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# **RESTORATIVE DENTAL POLYMER MATERIALS**

**A.S. Hurynava**

**For Foreign students of the 1-st year  
on a specialty 1-79 01 07 Stomatology**

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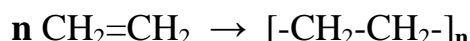
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# I. HIGHMOLECULAR COMPOUNDS. POLYMERS.

## 1.1. GENERAL CHARACTERISTIC OF HIGH MOLECULAR COMPOUNDS. MONOMER, POLYMER, OLIGOMER.

High molecular compounds are large group of natural and synthetic compounds with high molecular weight ranged from several thousand to several million. Their molecules are called macromolecules. A **polymer** is a large molecule (**macromolecule**) consisted of a number of smaller repeating units that are made from molecules called *monomers*.

Typical simple polymer is polyethylene that is a product of ethylene polymerization:

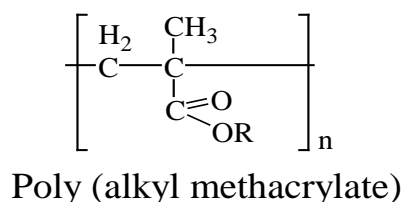
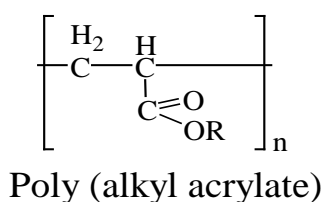


$n$  is a number of monomers and repeating units.

A *simple repeating unit* is a least structural unit repeated many times along macromolecular chain. A *monomer unit* is a repeating unit formed from a starting monomer molecule. The simple repeating unit of polyethylene is  $[-\text{CH}_2-]$ , but the monomer unit is  $-\text{CH}_2-\text{CH}_2-$  made from monomer ethylene.

Polymers affect our life in many ways. One of the most significant ways is in the natural chemistry of life processes. The DNA that is carrier of the genetic information in our cells is a macromolecule formed from four simple molecules known as nucleotides; the proteins which constitute much of the structural framework of muscle and bone, and enzymes which catalyze biochemical reactions are macromolecules formed from some twenty or so simple  $\alpha$ -amino acids; cotton (cellulose) and starch are macromolecules formed from simple carbohydrate molecules. One natural polymers is rubber that is a natural polymer of isoprene contained all Z (*cis*-) double bonds.

Another way is synthetic polymers. For example, polyacrylates made up from esters of acrylic and methacrylic acids:



A sample of a polymer contains the macromolecules with a range of molecular weights rather than a single molecular weight. There are two definitions of polymer molecular weight:

- 1) **Number Average Molecular Weight ( $M_n$ )** is the average mass of Avogadro's number of polymer molecules in a sample;

2) **Weight Average Molecular Weight ( $M_w$ )** is the average mass of a polymer molecule in a sample.

Both of these average molecular weights can be measured by appropriate physical methods, and both give a general idea of the size of the polymer molecules in the sample of polymer. The number average molecular weight  $M_n$  is more widely used. When values  $M_n$  and  $M_w$  of a polymer are close to each other, the polymer contains the molecules with very similar molecular weight. This polymer is characterized with narrow molecular weight distribution. If the values  $M_n$  and  $M_w$  are the same, polymer is termed **monodisperse**. When the values  $M_n$  and  $M_w$  are very different, the polymer consists of a mixture of molecules with a wide molecular weight distribution. This polymer is termed **polydisperse**. The ratio of  $M_n$  and  $M_w$  is measured as the **polydispersity** of the polymer.

The molecular weight of polymer macromolecules is characterized by **degree of polymerization (n)**. It is a measure of **the average number of monomer units in each polymer molecule**. Then molecular weight of polymer is obtained as:

$$\mathbf{M \text{ (polymer)} = n \mathbf{M \text{ (monomer unit)}}$$

Reactions occurring with a high degree of polymerization lead to high molecular weight polymers (high polymers). Polymerization reactions resulting from macromolecules with relatively low molecular weights are designated as occurring with a low degree of polymerization.

The extent to which the monomer has been consumed is called **degree of conversion**. The course of polymerization is characterized in terms of the amount of high polymer present at low conversion.

Macromolecules are broadly categorized by size based on degree of polymerization:

1. **dimers** contain two monomer units;
2. **trimers** contain three monomer units;
3. **tetramer** contain four monomer units;
4. **oligomers** are small macromolecules with 10-50(100) monomer repeat units;
5. **polymers** are macromolecules with more than 100 monomer repeat units.

Polymers may contain many thousand of monomer units of the polymer molecule; natural macromolecules contain millions of repeating units. Oligomers, contained different number of monomer units, have different physical and chemical properties.

## 1.2. POLYMER NOMENCLATURE.

There are some logical IUPAC rules for naming polymers. Chemists name the monomer and then add the **poly-** prefix. Usually chemists use common names of monomers more often than their IUPAC names. If the monomer's name includes more than one word, or if a letter or number precedes the name, the monomer's name is enclosed in parentheses (Table 1).

**TABLE 1. The name of monomers and polymers.**

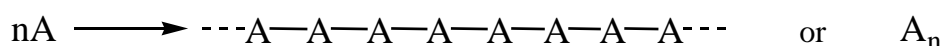
Monomer	Monomer name	Polymer	Polymer name
$\text{H}_2\text{C}=\text{CH}_2$	Ethylene	$\left[ \begin{array}{c} \text{H}_2 \\   \\ \text{---C---C---} \\   \\ \text{H}_2 \end{array} \right]_n$	Polyethylene
$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{CH}_3$	Propylene	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{CH}_3 \end{array} \right]_n$	Polypropylene
$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{CN}$	Acrylonitrile	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{CN} \end{array} \right]_n$	Polyacrylonitrile
$\text{H}_2\text{C}=\underset{\text{COOCH}_3}{\text{C}}-\text{CH}_3$	Methyl methacrylate	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{COOCH}_3 \end{array} \right]_n$	Poly(methyl methacrylate)
$\text{H}_2\text{C}=\underset{\text{O}-\text{C}(=\text{O})-\text{CH}_3}{\text{CH}}$	Vinyl acetate	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{O}-\text{C}(=\text{O})-\text{CH}_3 \end{array} \right]_n$	Poly(vinyl acetate)
$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{Cl}$	Vinyl chloride	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{Cl} \end{array} \right]_n$	Poly(vinyl chloride)
$\text{H}_2\text{C}=\underset{\text{C}_6\text{H}_5}{\text{CH}}$	Styrene	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---C---C---} \\   \quad   \\ \text{H}_2 \quad \text{C}_6\text{H}_5 \end{array} \right]_n$	Polystyrene
$\text{HO}-\underset{\text{H}_2}{\text{C}}-\underset{\text{H}_2}{\text{C}}-\text{OH}$ and	Ethylene glycol	$\left[ \text{O}-\underset{\text{H}_2}{\text{C}}-\underset{\text{H}_2}{\text{C}}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O} \right]_n$	Poly(ethylene terephthalate)
$\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OH}$	Terephthalic acid		

### 1.3. CLASSIFICATION OF POLYMERS.

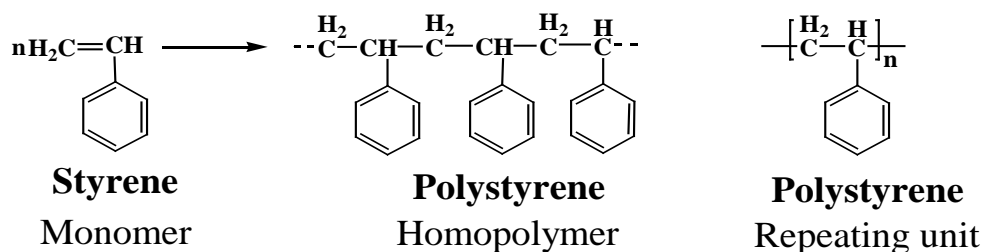
#### 1.3.1. Classification of polymers according to the composition.

The composition of polymer is a sequence of monomer repeating units that are covalently bonded together.

Repeating units of polymers have a variety of possible structures. When all repeating units in a polymer have the same structure, this polymer is called a **homopolymer**

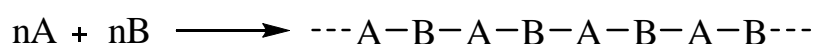


An example of a homopolymer is polystyrene:

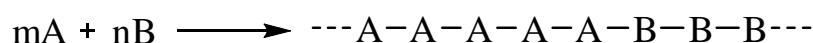


When the polymer chain consists of different repeating units, the polymer is called a **copolymer**. There are three types of copolymers:

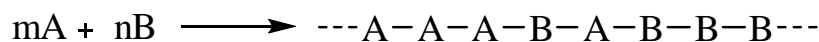
1. Alternating copolymer



2. Block copolymer

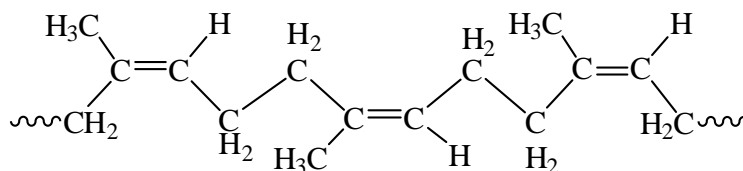


3. Random copolymer



### 1.3.2. Classification of polymers according to the nature of elements of main chain.

**Homochain polymers (carbochain)** have only carbon atom in a main chain of polymers. Examples are polyvinyl polymers like polyethylene, polypropylene, polyacrylonitrile, polyvinylchloride, polyacrylates, polystyrene (see point 1.2.) and polybutadienes like natural rubber.

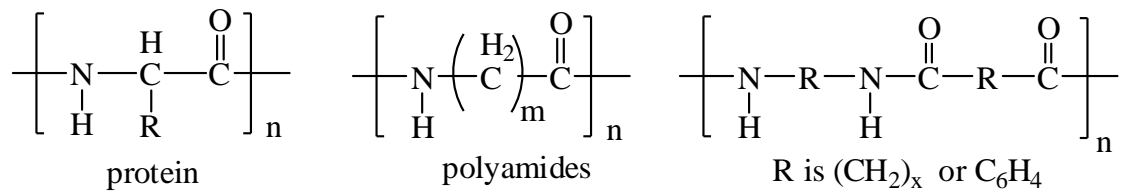


Natural rubber: *cis*-1,4-polyisoprene

**Heterochain polymers** have different atoms in a main chain of polymer. There are natural, inorganic and element-organic polymers. Heterochain polymers are also classified based on nature of heteroatom or functional group.

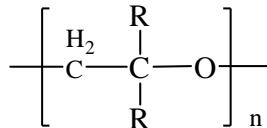
Examples of nitrogen containing polymers are both natural protein and synthetic polyamides (both are polyamides).



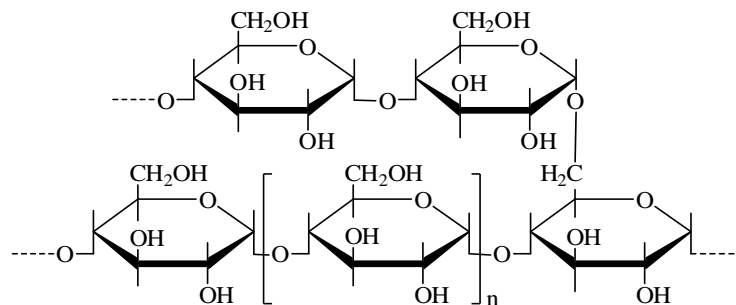


Examples of oxygen containing polymers are:

-ethers like polyethylenoxide

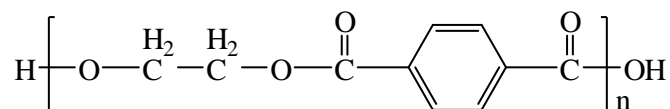


-polyacetals like natural polysaccharides, for example, amylopectin of starch ( $n = 20-25$ ) and glycogen ( $n = 10-12$ )

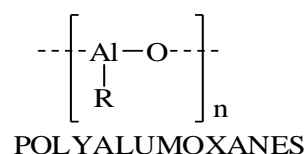
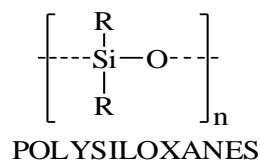


-nucleic acids.

-esters like polyethylenetherephtalate

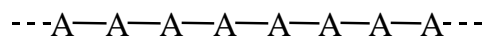


Element-organic polymers have only heteroatom in a main chain. For example polysiloxanes, polyalumoxanes

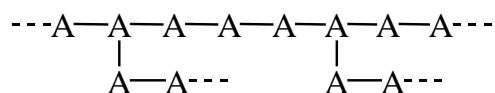


### 1.3.3. Classification of polymers according to structural characteristics.

1. A **linear polymer** is a molecule with a series of connected repeating units.

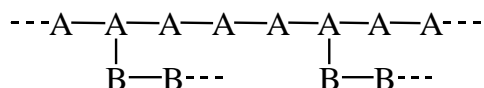


2. A **branched polymer** has bonds branching from the backbone of a linear polymer.

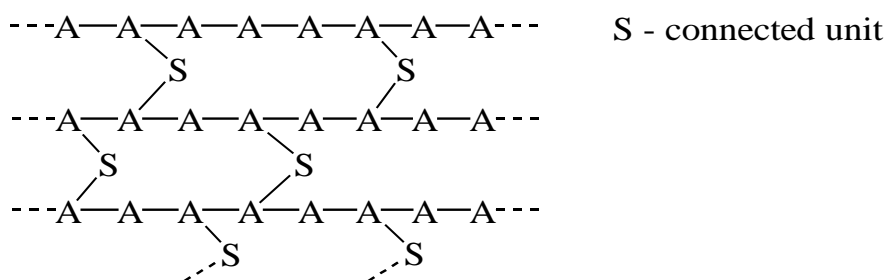


Examples of branched homopolymers are naturally occurring homopolysaccharides like amylopectin of starch and glycogen (see point 1.3.2.).

One polymer may be joined to the other as a branch from the main chain of the other polymer. The formed copolymer is called also a **graft copolymer**.



3. **Cross-linked polymers** are linear polymer molecules joined by a branching connection. Example is vulcanized rubber.

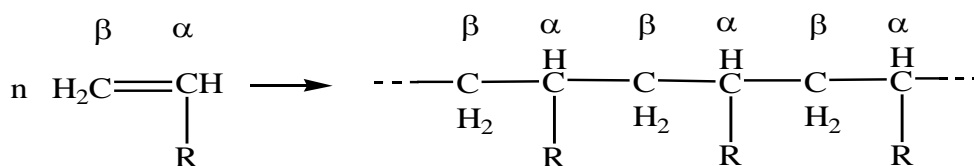


#### 1.3.4. Classification of polymers according to the constitutional isomerism and stereoisomerism.

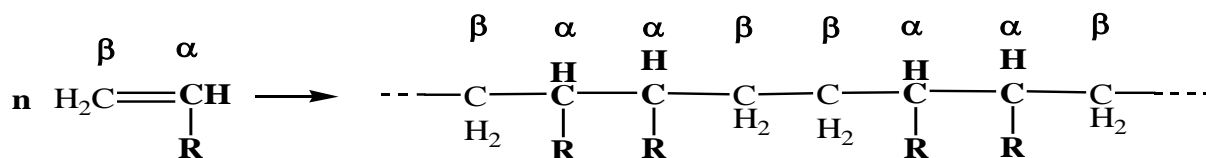
The three-dimensional structure and shape of macromolecule depend on its chemical structure and arrangement of monomer units and side chains to each other in a space. There are **regular** and **irregular** polymer structures. The **regular polymer** has the same three-dimensional structure of alternate monomer units along macromolecular chain. Change of this alternation lead to **irregular polymer** structure. Regularity and irregularity depend on type of addition and configuration of monomer units.

Polymerization of alkenes  $\text{CH}_2=\text{CH-R}$  lead to different way of addition:

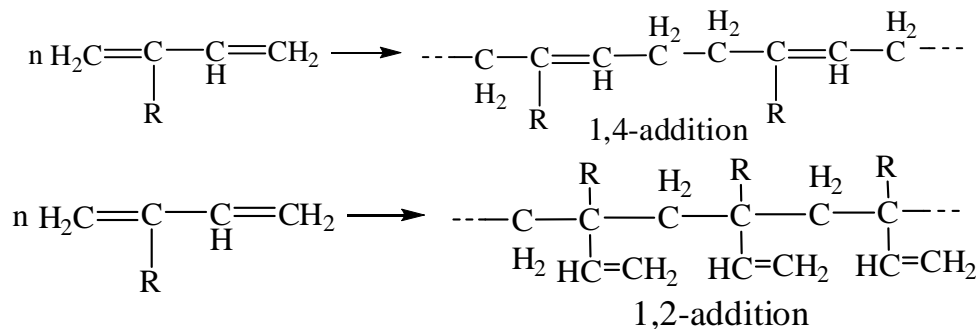
1. “Head to tail” ( $\alpha,\beta$ -addition)



2. “Head to head” ( $\alpha,\alpha$ -addition) and “tail to tail” ( $\beta,\beta$ -addition)

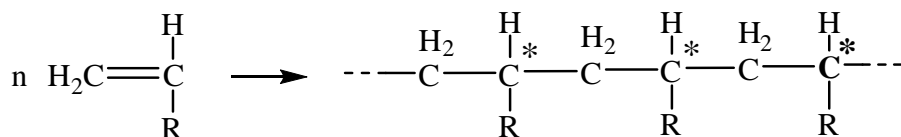


$\alpha,\beta$ -Addition,  $\alpha,\alpha$ -addition and  $\beta,\beta$ -addition form regular polymer. Polymerization of 1,3-butadienes by 1,4- or 1,2-addition forms regular polybutadienes.



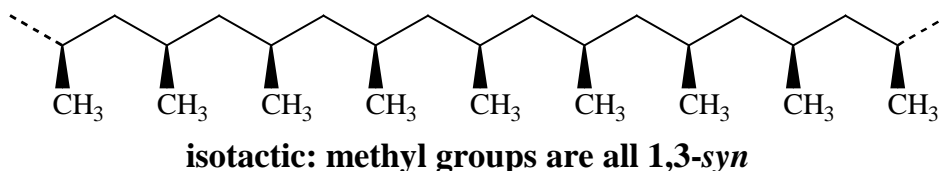
3. Random addition lead irregular alternation of  $\alpha,\beta$ -,  $\alpha,\alpha$ - and  $\beta,\beta$ -addition of poly ethylenes and 1,4-, 1,2-addition of poly butadienes.

The polymerization of monosubstituted alkenes involves the formation of a new chiral center with every molecule of alkene added to the growing polymer chain.

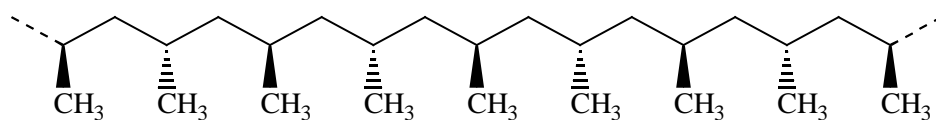


The stereochemical relationship among the side groups on the backbone of the polymer chain is called **tacticity**. There are three general ways in which every new chiral center can be introduced:

1. In the structure of an **isotactic polymer** the new chiral center is introduced with a configuration the same as that of the previous chiral center. An isotactic polymer arranges all its substituents on the same side of the polymer chain in a zig-zag conformation.

