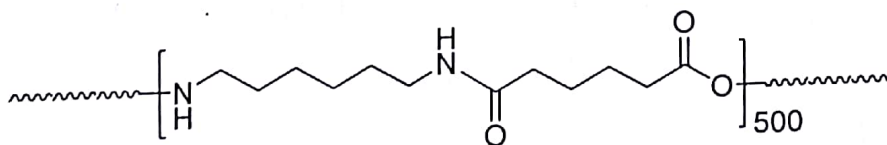
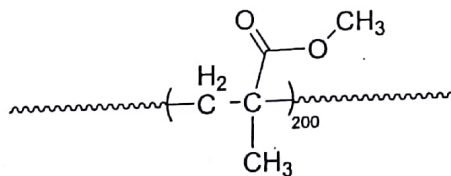
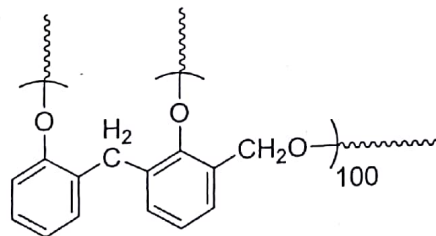
It should be noted that the growth of polymer chains is a **random process**, some chains grow **faster than** other, some are **terminated** before others. Thus not all chains have the same length, As a result, polymer contains a range of molecular sizes they have a distribution of molecular weights. Hence it is necessary to calculate the average degree of polymerization, (i.e., The quoted molecular weight for a polymer is an average value).

The average molecular weight ( $A_{Mw}$ ) is equal to the Degree of Polymerization multiplied by the molecular weight of the repeating unites( $ru$ ).

$$A_{Mw} = DP * Mw_{ru}$$

### W.H.

Calculate the ( $A_{Mw}$ ) of the structure of the following:



## 2-Physical state

In terms of physical state, polymers exist as:

- (a) Elastomers or rubbers,
- (b) Hard amorphous polymers(organic glasses),  
Poly(methyl methacrylate).
- (c) Hard partially crystalline polymers, Polyethylene.
- (d) Fibers, Nylon.

The first two of the above are most relevant to Dentistry.

Rubbers consist of long chain molecules that are coiled and in random thermal motion. These molecules may be linked on to one another at relatively isolated point by covalent bonds(cross-linked).

The specific feature of a rubbery polymer is that when the material is stretched the only work done is in uncoiling the molecules. Thus such materials are easy to deform, the deformation being largely reversible, although these materials are rubbery at room temperature,

the effect of intermolecular forces will increase as temperature decreases, and at a reasonably well defined temperature ( $T_g$ ; the glass transition temperature) the forces become so large as to inhibit ion coiling. Below the glass transition temperature the material will therefore be rigid just like polymers of type (b) above.

If a polymer of type (b) is heated, it is found to lose rigidity at a well defined temperature above room temperature, and become rubbery. In fact the difference between

polymers of types (a) and (b) is that the former have a  $T_g$  well below room temperature, whereas the  $T_g$  of the latter is above room temperature.

One of the most important properties that define a polymer (and hence to an adhesive) is its glass transition temperature, the value of the glass transition temperature is directly related to the mechanical properties (strength, hardness, brittleness and elongation,..... etc.) that the polymer (adhesive / plastic) presents at the temperature that is exposed, you've never seen in winter why some plastics become hard and brittle?, the explanation lies in its glass transition temperature.

Glass Transition Temperature ( $T_g$ ) is defined as the temperature at which the mechanical properties of a plastic / adhesive radically changed due to the internal movement of the polymer chains that form the plastic / adhesive.

### **3-Effect of molecular weight on properties**

In many polymers the chains are held together by secondary or Van der Waals forces and molecular entanglement. Materials of high (**MW**) have a greater degree of molecular entanglement and have greater rigidity and strength and higher values of ( $T_g$  and  $T_m$ ) than low (**MW**) polymers.