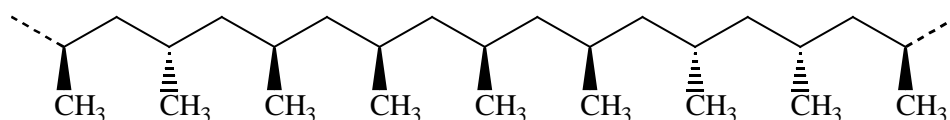


2. In the structure of a **syndiotactic polymer** the new chiral center is introduced with a configuration opposite to that of the previous chiral center. The substituents of a syndiotactic polymer are on alternating sides of the zig-zag structure.



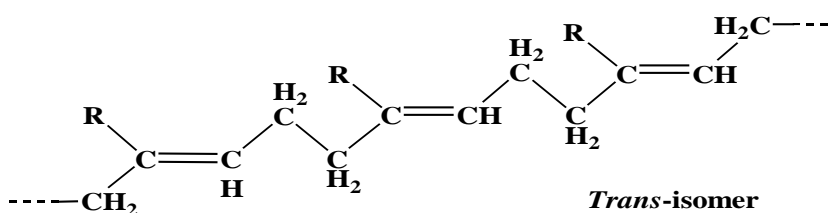
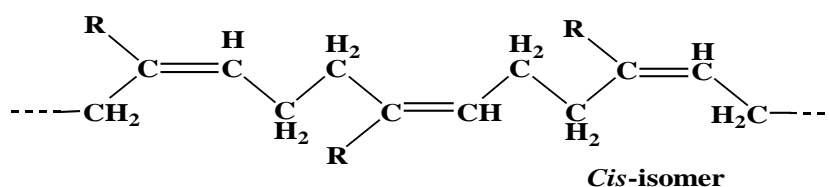
**syndiotactic: methyl groups are all 1,3-*anti***

3. The **atactic polymer** has its substituents arranged randomly on the chain.



**atactic: methyl stereochemistry is random**

Polymerization of conjugated alkadienes unlike simple alkenes leads to polymers (polybutadienes) contained double bond of every repeating monomer unit. There are *cis*-, *trans*-isomerism of monomer units.



Both *cis*- and *trans*-isomers are stereo regular. Random alternation of *cis*- and *trans*-configuration of monomer repeating units characterizes stereo irregular polymer.

### 1.3.5. Classification of polymers according to the melting behavior.

According to melting behavior polymers are classified into **thermoplastic** and **thermosetting polymers**.

The linear polymers become plastic at high temperatures and can be cast into a desired shape. Polymer materials are called **thermoplastic** if the cycle of heating, melting and casting into shape can be repeated many times.

Cross-linked polymers rather than a linear structure tend not to melt. Rather, they decompose in heating. These materials are called **thermosetting polymers**. They cannot be heated and molded, so their use requires them to be in the final shape when the polymerization reaction occurs. Once a thermosetting polymer has cooled in a particular shape, its shape cannot be altered by

heating. They tend to be stronger and tougher than thermoplastic materials. Most dental polymers are cross-linked and are thermoset.

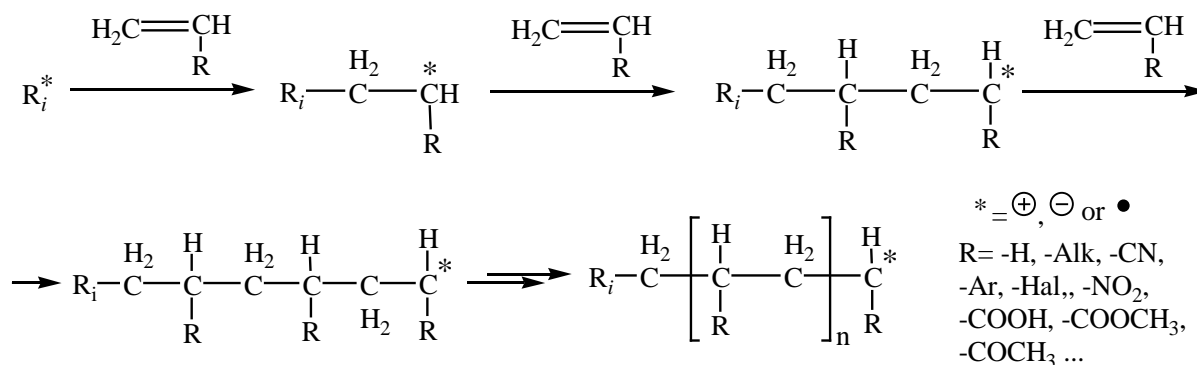
## II. GENERAL PRINCIPLES OF POLYMERIZATION REACTIONS.

### 2.1. TYPES OF POLYMERIZATION REACTIONS.

The chemical reaction that links the monomer together to produce a polymer (macromolecule) is called **polymerization**. There are two types of polymerization reaction mechanisms:

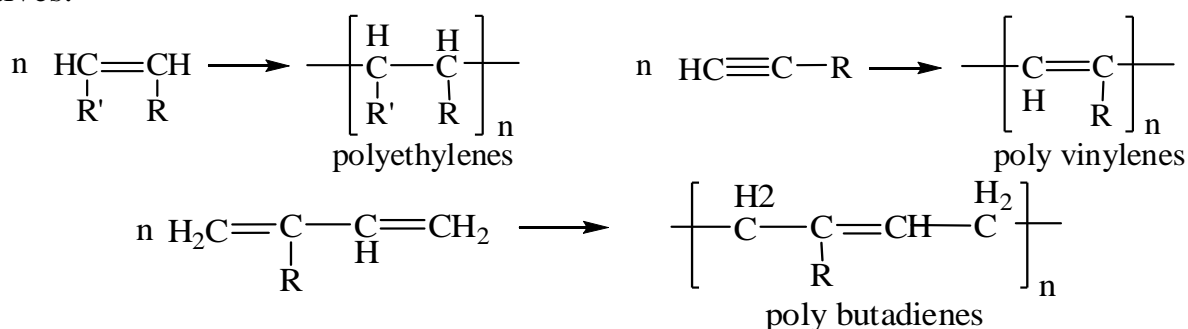
1. **Chain-growth polymerization (or addition polymerization).**
2. **Step-growth polymerization (or condensation polymerization).**

In a **chain-growth polymerization** one monomer reacts with another monomer that contains the same functional groups. The growing polymer chain is extended by addition reaction: the addition of reactive species – a free radical, a carbocation, or a carbanion – to the  $\pi$ -bond of an unsaturated monomer. In a result every monomer unit loses one  $\pi$ -bond. Chain-reaction polymerization of alkene monomers lead to formation of saturated macromolecules.



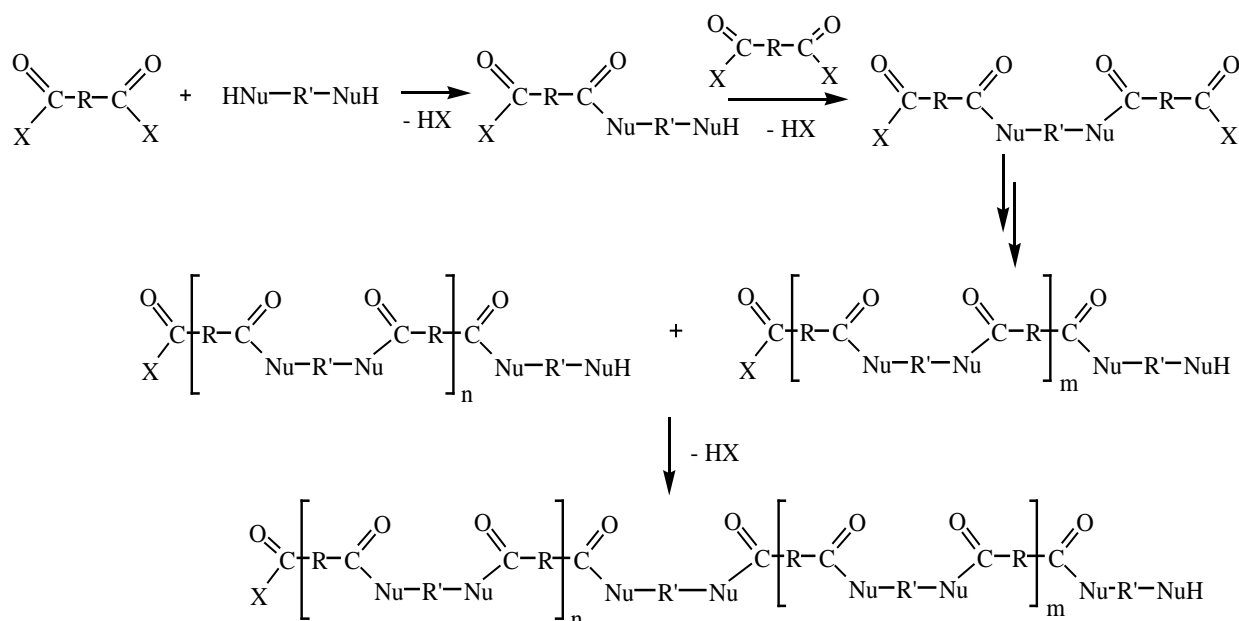
The main chain of the additional polymer doesn't have any functional group. Functional group can be only in a side chain, and they determine the chemical and physical properties of resulting polymer.

There are polymerizations of ethylene, acetylene and butadiene derivatives.

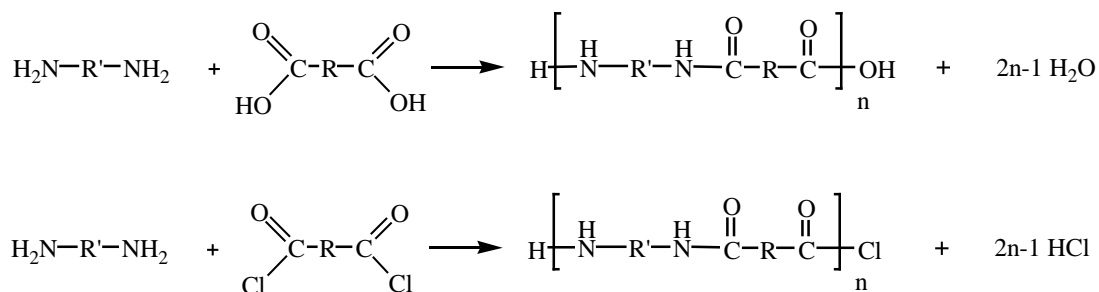


**A step-growth polymerization** takes place between monomers containing different functional groups. In the reaction mixture each functional group type can react with the other type but not with itself. The chain begins to grow when one monomer links to another monomer containing the other functional group type. The first monomer then reacts with the end of this two unit chain.

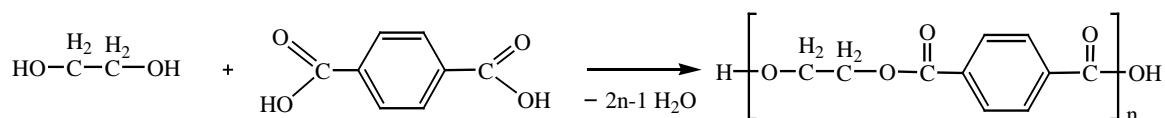
The polymer chain grows by the substitution reaction between the different functional groups with the elimination of one small molecule per monomer during each reaction. The polymer chain is extended not only during the condensation of monomer molecules with the growing macromolecule. Two growing polymer chains also frequently condense to form a larger macromolecule provided that the required two functional groups are present and accessible for reaction.



For example, the condensation polymerization of diamines and dicarboxylic acids (or their acid chlorides) lead to form poly amides.



The condensation polymerization of diols (ethanediol) and dicarboxylic acids (terephthalic acid) lead to form poly esters like poly (ethylene terephthalate).



Differences between two mechanisms are summarized in Table 2. In chain-reaction polymerization, the rate of polymerization depends on the number of active sites available for polymerization. The rate of polymerization is zero until the polymerization is initiated, and it rapidly rises to a maximum value limited by the number of active sites available. While the reaction is proceeding, its rate remains more or less constant until all the initiator is consumed. At this time it slowly decreases as the available monomer and the number of growing chains decreases. In contrast to this, the rate of polymerization in a step-reaction polymerization depends on the number of functional group available to participate in the polymerization reaction. This number is at its maximum value at the beginning of reaction, the rate of polymerization decreases continuously during reaction as the available functional groups are consumed.

**Table 2. Experimental Consequences of Mechanism of Polymerization.**

<b><u>Chain-Reaction Polymerization</u></b>	<b><u>Step-Reaction Polymerization</u></b>
<b>A. Chain Growth</b> Addition of monomer to a small number of active centers.	Coupling of any two species with the appropriate functional groups.
<b>B. Rate of Polymerization</b> Initial rate is zero; it increases rapidly to a maximum value which remains constant until the initiator is consumed, after which it slowly decreases. Monomer is still present at high conversion.	Initial rate is maximum; rate decreases continuously during the reaction. Monomer is rapidly converted to small oligomers which then slowly condense. Monomer is absent even at low conversion.
<b>C. Degree of Polymerization</b> High polymer present even at low conversions. Degree of polymerization may be extremely high.	High polymer not present until high conversion. Degree of polymerization seldom high.

## 2.2. CHAIN-REACTION (ADDITION) POLYMERIZATION

Chain-reaction polymerization, or addition polymerization, is mainly used for production of several economically important polymers: polyethylene, polypropylene, poly(vinyl chloride), polystyrene and many acrylic polymers.

The mechanism for a chain-growth polymerization involves initiation, propagation and termination steps.

Chain-reaction polymerization occurs through a reactive intermediate which may be a free radical, a cation or an anion. There are ionic or radical chain-growth polymerizations.

### **2.2.1. Free radical chain-growth polymerization.**

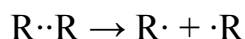
#### **2.2.1.1. Mechanism of free radical polymerization.**

In free radical polymerization, formation of macromolecule is initiated by adding free radical to an alkene or alkyne. Several polymers, such as polyvinyl chloride, polystyrene, acrylate polymers, and polyethylene, are made by free radical addition reactions. The most useful monomers for free radical chain-reaction polymerization are monosubstituted alkenes or 1,1-disubstituted alkenes. 1,2-Disubstituted ethylenes or more highly substituted ethylene derivatives are usually resistant to free radical polymerization.

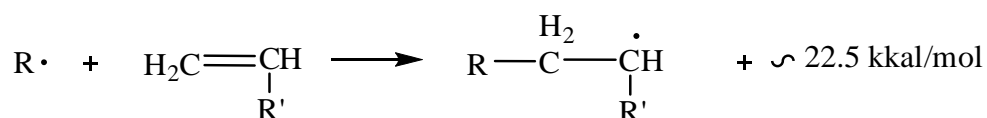
Free radical chain-reaction polymerization is a typical free radical chain reaction: it requires initiation to generate the chain carriers, and it will continue until the reaction chain is terminated by a reaction or reactions which remove the chain carriers from the reaction system. So, free radical polymerization reaction involves three steps: initiation, propagation and termination steps.

#### **1. Initiation step.**

The initiation can be thought of as two reactions. The first involves the homolytic cleavage of initiator molecule to form a free radical:



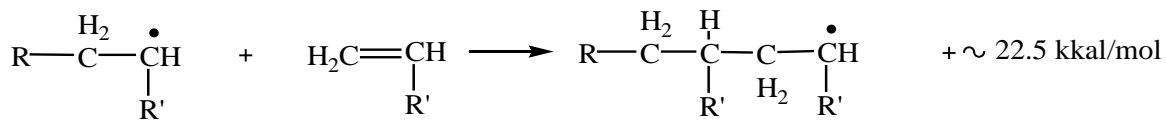
In the second reaction the free radical adds to the  $\pi$ -bond of the monomer molecule to make single C-C bond and another free radical on the end of the growing chain. So, the first "link" in the growing chain has been added.



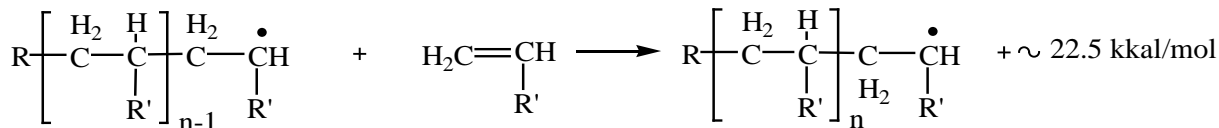
#### **2. Propagation step.**

Propagation step is the growth or lengthening of the chain. The free carbon radical of the "initiated chain" is added to the monomer and the chain is one monomer longer. The addition follows Markovnikov's rule: the more stable of two isomeric radicals are formed as major product. It is secondary or tertiary radical. The product is a free radical, so it can be added to the next monomer molecule to give a new radical.





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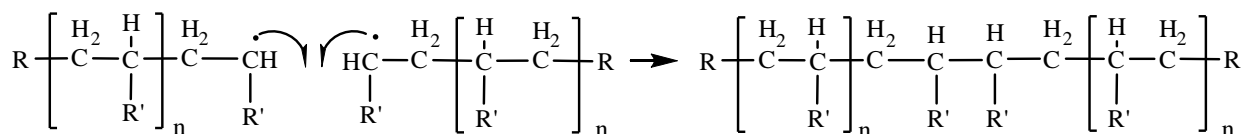


The addition reaction is repeated until all monomers are consumed or until the growth of the free radical polymer chain is terminated when the chain carrier is lost.

### 3. Termination step.

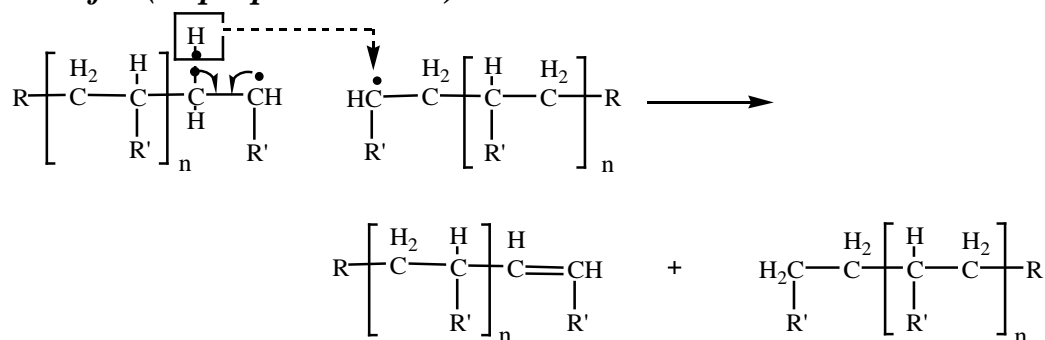
There are several potential chain termination reactions, but most common are two types. ***In the first type of termination reaction***, the free radical chain carriers are removed from reacting system by ***free radical coupling (combination)*** or ***atom transfer (disproportionation)*** to form non-radical product.

***Free radical coupling (combination):***



In a combination reaction two free radicals, either of the same or different lengths are combined to form a stable molecule.

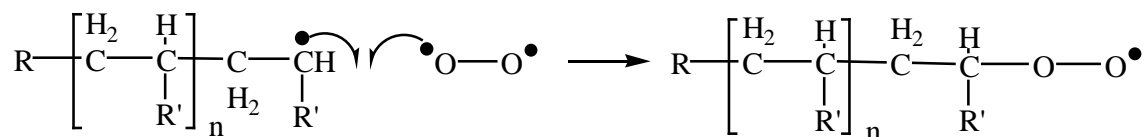
***Atom transfer (disproportionation):***



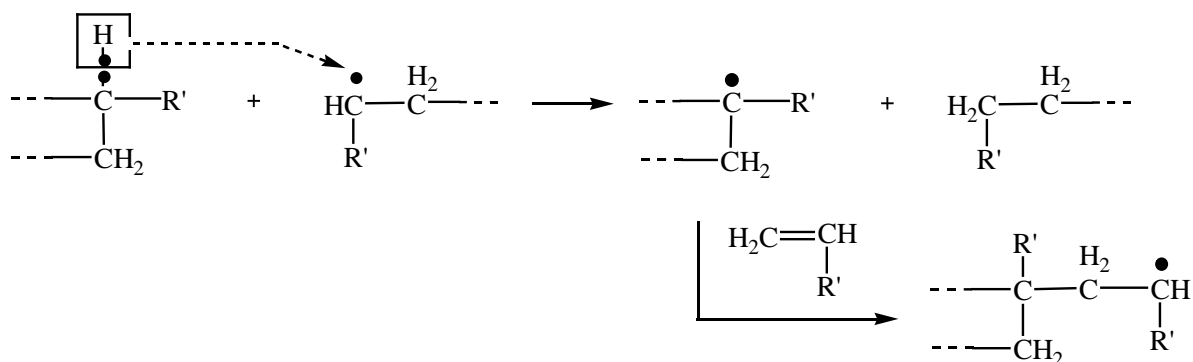
In a disproportionation reaction, one radical is oxidized to an alkene, while another is reduced to an alkane.

***In the second type of termination reaction***, the reactive free radicals react with molecules to give a new free radical, which is not reactive enough to add to the monomer, and the chain growth is halted. Such a powerful terminator of free radical chain reactions is molecular oxygen, because it is a stable biradical. The

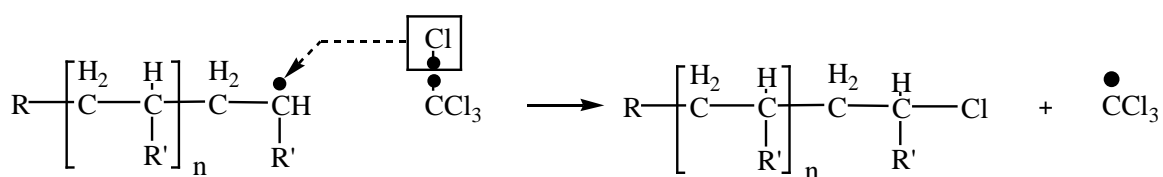
molecular oxygen from the air terminates free radical polymerization and provides residual monomer presence on the surface of polymer product.



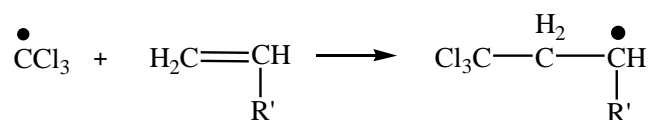
One important side-reaction that occurs during free radical chain-reaction polymerization of alkenes is phenomenon of **chain transfer**. In this reaction one growing macromolecule chain is terminated by transfer of a hydrogen atom from another molecule or from an atom within the same macromolecular chain. The result is creation of a new free radical, which then continues the chain-reaction polymerization. Chain transfer reactions give macromolecules with shorter chains and branching with irregular degree.



Certain solvents or impurities may also function as chain transfer agents, for example tetrachlormethane.



These new radicals then react with a monomer starting a new growing chain.



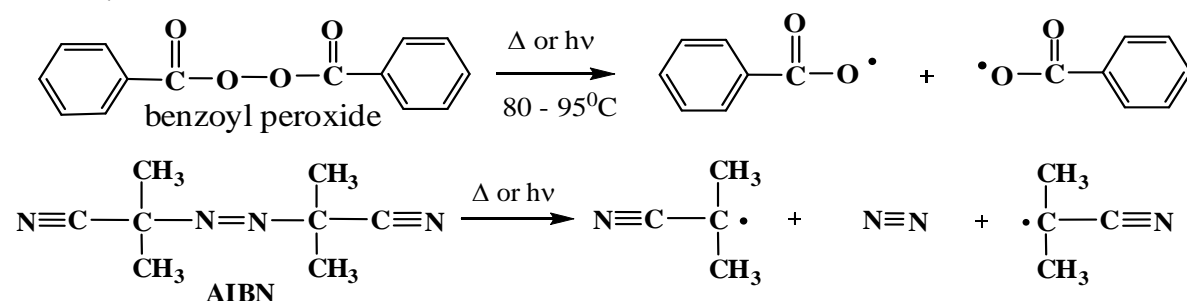
Termination reactions are irregular, so free radical polymerization leads to form polymers that are polydisperse in their molecular weight.

### 2.2.1.2. Free radical generating. Initiators, activators, fotosensibilizators.

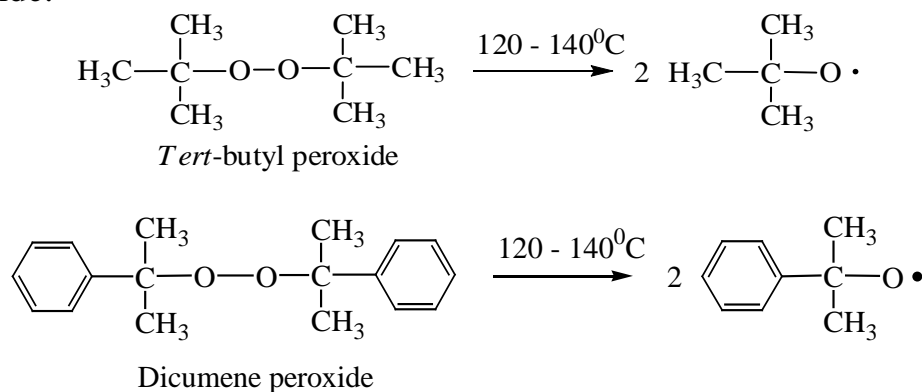
Excitement of monomer molecule leading to high reactive free radical in the initiation step of free radical polymerization requires much energy. There is several methods providing transmission of energy to activation of the monomer: 1) high temperature (heat initiation); 2) hard light (light initiation); 3) radiation; 4) initiators.

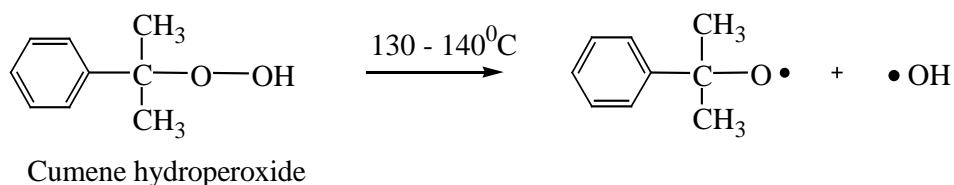
The initiation of free radical chain reactions involves the production of a free radical from a non-radical precursor that is an **initiator**. There are several methods for the formation of free radicals: homolysis of non-radical precursors, fragmentation, radical addition, atom abstraction and electron transfer.

Most **initiators** generate free radicals by **homolysis** of a relatively weak bond or by formation of an exceptionally stable molecule during the homolysis. The bonds most susceptible to homolysis are  $\sigma$ -bonds between heteroatoms having relatively low bond energy ( $\approx 25$  kkal/mol or 105 – 168 kJ/mol): Br-Br, Cl-Cl, N-O, O-O, O-Cl, N-Cl and so on. The most common compounds generating free radicals by homolysis are organic peroxides and hydroperoxides (the weak O-O bond which easy homolyzes) and organic azo compounds (homolysis produces  $N_2$  that is an extremely stable molecule despite C-N bond energy is enough high - 70 kkal/mol or 293 kJ/mol). The most popular radical initiators are benzoyl peroxide and azo-*bis*-isobutyronitrile (AIBN). Heating or irradiation with ultraviolet light of benzoyl peroxide or of AIBN gives two free radicals

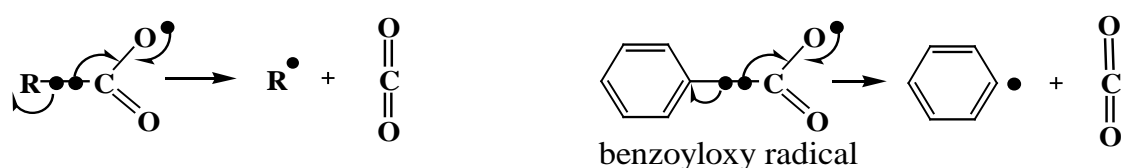


The alkyl peroxides and hydroperoxides undergo homolysis by the same way. Most typical are dicumene peroxide, *tert*-butyl peroxide and cumene hydroperoxide:



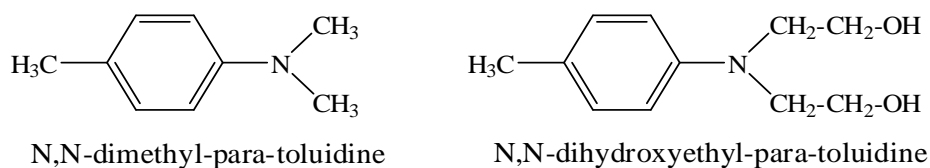


Oxygen-centered radicals – alkoxy radicals and carboxy radicals – are typically very high energy and extremely reactive. The high energy of these radicals provides their propensity to fragment to carbon-centered radicals and carbonyl compounds. Thus carboxy free radicals rapidly decompose by decarboxylation to give alkyl radicals and carbon dioxide. For example, benzoyloxy radical formed by homolysis of benzoyl peroxide is decarboxylated to give phenyl radical and carbon dioxide.



Homolysis of initiators can be carried out by heat, light or chemical reactions. As a result of various activation methods, polymerized (cured) materials are classified as heat-activated (also known as heat-cure), light activated (also known as photo-cure or light-cure) or chemically activated (also known as cold-cure or chemical-cure).

Chemically activated polymerization is accelerated by the presents of special compounds – redactors, which are called **activators**. Most common chemical **activators** are ferrous ( $\text{Fe}^{3+}$ ) and some other metals ( $\text{Cr}^{3+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Cu}^+$ ) salts, sulfites ( $\text{SO}_3^{2-}$ ), thiosulfates ( $\text{S}_2\text{O}_3^{2-}$ ), tertiary amines, both aromatic and aliphatic, for example N,N-dimethyl-p-toluidine or 4-vinyl-2-methylaniline.

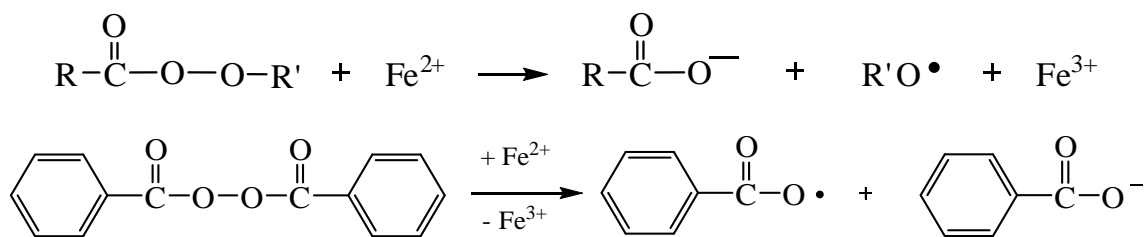


Oxidation – reduction reactions between initiator and activator form free radicals leading initiation step of polymerization reactions. Examples are the next:

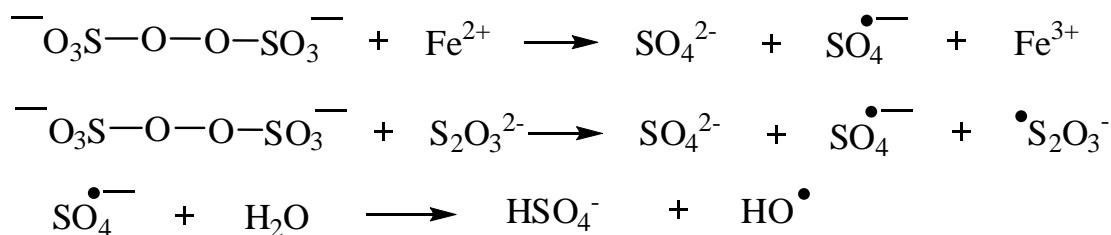
- Reaction between hydrogen peroxide and ferrous salts



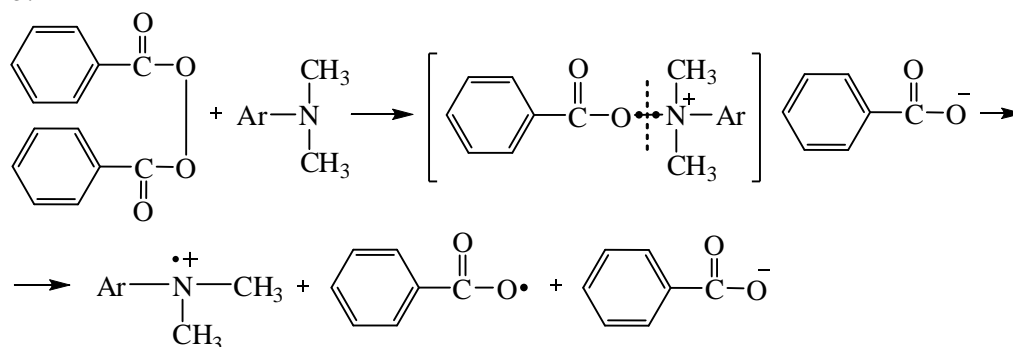
- Reaction between organic peroxide and ferrous salts



- Reaction between persulfates and ferrous salts, sulfites and thiosulfites

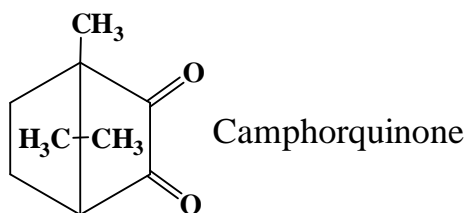


- Reaction between peroxide, for example benzoyl peroxide, and aromatic amine:



Oxidation – reduction reactions (chemical activation) require less activation energy (50 -84 kJ/mol) than heat activation (125 -170 kJ/mol), so chemical activation of polymerization is accomplished at room temperature.

Light-activated polymerizations use several activator and initiator compounds. The activator absorbs light and then reacts with the initiator. The polymerization process does not begin until the material is exposed to a very bright light source. Light activation is accomplished with blue light at a peak wavelength of about 465 nm, which is absorbed usually by a photo-sensitizer, such as camphorquinone.



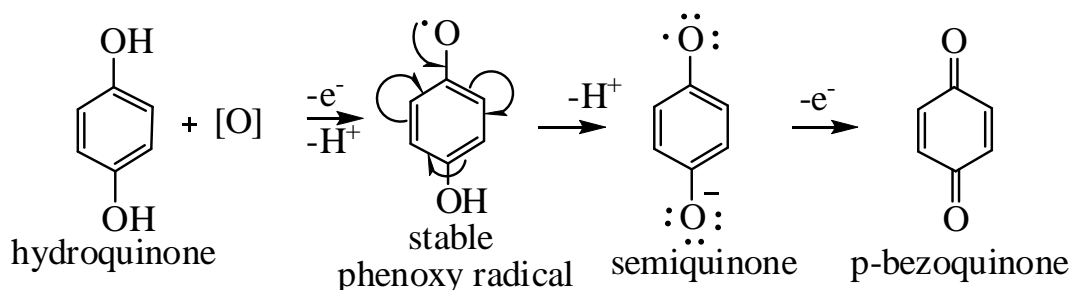
Several dental materials have both chemical and light-activated capabilities. These materials are called dual-cure materials. Polymerization is started with a curing light, but material that cannot be reached by the intense light sets by the chemical activation mechanism.

### 2.2.1.3. Inhibitors of free-radical reactions.

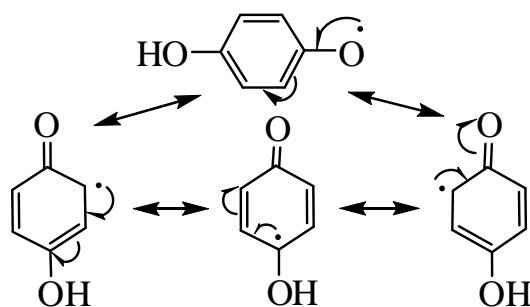
Polymerization reactions can occur very rapidly. For a polymerized (and dental also) material to be useful, the reaction must occur when desired or be delayed after mixing and occur somewhat slowly and also when monomers are stored. The reaction of chemically activated materials is initially delayed for several minutes by the presence of compounds called an **inhibitor**. **Inhibitors** are compounds that prevent the free radical chain mechanism from occurring and stop polymerization reaction. **Inhibitors** react with free radicals formed in the initiation or propagation step to form compounds or radicals that are not initiators of new chains due to high stability. This reaction competes with the polymerization reaction and wins. The competing reaction of inhibitor with free radicals delays polymerization and provides working time for placement, molding and shaping of the material. Without this delay, materials would set too fast for use. After a period of time the inhibitor is used up and polymerization begins to occur.

Typical inhibitors are polyhydric phenols (hydroquinone, catechol, pyrogallol), aromatic amines (N-phenyl-2-naphthylamine, 4-amino-1-naphthol), aromatic nitro compounds (1,3,5-trinitrobenzene, picric acid), sulfur, iodine and also copper, ferric, zinc salts of salicylic, acrylic and methacrylic acids.

The delayed effect of inhibitor depends on stability of its product with free radicals and structure of monomer. So, using of polyhydric phenols as inhibitors of polymerization reactions and antioxidants depends on their high reactivity in oxidation reactions. For example, hydroquinone is easily oxidized by free-radical mechanism to form intermediate phenoxy radicals and anion-radical semiquinone with high stability.



The phenoxy radical and semiquinone anion radical are stabilized by conjugation, which can be represented as resonance hybrid of four canonical forms

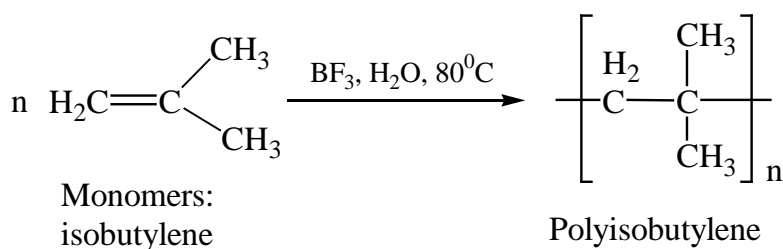


Semiquinone is relatively stable radical; it doesn't have ability to abstract atom with unpaired electron and initiate chain free-radical reaction. But semiquinone can accept chain carbon radicals and terminates free-radical reactions. That's why semiquinones are inhibitors of free-radical polymerization reactions.

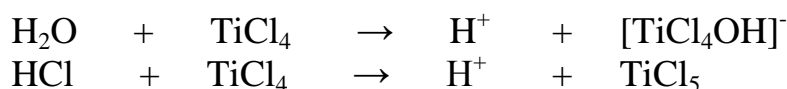
### 2.2.2. Cationic polymerization.

The chain reaction polymerization of electron-rich alkenes such as enol ethers, styrene and isobutylene can be carried out under conditions where the chain carrier is a carbocation rather than a free radical, because these alkenes can react with an electrophile to give a relatively stable cationic intermediate.