### **4. The effect of cross-linking on physical properties**

Cross-linking affects the physical properties of a polymer. A small degree of cross-linking limits the amount of movement of the polymer chains relative to each other when the material is stressed. Thus the deformation is



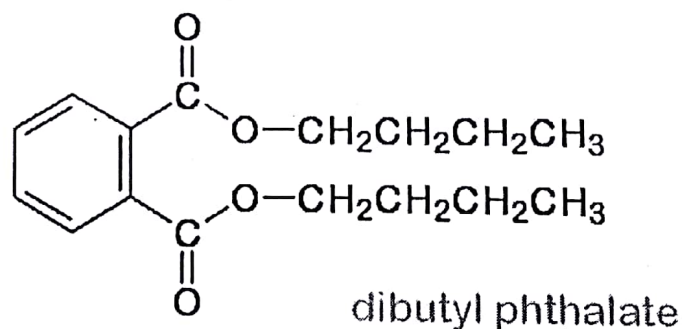
elastic rather than plastic. Also, the polymer may have a higher than value of  $T_g$ . Extensively cross-linked polymer are harder, more brittle and more resistant to the action of solvents than non-cross-linked materials.

## 5-Plasticisers

Liquids are able to penetrate between the randomly orientated chains of a polymer. As a result the molecules are further apart, and the forces between them are less. Such liquids are plasticizers. They soften the material and make it more flexible by lowering its  $T_g$ . If sufficient plasticizer is added, a polymer which is normally glassy at room temperature can have its  $T_g$  depressed to below room temperature, thus making it flexible and rubbery. This principle is used in producing acrylic soft lining materials.

Most polymers of high molecular weight are quite rigid.

These polymers can be softened and made flexible by adding plasticizers, usually dialkyl phthalate esters, such as dibutyl phthalate, a high boiling liquid.



The plasticizer separates the individual polymer chains from one another. It acts as a lubricant which reduces the attractions between the polymer chains.

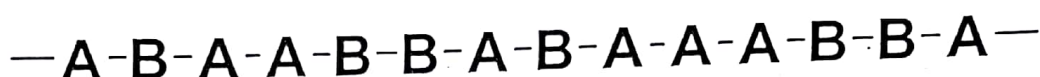
## 6. Copolymers

Polymer chains which two or more different types of monomeric units can be prepared these are termed co-polymers, or Several types of co-polymer are possible, for example, as below, where A and B represent different monomer units:

(a) alternating co-polymer



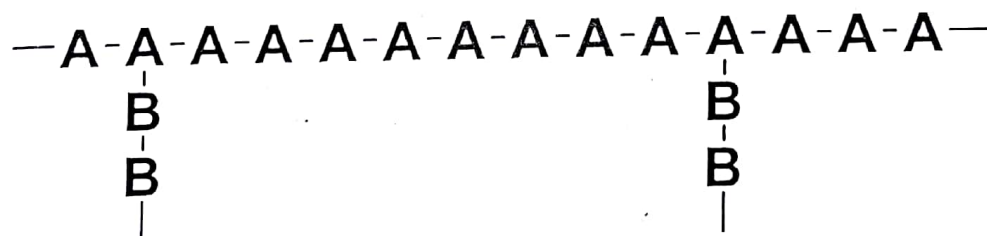
(b) random co-polymer



(c) block co-polymer



(d) graft co-polymer



Co-polymerization processes have enabled chemists to "tailor-make" molecules of predicted properties for special applications.



# THERMOPLASTICS

Thermoplastics can be softened or melted by heat and reformed (molded) into another shape.

Most addition polymers are thermoplastics.

The polymer chains are held together by weak interactions (noncovalent bonds) such as :

van der Waal's forces,  
London dispersion forces and  
Dipole-dipole attractions.

These interactions are disrupted by heating, allowing the chains to become independent of each other.