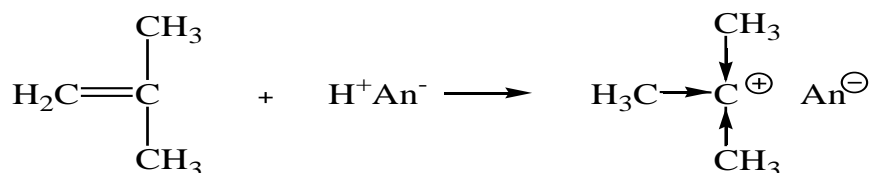
The example is cationic polymerization of isobutylene polymerization:



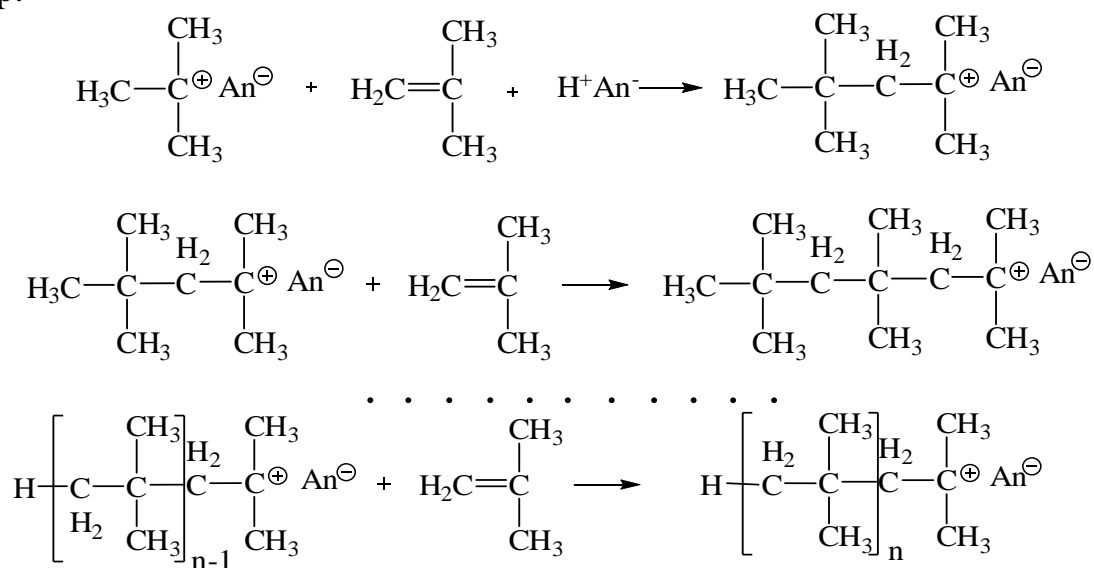
The most common **initiators** of cationic polymerization are protonic acids ( $\text{H}_2\text{SO}_4$ ) or Lewis acids ( $\text{BF}_3$  and  $\text{TiCl}_4$ ). Lewis acids are used together with lowmolecular compounds (co-catalysts) like the water or gaseous hydrogen chloride, resulted proton releasing:



**The initiation step** in a cationic polymerization of isobutylene is to add a proton to the double bond of alkene to form a carbocation. Electrophilic addition to each alkene monomer occurs with Markovnikov rule. The ease of polymerization parallels stability of the intermediate carbocation formed. In our example addition of proton to the double bond of isobutylene leads to formation of tertiary carbocation, stabilized by free electron releasing alkyl (methyl) groups.

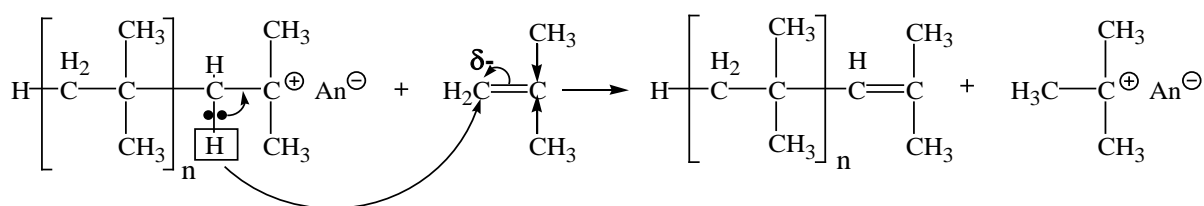


**The propagation step** involves reaction of a carbocation with a molecule of alkene to form a new most stabilized carbocation. This step repeats itself until the reaction either runs out of reactants or the polymers react in a termination step.

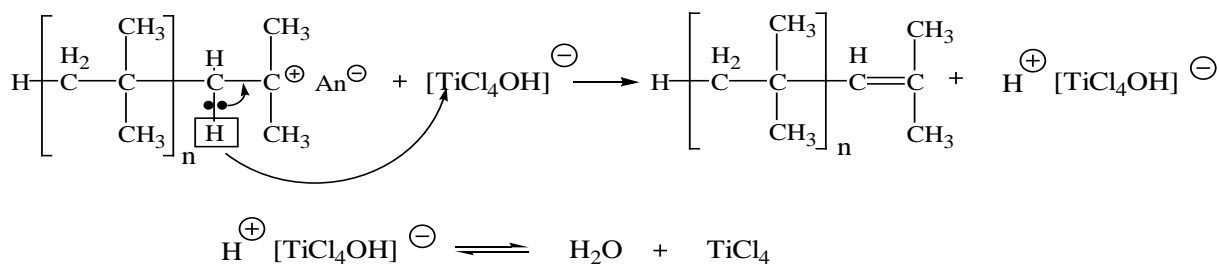


**The termination step.** The growing polymer chain may be terminated by loss of a proton from the carbon atom adjacent to the carbocation center as result of chain-transfer reactions:

1) Chain-transfer to the monomer as base.

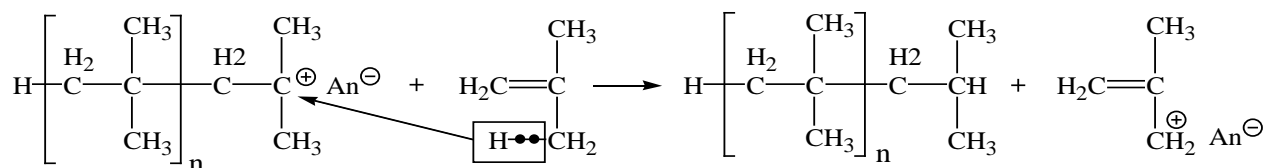


2) Chain-transfer to the anion formed as result of reaction between Lewis acid and co-catalist.



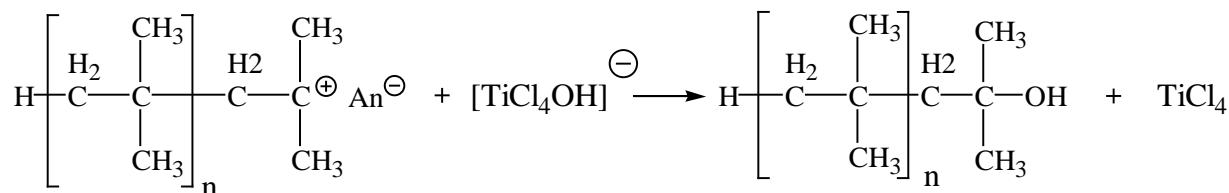


Another way of chain transfer reactions can be carbocation removing hydride anion from monomer or polymer molecule.



The chain-transfer reactions don't lead kinetic chain termination, because one of products is cation – carbocation or proton that can start to grow the new polymer chain.

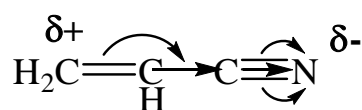
The kinetic chain termination may be resulted in reaction between the growing polymer carbocation and anion from Lewis acid:



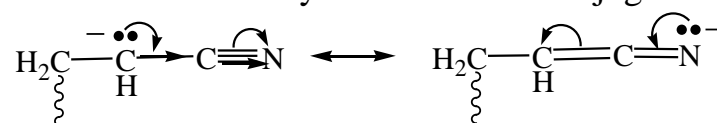
These termination reactions occur fairly readily, so cationic polymerization usually leads to lower molecular weight polymers than those obtained by free radical polymerization. But using Lewis acids and co-catalysts for cationic polymerization leads to the higher molecular weight polymers. The solvation and stability of carbocation reactive site and anion is increased, when the polarity of solvent is increased. That's why, probability of termination reaction decreases and higher molecular weight polymer formation occurs.

### 2.2.3. Anionic polymerization.

Alkenes are not normally susceptible to addition of nucleophiles because the  $\pi$ -bond electron density of simple alkenes is too high. But the presence of electron-accepting (withdrawing) groups such as a carbonyl or alkoxy carbonyl group ( $-\text{C}=\text{O}$ ,  $-\text{COOR}$ ), cyano group ( $-\text{CN}$ ) and nitro group ( $-\text{NO}_2$ ) in conjugation with the alkene  $\pi$ -bond make it more accessible to nucleophiles because conjugation of  $\pi$ -bond to these groups lowers its electron density as result of negative inductive and negative resonance (mesomeric) substituent effects, for example in the molecule of propenenitrile:

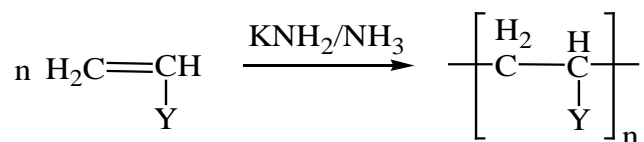


Electron accepting substituents can also stabilize an adjacent negative charge of intermediate carbanion by induction and conjugation, for example:



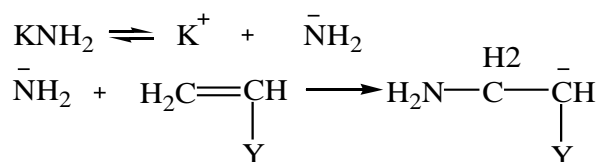
Common initiators of anionic polymerization are strong nucleophiles that are strong bases such as alkyllithiums and alkylsodiums or potassium amide. There are Ziegler-Natta catalysts prepared from transition metal halide on base elements of IV-VII groups of periodic table and metal alkyls based on elements of I-III groups of periodic table.

Anionic chain reaction polymerization occurs in much the same manner as free radical or cationic polymerization. One example of anionic polymerization is polymerization of ethylene derivatives with electron accepting groups in presence of potassium amide in liquid ammonia.

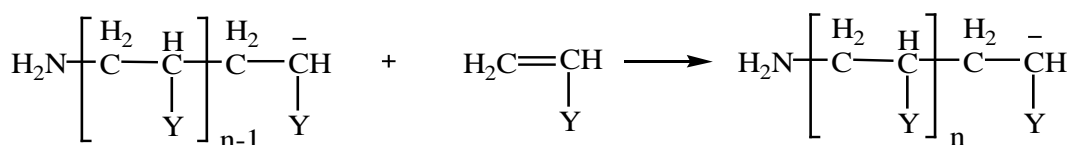
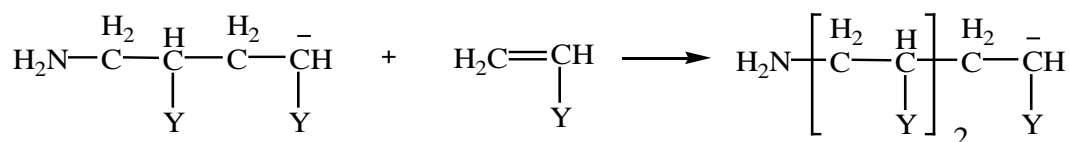
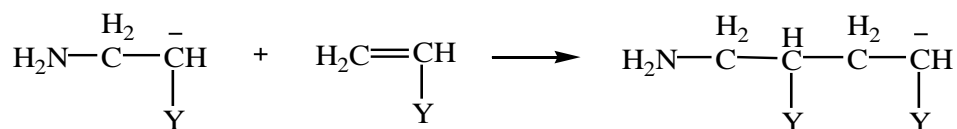


The mechanism of anionic polymerization involves initiation, propagation and termination steps.

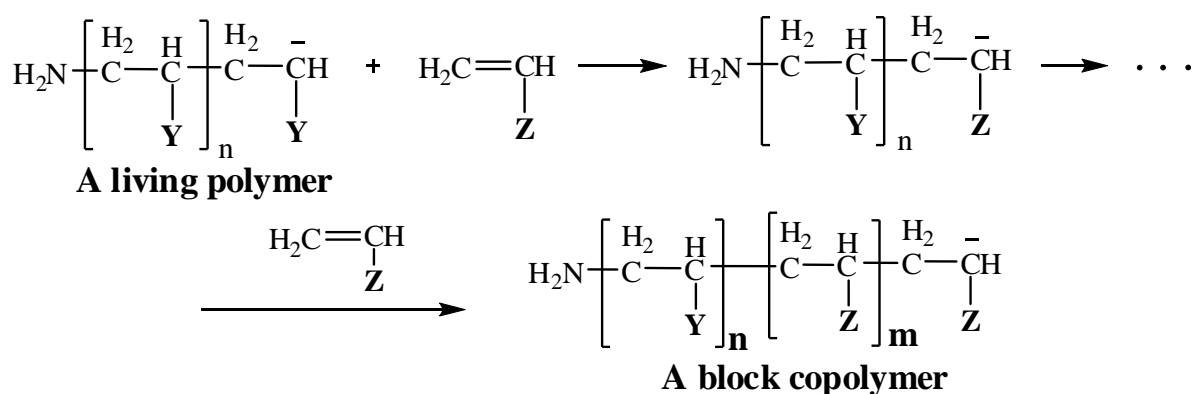
### *Initiation step*



### *Propagation step*

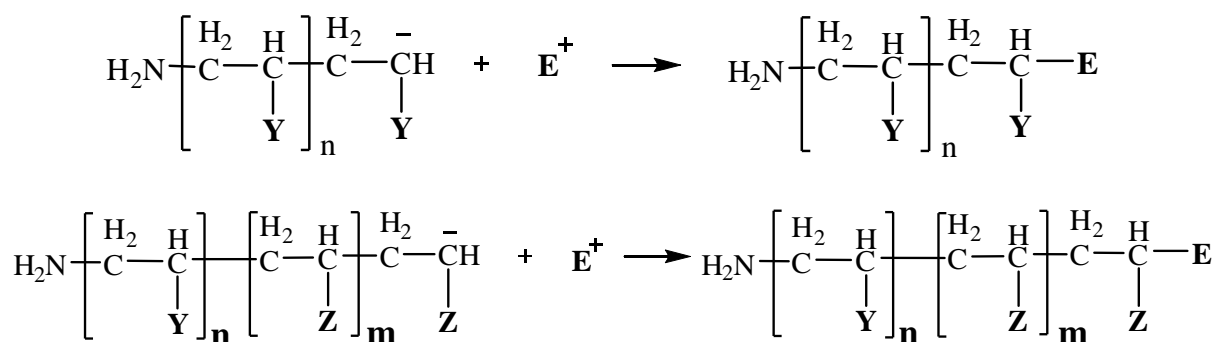


Unlike free radical or cationic polymerization there are no effective reactions for termination of anionic polymerization unless the addition of an electrophile to reaction mixture. The anionic polymers are called also as “**living polymers**”. The anionic polymerization reaction continues until all the monomer is consumed, at this time the polymerization reaction ceases. In the absence of termination reaction, the ends of polymer chains still carry the reactive anionic species, and the addition of more monomer to the reaction vessel results in the polymerization reaction beginning again – the polymer is “**alive**”. This characteristic of anionic polymerization is used for producing block copolymers: after the first monomer is consumed, the second monomer is added. This process can be repeated several times to give a block copolymer with desired properties.



### *Termination step*

Since the chain carriers in anionic polymerization are strong nucleophiles, a wide variety of electrophiles may be used to terminate the reactions such as acids, alkyl halides, esters and epoxides. Electrophiles are deliberately added to the reaction mixture to carry out termination reactions.



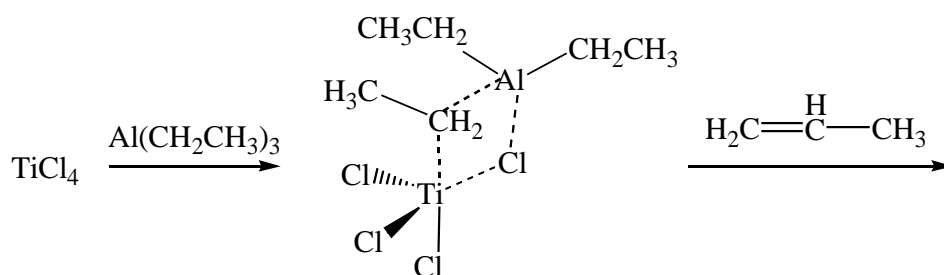
Sodium and potassium amides are common initiators for polymerization of derivatives acrylic and methacrylic acids such as methyl acrylate, acrylonitrile and methacrylonitrile.

### 2.2.4. Coordinative chain reaction polymerization: Ziegler-Natta polymerization.

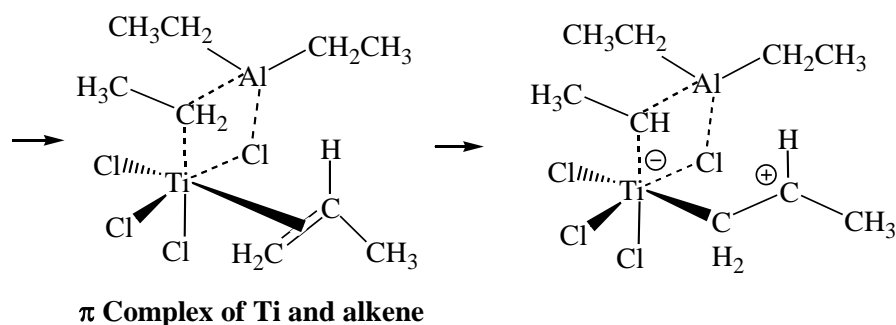
Free radical polymerization usually produces atactic polymers. Since many of physical properties of atactic polymers make them less desirable for commercial use than stereoregular (isotactic or syndiotactic) polymers, **coordinative chain-reaction polymerization** is more used. It is a catalytic, low-temperature and low-pressure polymerization of alkenes, which is known as **Ziegler-Natta polymerization** after its two discoverers, Karl Ziegler and Giulio Natta. Ziegler-Natta polymerization is catalyzed by a transition metal catalyst prepared from a transition metal halide and metal alkyl, more usually from titanium tetrachloride and triethylaluminum. Because the reaction occurs at a metal center, this method allows such high levels of control over the stereochemistry and molecular weight of the polymers produced simply by adjusting the experimental parameters. For example, one may produce either syndiotactic or isotactic polypropylene simply by varying the catalyst and reaction conditions.

The tacticity of polymer strongly affects polymer's properties. Syndiotactic and isotactic polypropylene are more crystalline than atactic polypropylene. Atactic polypropylene is a soft, low melting amorphous solid, but isotactic polypropylene is highly crystalline and melts at 170<sup>o</sup>C.

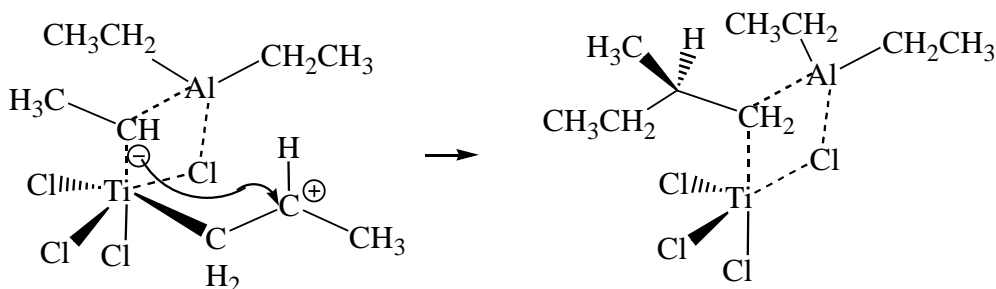
The mechanism with the Ziegler-Natta catalysis begins with formation of a complex between titanium and aluminum.



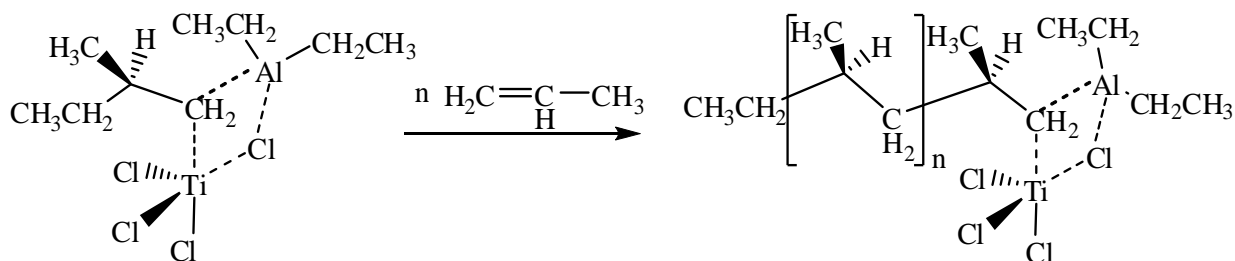
In this complex titanium has an empty orbit available for interaction with the  $\pi$  electrons in the monomer, thus, allowing formation of  **$\pi$ -complex**. The  $\pi$ -complex orients the methyl group away from the titanium and towards the aluminum. The  $\pi$ -complex then rapidly rearranges:



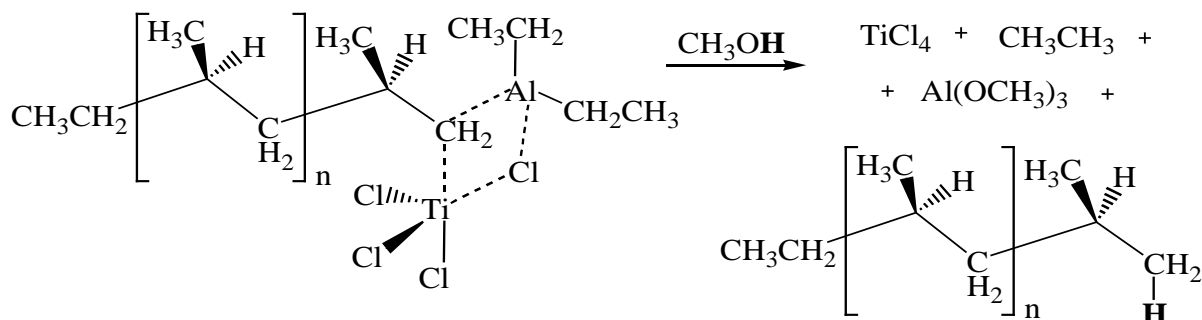
The alkyl group of aluminum rapidly transfers to carbocation so that it does not have time to rearrange. Thus, the titanium stereo-specifically inserts the propylene group between itself and the ethyl group.



The titanium complex continues to stereo-specifically insert additional propylene monomers between itself and the last ethyl group added to the chain. This repeating reaction forms the isotactic polymer.



To end the reaction, the complex is destroyed by treating it with methanol:



### III. POLYMER DENTAL MATERIALS.

#### 3.1. CLASSIFICATION OF DENTAL MATERIALS.

Polymer dental materials are classified by following categories:

1. Dental materials for the orthopedic stomatology:

- Impression materials for casts and models;
- Denture base resins, materials for crowns, a false tooth and bridges.

2. Direct restorative dental materials for the therapeutic stomatology:

- Materials for permanent restorations to repair anatomy shape and functions of tooth;
- Materials for temporary filling of cavity preparation during treatment of high caries activity;
- Materials for liners and bases before placement of permanent restorations;
- Root canal filling materials;
- Preventive materials: pit and fissure sealants to prevent decay and caries.

3. Prosthesis called complete dentures replaced missing teeth; bone and gingiva after the teeth have been lost or extracted.

#### 3.2. IMPRESSION MATERIALS.

Impression materials are used to make an accurate replicas (models or casts) or mold hard and soft oral tissues. Dentists take impressions of teeth and their supporting structures including gingiva, alveolar bone or residual ridge, hard and soft palate and frenums that are muscle attachments. The *impression* is a negative reproduction of tissues. Filling the impression with dental stone or other model material make a positive replica (cast) that is removed after the model material has set. The positive replicas (casts) are used to fabricate restorations and prostheses.

Impression materials set either by a chemical reaction or by a physical change. The chemical reaction involves chain lengthening, cross-linking or both to give thermosetting impression materials. Other impression materials set by a physical change when they cool, either by solidification or by gelation; they are thermoplastic. In general, thermoplastic materials are not as stable as thermoset materials. Impression materials set to form elastic or solid inelastic replica.

There are several types of impression materials:

- 1) Aqueous elastomeric impression materials:
  - a. Alginate (irreversible hydrocolloid) - thermoset.
  - b. Agar (reversible hydrocolloid) - thermoplastic.
- 2) Nonaqueous elastomeric impression materials – either are thermoset:
  - a. Polysulfides.
  - b. Condensation silicones.
  - c. Polyethers.

- d. Addition silicone.
- 3) Inelastic impression materials:
  - a. Wax and impression compound - thermoplastic.
  - b. Plaster and zinc oxide-eugenole - thermoset.

### ***3.2.1. Aqueous elastomeric impression materials.***

Aqueous elastomeric impression materials are based on two polysaccharides - salts of alginic acid and agar-agar. Both are considered to be hydrocolloid materials. Setting of these materials forms a colloid of gel type. Colloid is a substance containing two or more phases with the units of at least one of the phases having a dimension slightly greater than simple molecular size (1 to 500 nm). Thus colloidal systems are fine dispersions - sols, gels, films, emulsions or foams.

Alginate and agar impression materials change from the sol colloid state to the gel colloid state. A *sol* resembles a solution, but it is made up of colloidal particles dispersed in liquid; sol is a viscous liquid. When sol is cooled or caused to react by adding any compounds, it is transformed into a semisolid, rubbery state, called a gel. A **gel** has an entangled framework of solid colloidal particles with liquid that is trapped in interstices and held by capillarity. Because the liquid phase of sols and gels is the water, alginate and agar are called hydrocolloid impression materials.

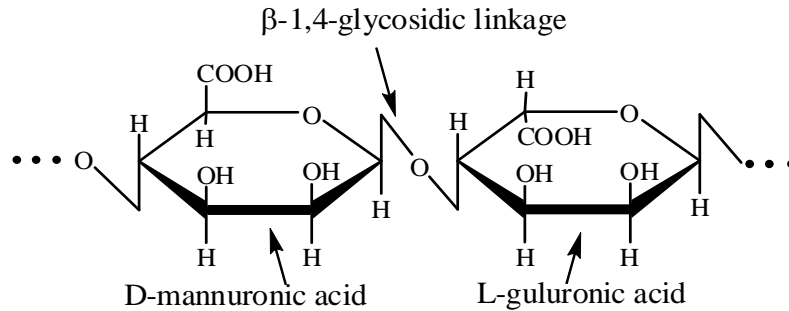
There are reversible and irreversible hydrocolloids. *Alginate* impression material set via chemical reaction, it is called ***irreversible hydrocolloid***. Heating of setting alginate results in warm alginate, it does not reverse back to the sol state. *Agar* gels by physical change in cooling, it is called ***reversible hydrocolloid***. This impression material reverse back to the sol state when heated, then change again to the gel state when cooled.

Gels with water liquid phase are hydrophilic and tend to imbibe large quantities of water when allowed to stand submerged. The imbibition leads to swell and change physical dimensions. In dry air the gel loses water with an accompanying shrinkage. This property of gel makes some advantages and disadvantages for hydrocolloid impression materials.

One of the advantages is that reversible and irreversible hydrocolloids will wet a tooth surface that is contaminated by oral fluids. Hydrocolloid material absorbs a limited amount of oral fluid. Pouring the impression with dental plaster to make gypsum casts or models is easier than with elastomeric impression material. The gypsum product mixed with water also easily wets the surface of the impression material. Disadvantage of this material is that water evaporates from the surface of impression in air. As the result the impression shrinks and is no longer accurate.

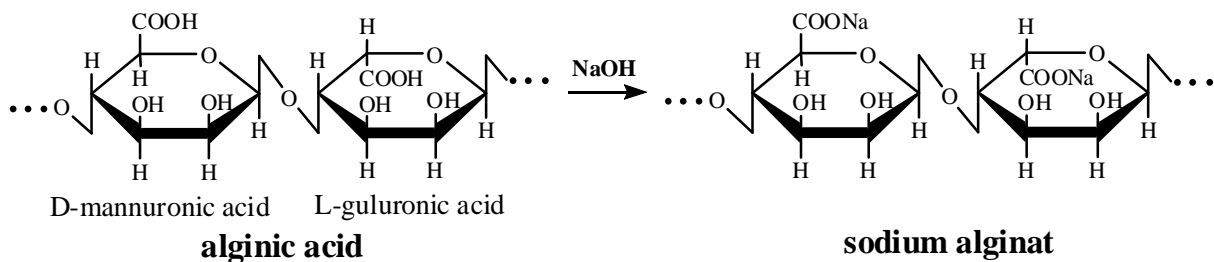
### 3.2.1.1. Alginate - irreversible hydrocolloid impression material.

Potassium and sodium salts of alginic acid have properties that make them suitable for compounding a dental impression material. Alginic acid is prepared from marine plant algae. Alginic acid is a high-molecular-weight block copolymer of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid joined together by 1,4-glycosidic linkages.

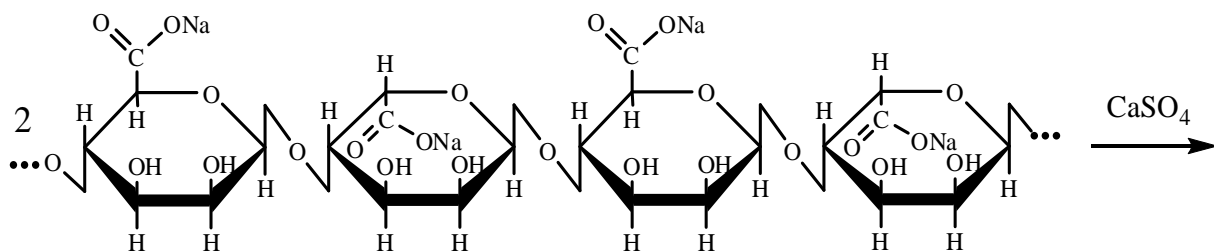


Properties of alginate materials depend on degree of polymerization and ratio of guluronan and mannuronan block in macromolecules. The mannuronan residues are stretched and flat, the guluronan residues contribute less flexibility.

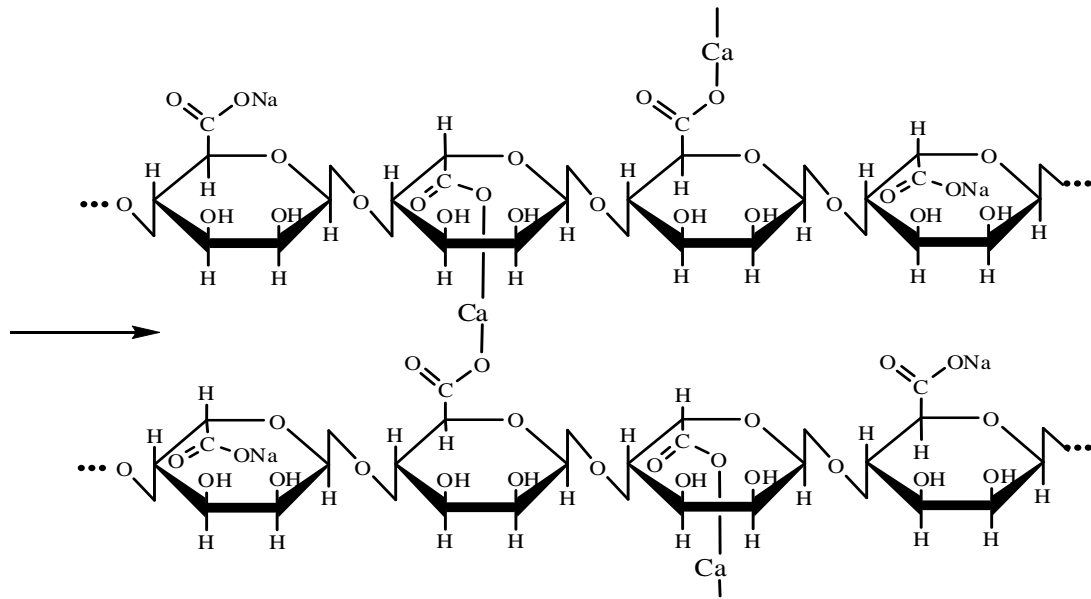
Potassium and sodium alginates are line extended molecules.



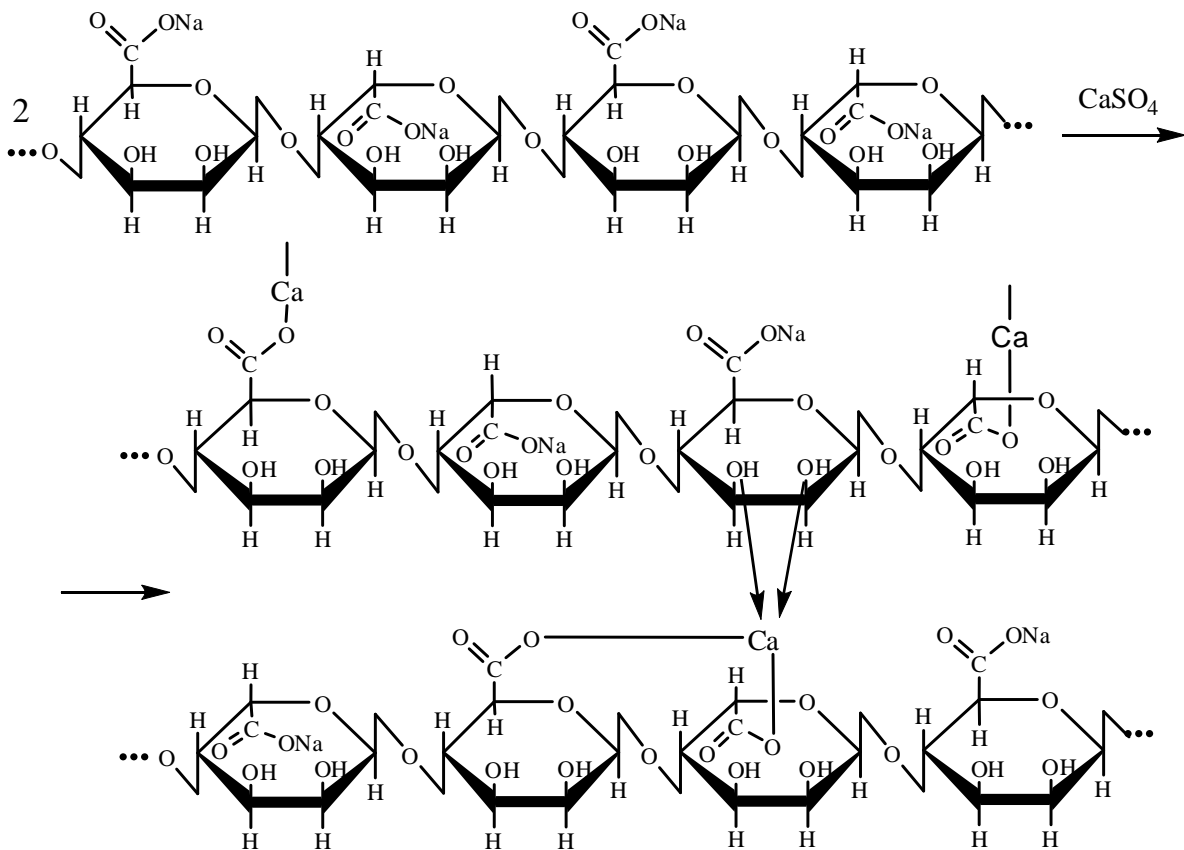
When line alginate salt molecules react with polyvalent metal cations the cross-linked network polymer is obtained. Cross-linkages are formed between carboxylic groups of two macromolecules:







Macromolecules can be cross-linked by chelate complex formation between two vicinal hydroxyl groups of one macromolecule and cation formed salt with two carboxyl group of other macromolecule.



Upon mixing with water, the alginate impression material first forms viscous sol. In following cross-linking reaction with calcium sulfate the water

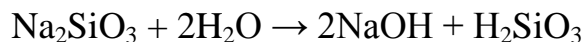
molecules disperse into the small pockets between linked macromolecules to form an insoluble elastic gel called calcium alginate. The ability of alginates to form gel is mainly related to proportion of L-guluronan blocks that mainly bind with  $\text{Ca}^{2+}$ . Thus alginates contained predominantly guluronan residues form strong and brittle gel, alginates rich in mannuronan form weaker and more elastic gels.

The quality of gel structure depends on nature of cross-linking cation and the rate of its addition. Slow addition of cation leads to formation of polymolecular and under-molecular structures (gel particles) and following linking between this gel particles to give tree-dimensional gel structure. This method is preferred for impression preparation. That's why manufacturers use partially water soluble salts; it allows slow movements of cations to the solution and slow reaction. The quality and strength of cross-linkages depends on complex-forming ability of polyvalent cation. Usually manufacturers use partially soluble salts of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$  cations:  $\text{CaSO}_4$ ,  $(\text{CaSO}_4) \times 2\text{H}_2\text{O}$ ,  $\text{BaSO}_4$ ,  $\text{BaCO}_3$ ,  $\text{SrSO}_4$ ,  $\text{PbSiO}_3$ .

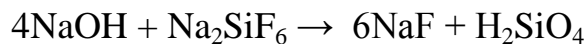
Setting times of alginate impression materials range from 1 to 5 minutes. But cross-linkages formation begins immediately after mixing of powder and water. There are two systems that delay cross-linking reactions:

1. Alkaline component – acid component system;
2. Retarder – cross-linking agent system.

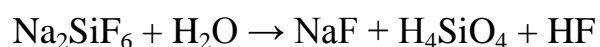
In the first system the alkaline component is usually sodium hydroxide or salts of alkaline elements and weak acids ( $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SiO}_3$ ) that have alkaline solution in water (pH = 12.0 – 13.0). For example



In alkaline solution the alginate macromolecules don't react with calcium or barium cations and cross-linking don't occur. Working time is provided by addition of acid component in excess towards the alkaline component that reacts each other slowly during tasked time until solution becomes almost neutral with pH = 7.0 – 8.0. Acid components are usually sodium or potassium silicafluorides or titanofluorides. For example, sodium silicafluoride as acid component neutralizes alkaline sodium hydroxide:



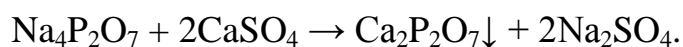
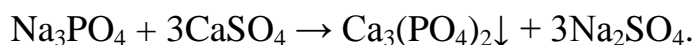
Formed silicic acid is water insoluble; it is dispersed in water and positively affects to set of material. Excess of sodium silicafluoride ( $\text{Na}_2\text{SiF}_6$ ) react with water as following:



Formed sodium fluoride promotes stickiness missing.

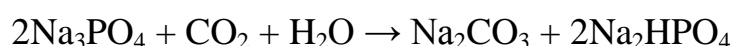
The working time of material with delaying system alkaline – acid components is the time in which pH decreases from 12.0 – 13.0 to 8.0 and cross-linking reaction has occurred. Alginate impression powder includes special indicators to control this pH change and process of impression setting. For example, alginate impression material “Kromoran” of Italian firm “Lascod” contains two indicators: phenolphthalein and thymolphthalein. Russian materials “Стомальгин” and “Альгэласт” also contain phenolphthalein as indicator. Mixing the white material powder with water gives paste that is alkaline and blue-violet colored. While pH is decreased due to reaction of alkaline component with acid component, past color changes to light-pink. In the moment when color is disappeared at pH = 7.0 – 8.0 setting reaction is started. In the same moment material on the tray is carried in the mouth and after 40 – 50 second set impression must be removed from the mouth.