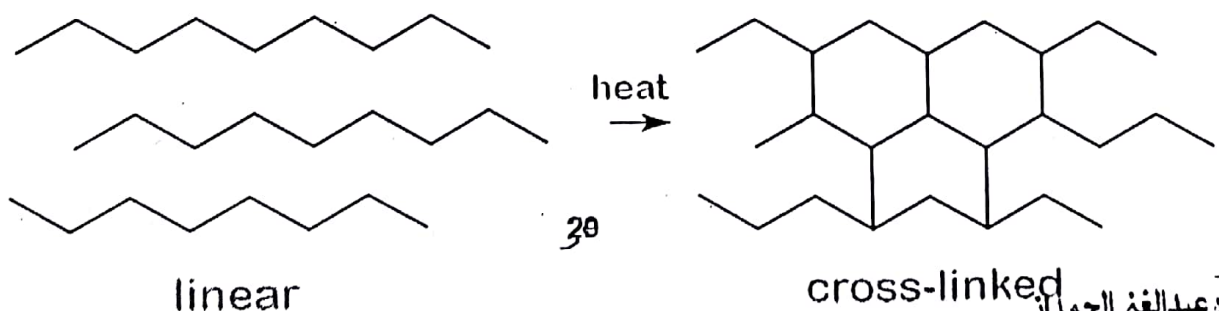
Heating and reforming can be repeated indefinitely (if degradation doesn't occur). This allows recycling.

# THERMOSET PLASTICS

Thermoset plastics melt initially, but on further heating they become permanently hardened.

Once formed, thermoset plastics cannot be remolded, and they cannot be recycled.








On heating, thermoset plastics become cross-linked (covalent bonds form between the chains). The cross-linked chains form a rigid network



د. عماد عبد الغني الحمداني  
04 MAY 2014

## RECYCLING CODES

The code are frequently stamped on the bottom of containers as the following:

	PETE	polyethylene terephthalate	soft drink bottles
	HDPE	high-density polyethylene	milk and beverage containers, products in squeeze bottles
	V	polyvinyl chloride	bottles with cleaning agents in them, some shampoo bottles
	LDPE	low-density polyethylene	thin plastic bags, plastic wrap
	PP	polypropylene	heavy-duty, microwavable containers used in the kitchen
	PS	polystyrene	foam beverage cups, envelope windows
	Other	All other resins, multilayered materials, containers made of other materials	ketchup bottles, snack containers, mixtures where the top differs from the bottom

### Some Common Terms

A retarder is a substance that "slowly" reacts with a radical to form products nearly incapable of reacting with monomer.

An inhibitor is a "retarder" that reacts **rapidly** with active radicals to form **stable** compounds (BX.) unable of addition to monomer completely stops or "inhibits" polymerization.

Chain transfer – An atom is transferred to the growing chain, terminating the chain growth and starting a new chain.

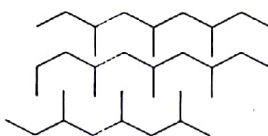
## HIGH-DENSITY POLYMERS

Linear polymers with chains that can pack closely together. These polymers are often quite rigid.



## LOW-DENSITY POLYMERS

Branched-chain polymers that cannot pack together as closely. There is often a degree of cross-linking. These polymers are often more flexible than high-density polymers.



### Methods of fabricating polymers:

#### 1-Condensation polymers

When these used dentally, they were supplied in an intermediate stage of condensation, and moulded by the application of heat and pressure to the required shape; during this process the condensation on process continued.

#### 2-Compression moulding

The products of addition polymerization are usually *thermoplastic*; that is, they soften on heating and harden on cooling, without chemical change, ( contrast to *thermosetting* polymers, which do not soften, but burn or decompose on heating). Thermoplastic polymers can be moulded by the application of heat and pressure.

#### 3-Injection moulding

Industrially, thermoplastic materials are often moulded by heating the polymer until it is soft enough to be injected into a mould of the required shape. This method is used dentally, through not frequently.

#### 4-Dough technique

This method is widely used dentally in the moulding of poly(methylmethacrylate) for dentures. A dough is formed from a mixture of the monomer (liquid) and polymer (powder); this is packed into a mould and the monomer is polymerized under the appropriate conditions of activation and initiation to give a solid material.