In the second system working time is provided by a competing reaction, that initially delays cross-linking. In a powder of an alginate impression compound soluble alginate, the cross-linking agent, for example calcium sulfate dehydrate and retarder sodium phosphate are included. After mixing powder with water all components are disassociate. Calcium ions from the calcium sulfate dehydrate reacts preferentially with phosphate ions from the sodium phosphate or pyrophosphate to form insoluble calcium phosphate:



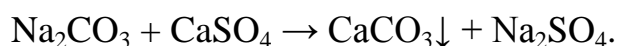
Calcium phosphate is formed rather than calcium alginate because it has a lower solubility. The calcium ions do not react with alginate until all phosphate ions have reacted.

Sodium phosphate can react with carbon dioxide dissolved in water.



Sodium hydrophosphat in resulting impression delays setting of plaster material and decreases its surface strength.

Sodium carbonate is also used as retarder:



Water insoluble calcium phosphate and calcium carbonate serves also as filler in the resulted impression. Manufacturers adjust concentration of sodium phosphate to produce regular- and fast-set alginates.

After retarders - phosphate or carbonate ions – are depleted the calcium ions react with the soluble alginate to form the insoluble calcium alginate, which together with water forms the irreversible calcium alginate gel. This reaction is irreversible; it is not possible to convert the calcium alginate to a sol after it has set.

Certain particles of calcium sulfate or other cross-linking compound are covered by calcium alginate formed in reaction. As result the calcium sulfate becomes isolated from the water environment and it does not react with other molecules of sodium alginate. Therefore, cross-linking agent ( $\text{CaSO}_4$ ) is used in fine particles state.

The use of suitable fillers in correct quantities produces a consistency that is suitable for various clinical uses. Manufacturers adjust the concentration of filler to control the flexibility of the set impression materials from soft-set to hard set. Addition of fillers reduces shrinkage and stickiness. The fillers in most alginate materials are diatomaceous earth or fine siliceous particles.

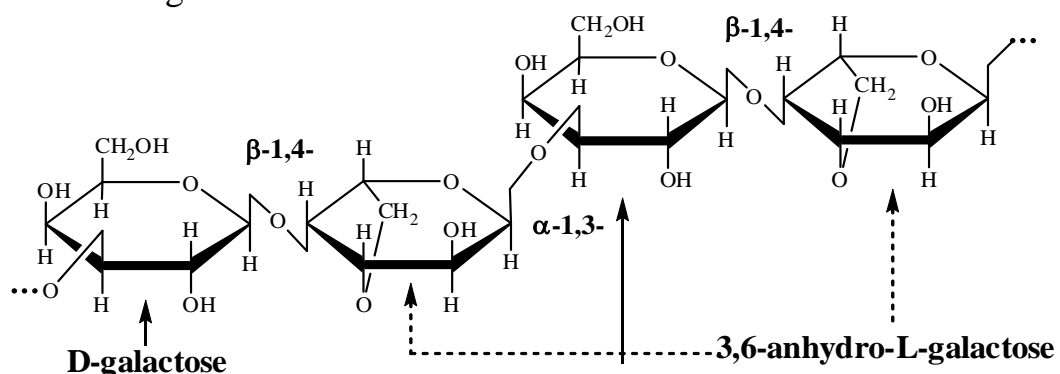
Alginate impression material is powder contained all required ingredients. Preparation for use requires only the mixing of measured quantities of powder and water.

Alginate impression materials are used for a variety of purposes. It is inexpensive and easy to use but lacks the accuracy for precisely fitting restorations. Proper mixing and handling will result in acceptable study models and casts on which to fabricate provisional restorations and removable dental prostheses.

### 3.2.1.2. Agar - reversible hydrocolloid impression material.

Reversible hydrocolloid impression material is premixed by a manufacturer and supplied as a semisolid material in tubes and sticks. These sticks feel wet because of their high water content. Reversible hydrocolloid impression material is predominantly water with added agar. Agar or agar-agar is polysaccharide material prepared from red seaweed. Agar contains 50-80% agarose and agaropectine.

Agarose is linear polysaccharide made up of D-galactose and 3,6-anhydro-L-galactose units joined together alternatively by  $\beta$ -1,4- and  $\alpha$ -1,3-glycosidic linkages:



Agaropectine is agarose contained acid groups; they are preliminary sulfate groups formed esters with any alcohol hydroxyl groups of monosaccharide units.

Other components of reversible hydrocolloid are colorants, flavors, mold inhibitors and sulfate compound. The sulfate compound improves the hardness of the gypsum material when it is poured into the impression.

Agar is not soluble in cold water, but it is soluble in boiling water. Important property of agar is that its water solution forms gel in cooling. Agar gel does not melt at the same temperature at which it is formed. It melts at a higher temperature than that of boiling water. Melting agar gel forms again in cooling.

For use the agar as reversible hydrocolloid is boiled to change the gel state into a viscous liquid sol. Then the material is stored in a 65°C water bath until needed. Material can be stored for several days. Several minutes before use for taking an impression, the material is placed in a 45°C water bath. It lowers the temperature to a point at which the oral tissues are able to tolerate the impression material. At mouth temperature the material gels and returns to its elastic state.

Reversible hydrocolloid itself is very inexpensive and results in a very accurate impression; it is good material in a wet environment. So it is very useful for taking impression when the margins of a crown preparation are subgingival or not easily kept dry. Some dentists wet the teeth with water just before taking the impression. Disadvantage of reversible hydrocolloid is requirement of special equipment for use and also that they have poor tear strength compared with nonaqueous elastomeric impression materials.

### ***1.2.2. Nonaqueous elastomeric impression materials.***

Nonaqueous elastomeric impression materials are also known as rubber base materials because they set via polymerization reaction. They are more stable than hydrocolloid materials, but more expensive. There are four types of synthetic elastomeric impression materials: polysulfides, condensation and addition silicones, polyethers.

Elastomeric impression materials are typically supplied in several consistencies (viscosities) depending on quantity of fillers and concentration of inorganic reagent. Polysulfides and polyethers are available in low, medium, high consistency. Addition silicones are available in extra-low, low, medium (regular), monophasic, high (tray) and putty (extra-high) consistencies. Condensation silicones are low and very high consistency.

#### ***1.2.2.1. Polysulfides.***

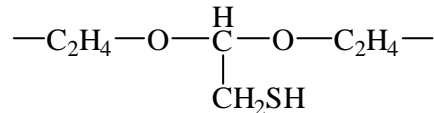
Polysulfides or thiokol rubbers were the first nonaqueous synthetic impression materials developed for dentistry since 1950 year. Polysulfide impression materials are supplied as two pastes in tubes. One paste is “base”, it is white; this paste contains a low-molecular-weight polysulfide oligomer mixed with inorganic filler - titanium oxide. The second paste, brown colored, is “accelerator”. It contains the reagent lead oxide and “oily” organic compound that is not react-

ing. The “accelerator” paste contains also a small percentage of sulfur because it promotes the polymerization reaction.

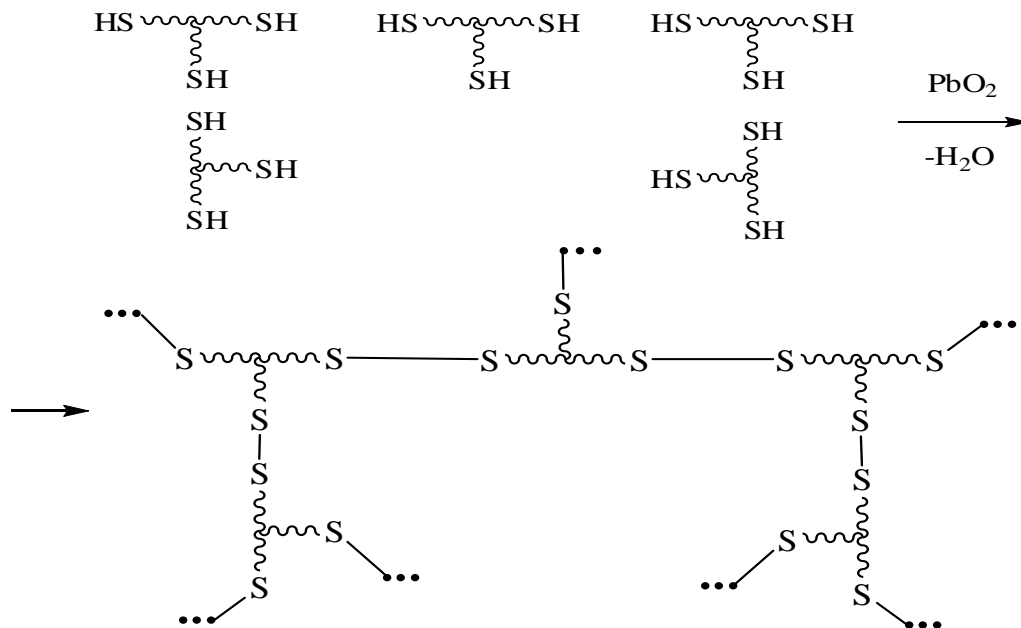
The typical structure of a low-molecular-weight polysulfide polymer is the following:



or, for example



The polymerization reaction starts when mixing begins and proceeds slowly. The reaction occurs as a series of simple oxidation reactions with releasing of water. Oxidation of terminal thiol-groups lengthens the polymer chain, while oxidation of pendant thiol groups cross-links the polymer chains. The polycondensation reaction corresponds to the following scheme:

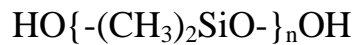


Polysulfide impression materials are relatively inexpensive, elastic and much more accurate than alginate, but less accurate than other nonaqueous elastomeric materials. Polysulfide impression materials are used for inlays, crowns and bridges.

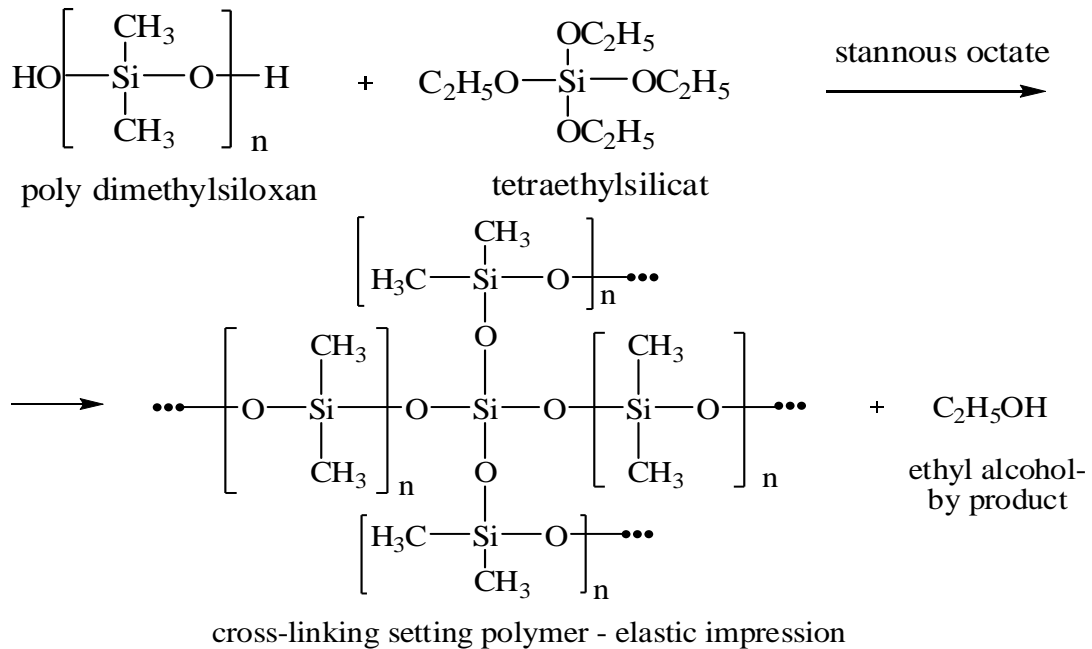
#### 1.2.2.2. Silicones.

A setting process for impressions based on silicone polymers are the result of two types of reactions: 1) polycondensation and 2) addition polymerization reaction. Condensation silicones were made available to dentists in 1955 and addition silicones in 1975 years.

Condensation silicone impression materials are supplied as two pastes in tubes or as complex of “base past” and “catalyst liquid”. The “base” is a linear polymer poly dimethylsiloxane with the ending hydroxyl groups:

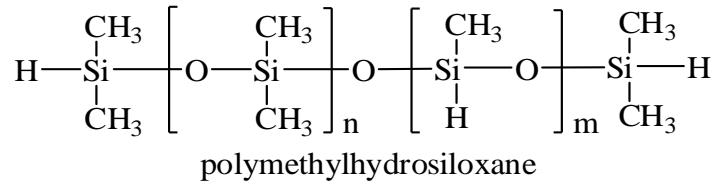


The “catalyst liquid” or “catalyst past” contains cross-linking agent tetraalkyl (tetraethyl) silicate and catalyst, that is stannous or titanium organic salts. Setting reaction is substitution reaction that cross-links polymer molecules. It has occurred when base past and catalyst liquid are mixed.

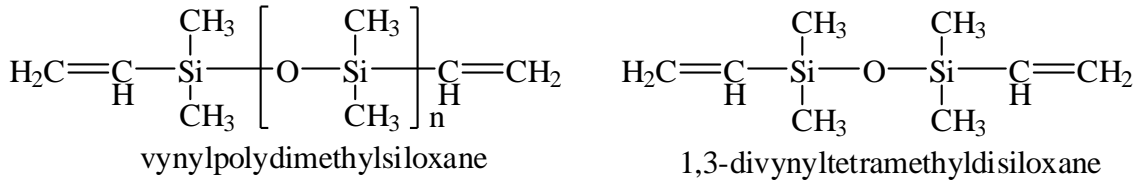


Condensation silicones are elastic, hydrophobic materials. They are cleaner materials to use, but it is difficult to pour a model without voids and bubbles. As with polysulfide materials, setting reaction results by-product (alcohol) formation, which loss the reaction through evaporation. It results in shrinkage and distortion. So, condensation silicone impression must be poured immediately.

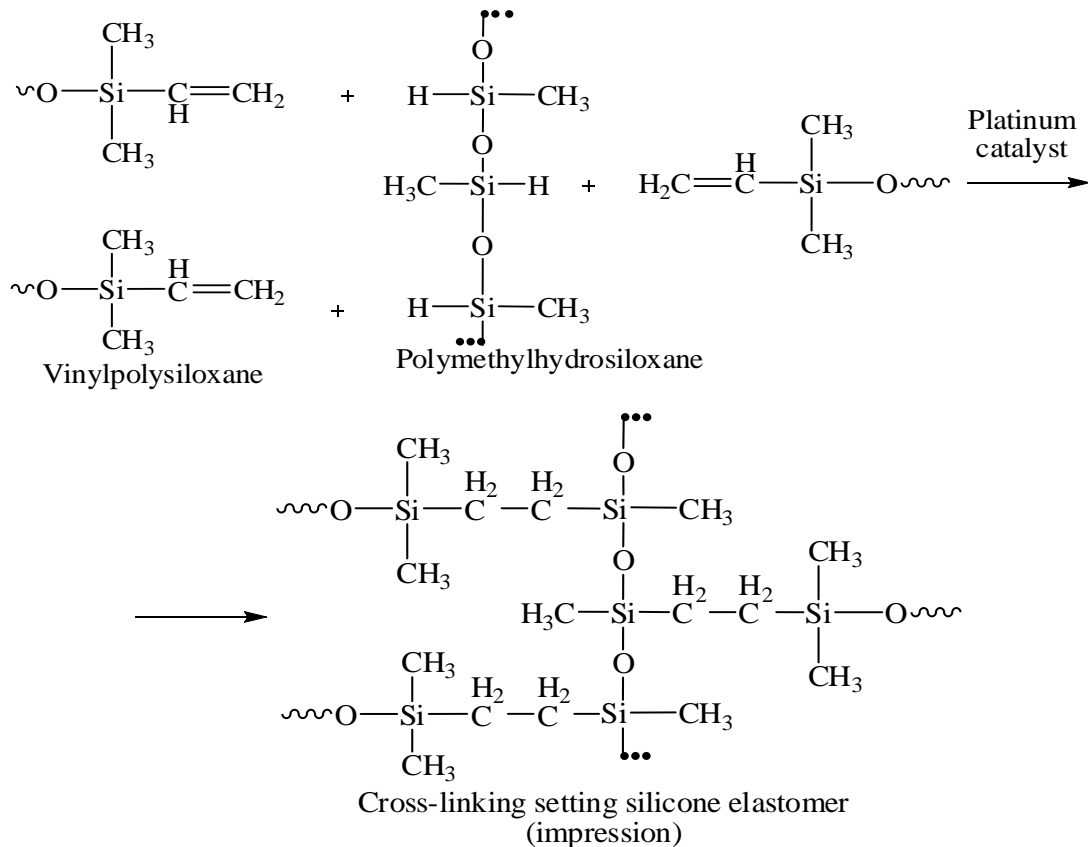
The most popular type of elastomeric impression materials is addition silicones. They are used especially for crown and bridge impressions. Addition silicones are clean and don't have unpleasant taste or smell. They are the most accurate and stable because addition setting reaction unlike condensation reaction doesn't result any by-products and, therefore, doesn't lead to shrinkage and distortion. But they are expensive. Manufacturers produce addition silicone materials in five viscosities: extra low, low, medium, heavy and very heavy consistency. To obtain the proper viscosity fillers are added, like cristobalite, talc. Addition silicon materials are supplied in two different-coloured pastes. The base past contains a moderately low-molecular-weight polymer polymethylhydrosiloxane with more than 3 and up to 10 pendant or terminal hydrosilane groups per molecule. The base past also contain filler.



The catalyst (accelerator) paste and the base paste contain a dimethylsiloxane polymer with vinyl terminal groups and filler. The catalyst paste also contains a platinum catalyst that is a complex compound consisting of platinum and 1,3-divinyltetramethyldisiloxane.



The polymerization reaction occurs as addition reaction with platinum catalyst when two reactive pasts are mixed:



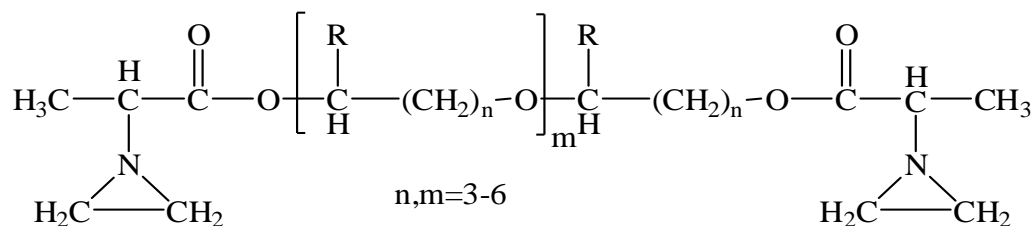
Addition silicones are hydrophobic and have problem in contact with hydrophilic gypsum material. Surfactants addition makes pouring the model easier.

### 1.2.2.3. Polyethers.

Polyether impression materials were developed in late 1960s to be used as dental impression materials. Polyethers are supplied as two pastes in tubes. The

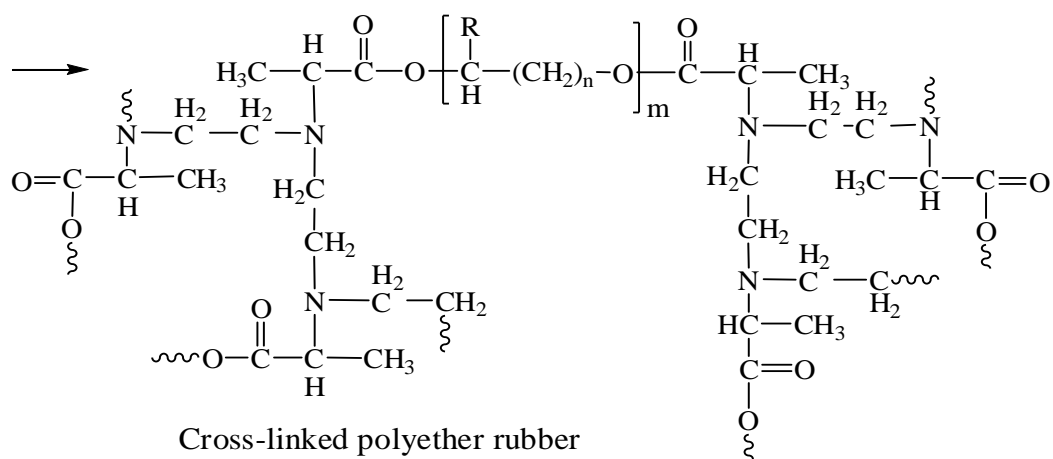
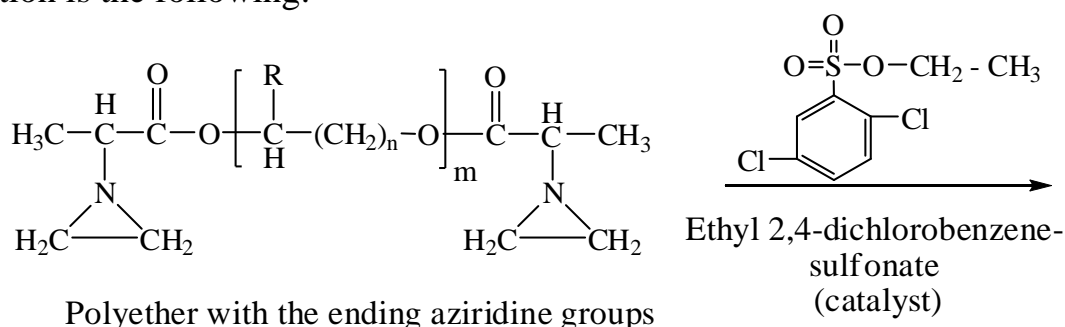


base past contains a long chain polyether copolymer with alternating ether fragments and reactive aziridine (or ethylenimine) ring terminal groups.



Other additives are a silica filler, compatible plasticizers and triglycerides. The catalyst paste contains the former (catalyst) that is alkyl (usually ethyl) 2,5-dichlorobenzene sulfonate. The catalyst paste also included silica filler and plasticizers. The required viscosity is regulated by addition of fillers in corresponding concentration. There are low, medium and heavy-body consistency polyether impression materials.

While the base and catalyst pasts are mixed the elastomer is formed by cationic polymerization with opening of the reactive terminal aziridine ring to make cross-linked polymer network. The general scheme of polymerization reaction is the following:



Polyether impression materials are comfortable to use and have many advantages. They are naturally hydrophilic due to polyether fragments. Polyethers have low shrinkage after polymerization, like addition silicones, because there is no loss of byproducts. However these materials make difficulty to remove set-

ting impression from the mouth and the gypsum cast from the impression. Polyethers are very expensive and may cause allergic reaction due to aromatic sulfonic ester used.

### 1.2.3. Inelastic impression materials.

Inelastic impression materials set by a physical change when they are cooled, usually by solidification. Solidification occurs, when molten material is cooled and goes from a liquid state to a solid state. Such impression materials are thermoplastic; they reverse to the liquid state in heating. Waxes, paraffin, stearin and gutta-percha are typical bases of thermoplastic inelastic impression materials.

#### 1.2.3.1. Waxes. Composition of waxes.

Most waxes are esters of long-chain fatty acids and long chain alcohols. Beside of this, waxes always contain free fatty acids, free long-chain alcohols and long-chain hydrocarbons.

**TABLE 3. Saturated fatty acids of waxes.**

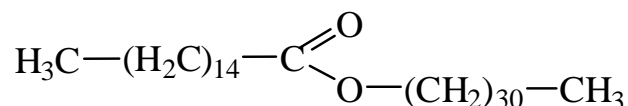
Common name	Structural formula	Systematic name	Melting point, °C
Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	dodecanoic acid	44
Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	tetradecanoic acid	54
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	hexadecanoic acid	64
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	octadecanoic acid	70
Arachidic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	eicosanoic acid	75
Eicosanecarboxylic acid	$\text{CH}_3(\text{CH}_2)_{19}\text{COOH}$	heneicosanoic acid	
Behenic acid	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$	docosanoic acid	80
Lignoceric acid	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$	tetracosanoic acid	84
Cerotic acid	$\text{CH}_3(\text{CH}_2)_{24}\text{COOH}$	hexacosanoic acid	88
Melissic acid	$\text{CH}_3(\text{CH}_2)_{28}\text{COOH}$	triacontanoic acid	94

**TABLE 4. Saturated alcohols of waxes.**

The common name	Number of carbon atoms	Structural formula	Systematic name
	10	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$	1-decanol
	11	$\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{OH}$	1-undecanol
Lauryl alcohol	12	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$	1-dodecanol
Myristyl alcohol	14	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{OH}$	1-tetradecanol
Cetyl alcohol	16	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OH}$	1-hexadecanol
Stearyl alcohol	18	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OH}$	1-octadecanol
Ceryl alcohol	26	$\text{CH}_3(\text{CH}_2)_{24}\text{CH}_2\text{OH}$	1-hexacosanol
Myricyl alcohol	30	$\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{OH}$	1-triacontanol
	31	$\text{CH}_3(\text{CH}_2)_{29}\text{CH}_2\text{OH}$	1-hentriacontanol

### 3.2.3.2. *Examples of waxes to compose inelastic impression materials.*

Beeswax is animal wax; it is produced by specific bee's glands. Beeswax is obtained from honeycomb and wax growths in hives. Beeswax is mixture of esters (72%), saturated unbranched alkanes C<sub>21</sub>-C<sub>35</sub> (12-15%) and fatty acids C<sub>16</sub>-C<sub>36</sub> (15%). The main component of beeswax is ester myricyl palmitate:



Cleaned beeswax has density 0.95-0.97 g/cm<sup>3</sup>, softening temperature is 37-38<sup>0</sup>C and melting point is 62-64<sup>0</sup>C. A relatively great temperature difference between the temperatures of softening and melting is important advantage to use it as inelastic impression materials.

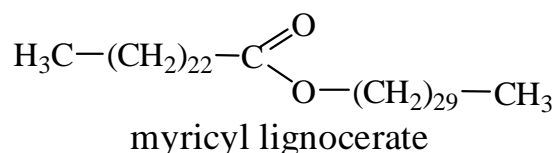
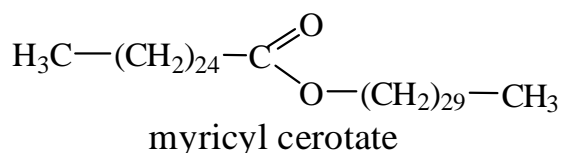
Wax is cheap, clean and easy to use. It is hydrophobic, insoluble in cold ethyl alcohol, but soluble in benzene, chloroform, diethyl ether. Wax used for taking impressions is solid at mouth temperature but is moldable at a temperature that is tolerated by oral tissues. Some wax is filled with special fillers to improve handling and stability. Fillers are natural or synthetic resins, talc, chalk, zinc oxide. Wax with fillers becomes stronger and more brittle and, when softened, flows much less compared with clean wax. Filled wax is softened at comfortable to the mouth temperature (50-60<sup>0</sup>C) and set in a mouth at t<sup>0</sup>=37-38<sup>0</sup>C.

Wax is supplied in many forms as sticks, strips, tubes or cakes of materials. Wax is softened or melted in water bath and then is placed in an impression tray, resoftened and seated in the mouth. When the material has cooled to mouth temperature, it returns to a rigid state and is removed.

Waxes as inelastic impression materials set hard and rigid compared with elastic impression materials. Therefore wax impression materials are used by many dentists to make preliminary impressions for complete dentures on edentulous patients. More commonly waxes are used as adjunctive materials in the dental laboratory for the fabrication of crowns, bridges and other restorations.

**Stearin** is material like wax that is obtained from animal fat by hydrolysis. Chemically it is the mixture of stearic, palmitic and other fatty acids. Cleaned stearin is solid compound with density 0.93-0.94 g/cm<sup>3</sup>, softening temperature 50-55<sup>0</sup>C and melting point near 70<sup>0</sup>C. Stearin is soluble in benzene and chloroform; it is brittle. Stearin is used as additional component of wax mixtures to give them less plasticity and higher melting point.

**Carnauba wax** is vegetable wax; it is found as protecting coating on leaves of palm-tree *Copernicia cerifera*. Major components of carnauba wax are esters (80%) myricyl cerotate and myricyl lignocerate:



Carnauba wax contains also long carbon chain alcohols (10%); 1-octacosanol  $\text{CH}_3-(\text{CH}_2)_{27}-\text{OH}$  and 1-heptacosanol  $\text{CH}_3-(\text{CH}_2)_{26}-\text{OH}$  are among them. It contains 1-1.5% long chain hydrocarbons.

Cleaned carnauba wax is solid brittle compound with yellow green color that is soluble in diethyl ether. It has density  $0.999 \text{ g/cm}^3$ , softening temperature  $40-45^\circ\text{C}$  and melting point near  $83-91^\circ\text{C}$ . Carnauba wax is used as additive of wax mixtures to make them harder, less plastic and to increase melting point.

Paraffin, ozokerite and ceresin are mineral waxes.

**Paraffin** is a mixture of solid alkanes  $\text{C}_{18}\text{H}_{38}$  and  $\text{C}_{35}\text{H}_{72}$  obtained by distillation of petroleum. Cleaned paraffin is colorless product without smell and taste that is soluble in most organic solvents. Paraffin density is  $0.907-0.915 \text{ g/cm}^3$ , its melting point is  $45-65^\circ\text{C}$ . Paraffin is almost not softened before melting; it is brittle, less plastic than other waxes, but it can be good scraped by sharp instrument. Paraffin is used in dentistry as component of wax mixtures for prepare models in fabrication of prosthesis bases, crowns.

**Ozokerite** or mining wax is naturally occurring mineral wax of petroleum group or petroleum bitumen group that is mixture of high long chain saturated hydrocarbons contained 85-87% of carbon and 13-14% of hydrogens. Ozokerite density is  $0.85 - 0.95 \text{ g/cm}^3$ , melting point is  $58-100^\circ\text{C}$ , congealing point is  $57-100^\circ\text{C}$  and penetration is 2-15. Color of ozokerite varies from light yellow to dark brown, sometimes green. Consistence of ozokerite also varies from soft and plastic to hard and brittle.

**Ceresin** is obtained from petrolatum and from ozokerite by specific cleaning with sulfuric acid and charcoal. Ceresin is a mixture of saturated long chain hydrocarbons contained 36-55 carbon atoms and slightly branched. It is white or yellow colored compound with density  $0.91-0.94 \text{ g/cm}^3$ , melting point  $65-85^\circ\text{C}$ , congealing point  $64-84^\circ\text{C}$  and penetration 5-15.

Ceresins and ozokerites are non-toxic, non-irritating, and non-hazardous. Both are soluble in benzene, acetone, chloroform, insoluble in water and alcohol. Ozokerite and ceresin are used in dentistry as additional components of wax mixtures to increases melting point, viscosity and hard.

### 3.3. RESTORATIVE DENTAL MATERIALS.

#### 3.3.1. Classification of restorative dental materials by location and fabrication.

Depending on the degree of tooth destructions, different restorations or filling are used to replace lost tooth structures. Some restorations replace a small

amount of tooth structure and are supported by the remaining tooth structure. These restorations are held in the tooth by undercuts (mechanical lock), adhesion or both. Crowns are used to restore teeth when a substantial amount of tooth structure is missing. If one tooth or several teeth are lost, dental bridges or dental prosthesis (complete or partial dentures) are used. Dentists classify restorative materials by location and fabrication to two categories:

1. Direct restorative materials.
2. Indirect restorative materials.

Direct restorative materials are constructed directly in the oral cavity to make filling of tooth. A direct restorative material is usually placed in the “cavity preparation” that was prepared by the dentist to remove the decay. When initially placed, a direct materials sets to become a hard, strong material. Polymer direct restorative materials are composites and glass ionomer cements that are polymerized in a mouth by chemical reactions.

Indirect restorative materials are fabricated outside the mouth. They are cured at elevated temperatures and under high pressures. Indirect restorative materials are used to make inlays, crowns, bridges and dental prosthesis (dentures) indirectly in a dental laboratory on a replica of the patient oral tissues.

### ***3.3.2. The performance criteria of direct restorative materials.***

In order to have good clinical service life the direct restorative materials have to meet certain performance criteria. Their important clinical, physical and mechanical properties are the following:

1. Absence of toxic or irritant constituents, indifference to tooth tissues;
2. Absence of solubility in the mouth liquid;
3. Adequate working and setting time that allows material to be plastic while restoration is formed and to set during 15-30 minutes;
4. Stable adhesion to tooth tissues, metals and ceramics in wetting environment;
5. Linear coefficient of thermal expansion that is much closer to this of tooth tissues.
6. Ability to set on walls of cavity preparation in presence of small amount of water or saliva;
7. Small value of thermal conductivity;
8. Low water sorption;
9. High color stability;
10. Adequately imitate properties of tooth tissues after setting;
11. pH~7 during setting and after setting;

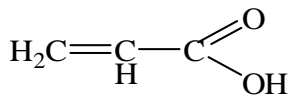
12. The much low shrinkage that strains the interfacial bond between the restoration and the tooth. It leads to a very small gap that can allow marginal leakage of saliva and microorganisms; it can result recurrent caries.
13. The compressive and flexural strength that much closed to the enamel;
14. Good wear and abrasion resistance.

### 3.3.3 .Polymers on base acrylic and methacrylic acids and their esters.

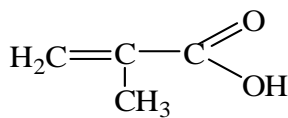
#### 3.3.3.1. Acrylic and methacrylic acid and their esters.

Both direct and indirect restorative polymer material are more commonly based on polymers and copolymers made up based on acrylic and methacrylic acids and their esters.

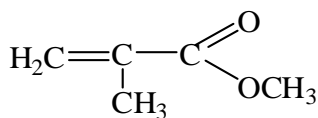
#### Monomers



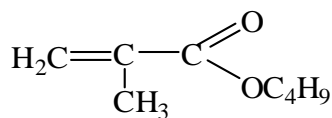
Acrylic acid  
(propenoic acid)



Methacrylic acid  
(2-methylpropenoic acid)

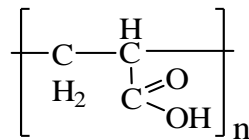


Methyl methacrylate  
(methyl 2-methylpropenoate)

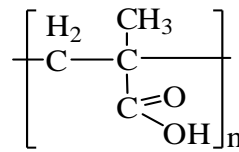


Butyl methacrylate  
(butyl 2-methylpropenoate)

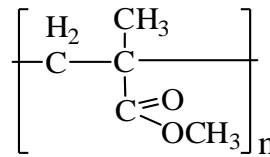
#### Polymers



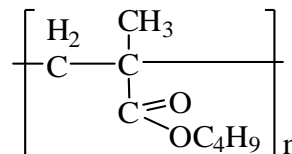
Poly(acrylic acid)  
poly(propenoic acid)



Poly(methacrylic acid)  
poly(2-methylpropenoic acid)



Poly(methyl methacrylate)



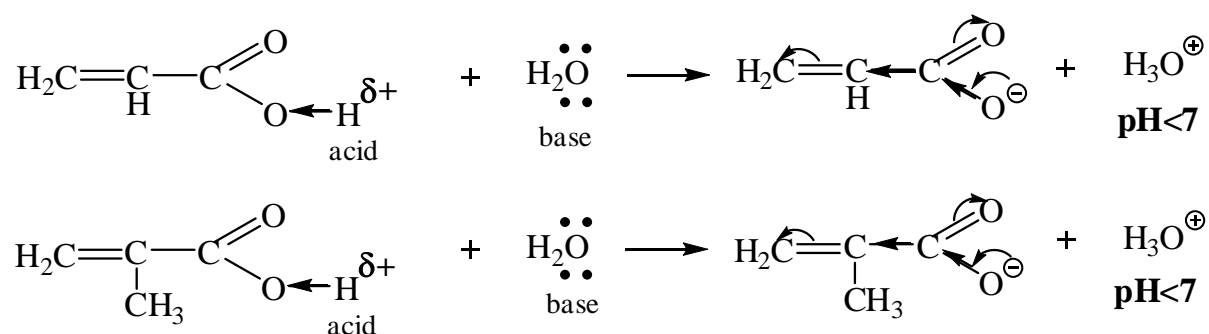
Poly(butyl methacrylate)

Acrylic and methacrylic acids both are liquids with sharp smell.

**TABLE 5. Physical properties of acrylic and methacrylic acids and their derivatives.**

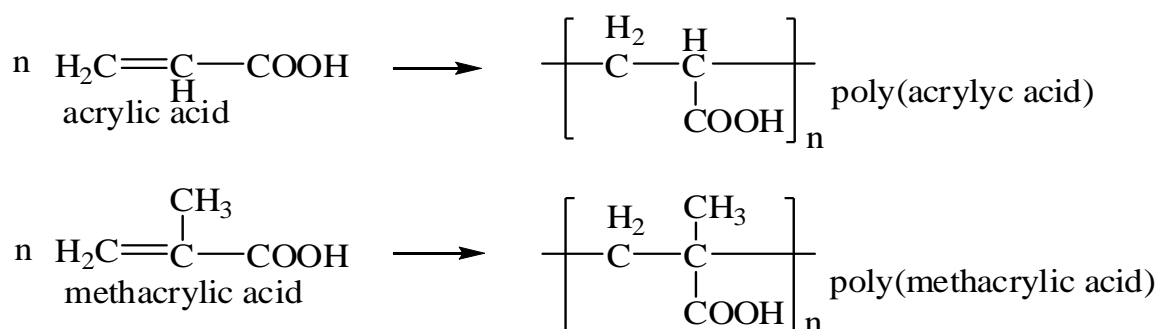
The name	pKa	Melting point, °C	Boiling point, °C	Boiling point of methyl esters, °C
Acrylic acid	4.25	12.3	141.9	80.5
Methacrylic acid	4.32	16	163	100

Acrylic and methacrylic acids both are classified as  $\alpha,\beta$ -unsaturated carboxylic acids. Their chemical properties are provided by presence of carboxylic group and double bonds in molecules simultaneously. In the water environment acrylic and methacrylic acids dissociate to make weak acidic solutions:



Acrylic and methacrylic acid are stronger acids than correspondent saturated carboxylic acids -propanoic ( $\text{pK}_a=4.87$ ) and 2-methylpropanoic ( $\text{pK}_a=4.84$ ) acids because the anions of acrylic and methacrylic acids are stabilized by conjugation. Conjugation provides more effective delocalization of negative charge of carboxylate anions, it decreases its energy and increases stability.

Typical property of acrylic, methacrylic acids and their esters is ability to polymerization reactions that is used to synthesis of their esters.

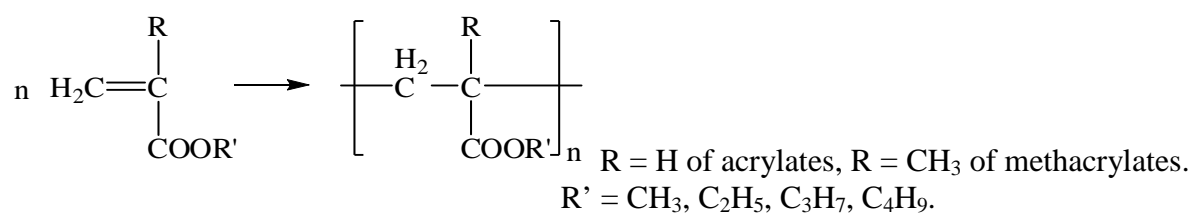


Polymers based on acrylic and methacrylic acids have chemical properties of carboxylic acids. Poly(acrylic acid) and poly(methacrylic acid) are water soluble due to much number of polar carboxylic groups along the macromolecular chains that are dissociate in water. Homo- and copolymers based on acrylic and methacrylic acids are used as matrix of restorative materials that set by reaction

to complex formation with oxides and salts of several metals (ZnO, CaO, Al<sub>2</sub>O<sub>3</sub>). This system is used to make glass ionomer direct restorative materials.

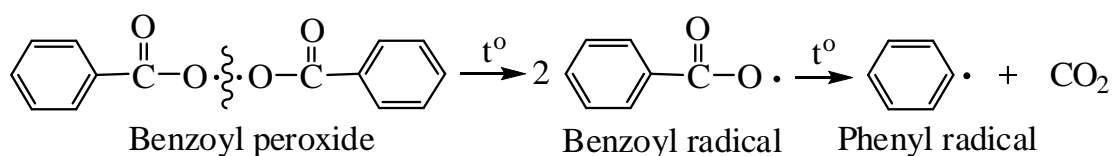
### 3.3.3.2. The mechanism of acrylates and methacrylates free radical polymerization. Polymers of heat cured and cold (chemical) cured. Depolymerization.

The polymer networks of polyacrylates and poly(methyl methacrylates) are formed by free-radical addition polymerization of the corresponding monomers that are esters of acrylic and methacrylic acids according to the following general scheme of reaction:

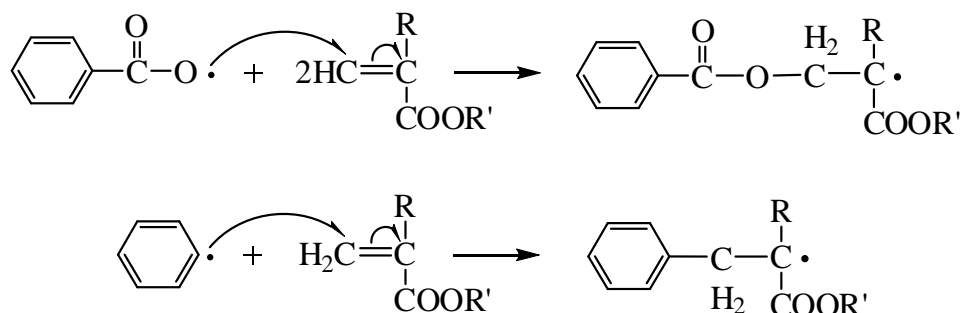


The radical polymerization reaction takes place in three stages: initiation, propagation and termination.

1. **Initiation stage** involves the homolysis of less resistant O-O bond of initiator benzoyl peroxide when initiator molecule becomes activated by heat, light or chemical reactions. Resulted benzoyl radical is decarboxylated to give phenyl radical and carbon dioxide.

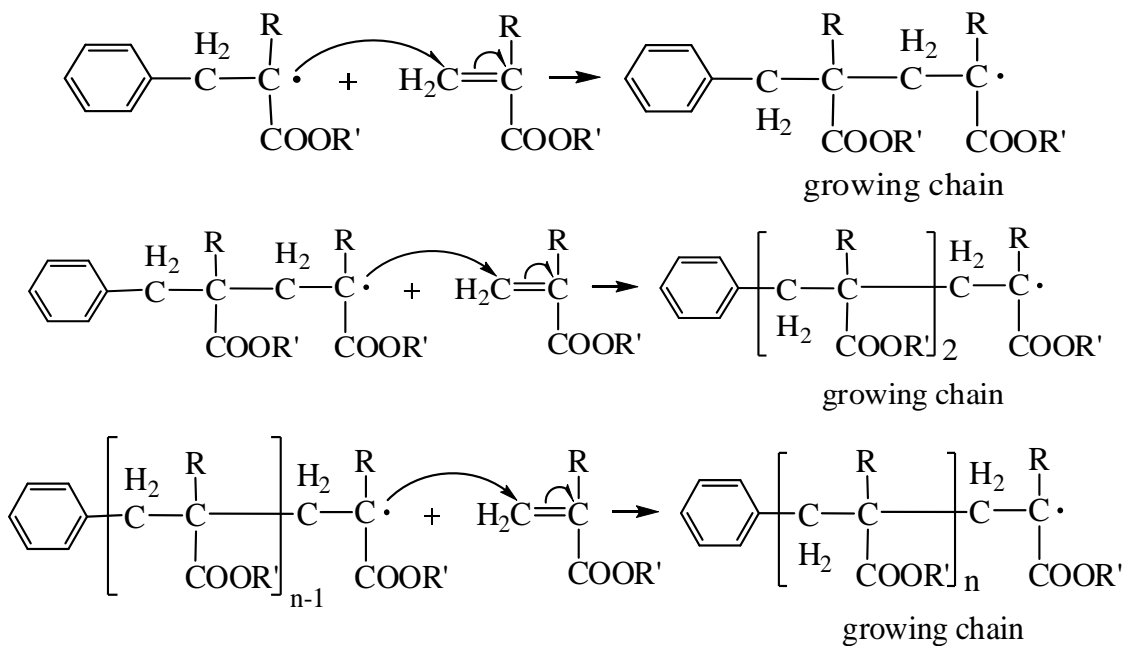


The free radicals add to a π-bond of a monomer species generating an active centered monomer radical:



2. During the following **propagation stage** rapid addition of other monomer molecules to the active center occurs to provide the growing polymer chain:

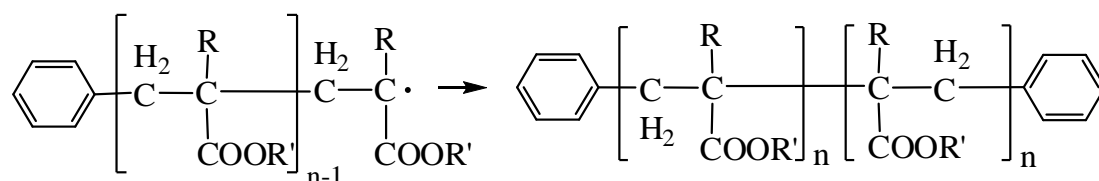




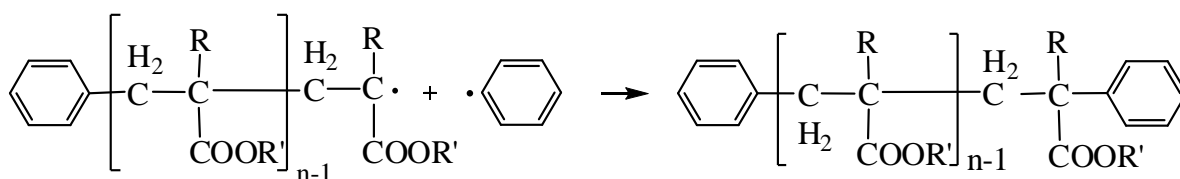
The propagation reaction continues to build molecular weight until the growing free radical is terminated.

3. Termination step takes place by one of the following reactions:

a) Recombination of two growing free radicals:

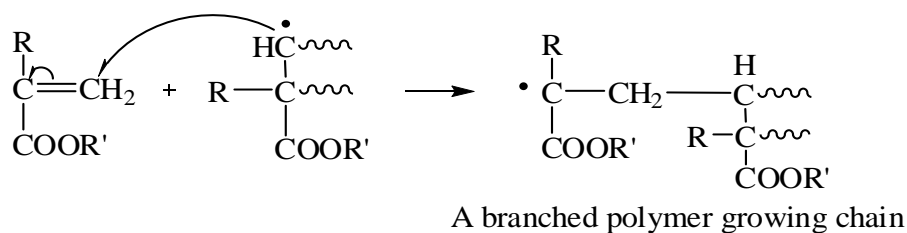


b) Recombination of growing free radical and initiator free radical, for example benzene radical:

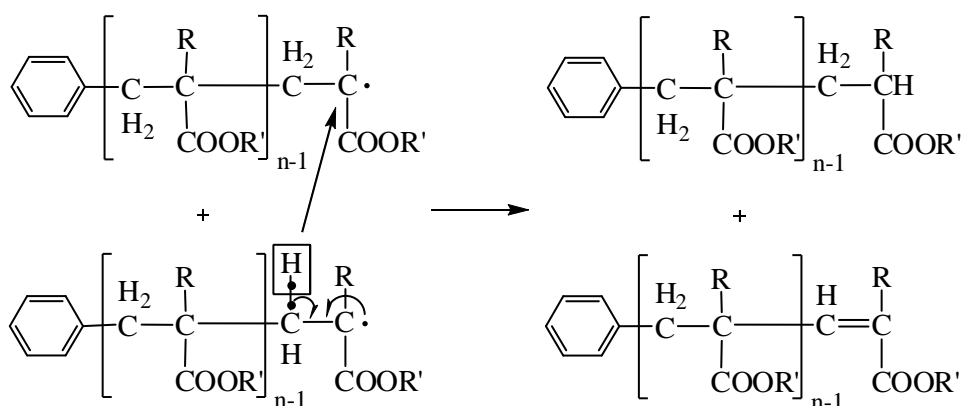


c) Chain transfer reaction to other growing chain that leads to formation of branched polymer chain and cross-linking:





d) Disproportionation (hydrogen atom transfer) reaction:



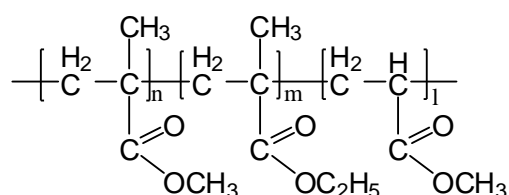
Acrylic polymers have many applications in restorative dentistry as denture bases, artificial teeth, denture repair materials, impression trays, provisional restorations and maxillofacial appliances for skeletal defects in orthopedic stomatology and as composites for direct restorations in therapeutic stomatology.

Acrylic resin systems are commonly supplied as powder and liquid or two paste system of filled composite restorative materials. This material sets by polymerization reaction that can be activated in heating, by chemical reaction or light. The powder and liquid may contain the components listed in table 6.

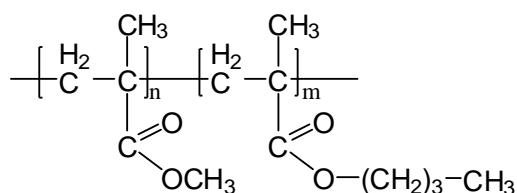
**TABLE 6. Principal ingredients of acrylic resin systems.**

	Heat - cure	Cold (chemical) - cure
Powder	Acrylic polymer (copolymer) beads	Acrylic polymer (copolymer) beads
	Initiator	Initiator
	Pigments, dyes	Pigments, dyes
	Opacifier	Opacifier
	Plasticizer	Plasticizer
	Dyed organic fiber	Dyed organic fiber
	Inorganic fillers	Inorganic fillers
Liquid	Monomer	Monomer
	Inhibitor	Inhibitor
	Plasticizer	Activator
		Plasticizer
		Cross-linking agent

**The powder** of most commercial material m,s contains poly(methyl methacrylate), modified with small amounts of ethyl, butyl or other alkyl methacrylates and alkyl acrylates. The different alkyl groups in ester group provide physical and mechanical properties of polymers. The alkyl group contained greater number of carbon atoms increases plasticity and resists to fracture by impact and decreases density. Poly(methyl acrylates) are usually more hard and less plastic than polyacrylates. Polymer with desirable plasticity is made as copolymer of different esters of methacrylic and small amount of acrylic acids. For example, dental material with internal plasticizing *ethacril* bases on copolymer of methyl methacrylate (89%), ethylmethacrylate (8%) and methylacrylate (2%):



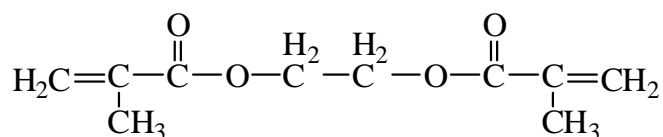
The main constituent of powder of the same direct restorative material as noracryl-100 and acryoxide is copolymer of methyl methacrylate and butyl methacrylate:



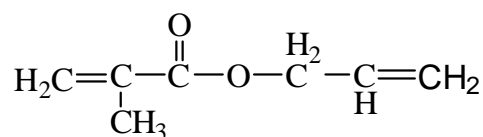
Pure polymers such as poly(methyl methacrylate) are clear and are adaptable to a wide range of pigmentation. Colorants are added to obtain various tissue-like shades; zinc or titanium oxides are used as opacifiers.

**The liquid** component of powder-liquid type acrylic resins is mostly monomer methyl methacrylate or mixture of monomers.

If a cross-linked polymer is desired, organic compound that cross links polymer macromolecules to each other are added to the monomer in liquid. Cross-linking agent is a compound contained two double bonds at the opposite ends of the molecule end serving to link long polymer molecules to each other. Typical cross-linking agents are the following:



Ethylenglycol dimethacrylate



Allyl methacrylate

Use of cross-linking agents provides greater resistance to minute surface cracking and may decrease solubility and water sorption. A linear resin without any cross-linking agent is brittle. Addition of cross-linking agent improves the toughness of material. Cross-linking compound may be present in amounts of 2% to 14%, but have little effect on the tensile strength, flexural properties or hardness of acrylic plastics.

During storage of restorative material or by heat, light and traces of oxygen the monomer may be polymerized. To prevent this undesired polymerization and to give the liquid adequate shelf-life the inhibitor is added. The most commonly used inhibitor is hydroquinone in concentrations of 0.003% to 0.1%.

A chemically activated or cold-cure (or self-cure) material has redox systems contained initiator (benzoyl peroxide or diisobutylazonitril) and activator (ferrous ( $\text{Fe}^{2+}$ ) salts or tertiary aromatic amines). Initiator is added to the powder when it is synthesized. Activator is added to the liquid. When powder and liquid are mixed activator reacts with initiator.

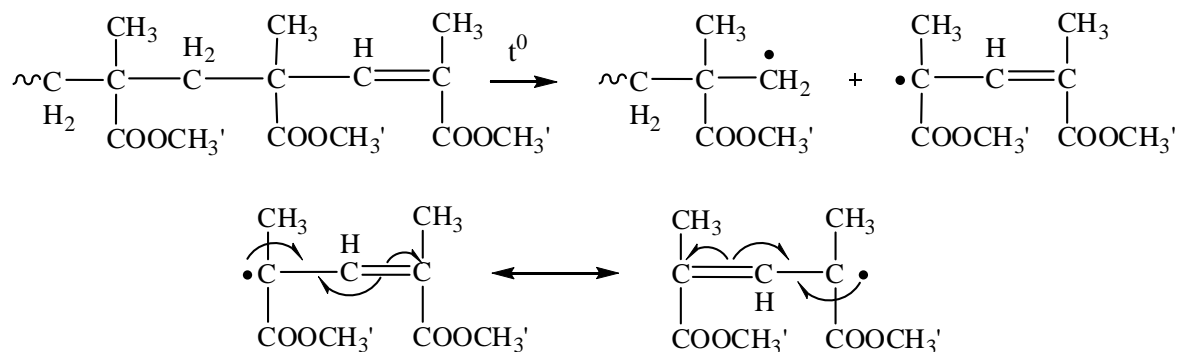
Polymerization reaction can occur very rapidly if only small amount of free radicals is formed. For a cold-cure dental material to be useful the reaction must be delayed after mixing and occur slowly. The reaction of chemically activated material is initially delayed for several minutes by the presence of inhibitor. An inhibitor, typically hydroquinone, reacts with the first free radicals that are produced during the initiation process and destroy them. The reaction of free radicals destruction competes with polymerization reaction and wins. The competing reaction of inhibitor with free radicals delays polymerization and provides working time for placement, molding and shaping of the material. The working time of acrylic resins is from 4 to 15 minutes.

Chemically activated acrylic resins are used to make temporary crowns, custom impressions trays, orthodontic retainers and many other dental devices.

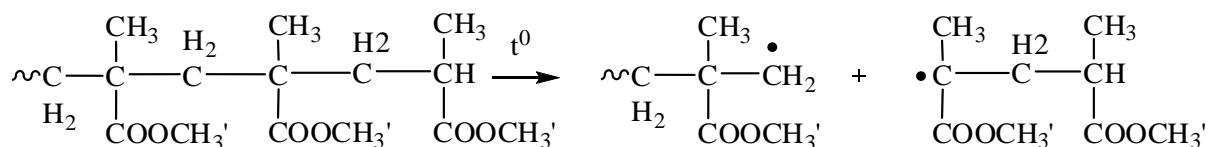
At high temperature ( $\sim 300^\circ\text{C}$ ) polymer can lose monomer at the end of the macromolecular chain. This process is called **depolymerization**. The degree of depolymerization depends on monomer structure, condition of polymer synthesis and condition of thermal destruction.

The heat (enthalpy change) of polymerization of  $\alpha,\alpha$ -disubstituted ethylenes, for example methyl methacrylate, that leads to formation of polymers containing quaternary carbon atom is small; it is  $\sim 10$  kkal/mol (41.8-54.3 kJ/mol). It is less than the heat of polymerization of monosubstituted ethylenes, for example methyl acrylate that is  $\sim 20$  kkal/mol (83.6 kJ/mol). Therefore depolymerization of polymers containing quaternary carbon atoms like poly(methyl methacrylate) takes place easier than polymers containing tertiary (poly(methyl acrylate)) or secondary (polyethylene) carbon atoms. On the other side tertiary carbon radical that is intermediate of poly(methyl methacrylate) depolymerization is more stable than secondary (poly(methyl acrylate)) or primary (polyethylene) carbon radicals.

One of termination reactions of poly(methyl methacrylate) polymerization is disproportionation. That's why some of polymer macromolecules contain double bonds at the end. Depolymerization of these macromolecules can start with homolysis of  $\sigma$ -bond to give a resonance stabilized allyl radical:

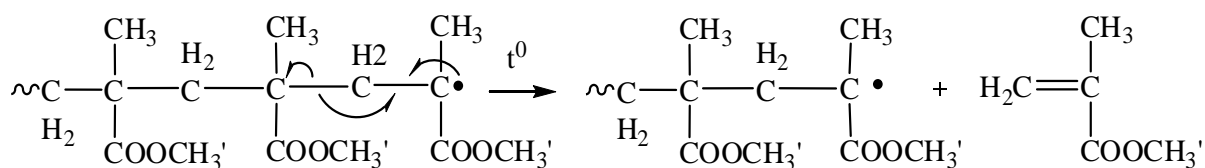


Homolysis of macromolecule that doesn't have double bond on the end of chain lead to formation of less stable carbon radical.



Because the stability of saturated carbon radical is less than conjugated carbon radical homolysis of saturated macromolecule is slower than macromolecule with double bond on the end of the chain.

Both of these reactions followed with losing of monomers:



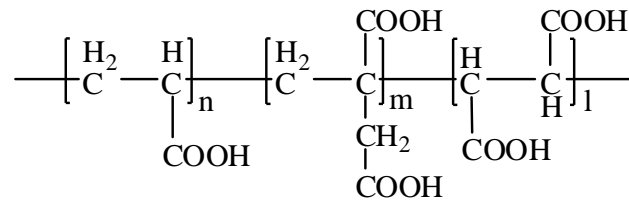
Depolymerization reactions destroy the polymer macromolecules and it are not desirable. The depolymerization reaction can be delayed by synthesis of copolymers containing monomer units that are less allowed to depolymerization. For example copolymers of methacrylates and acrylates are less allowed to depolymerization reactions, because this process is almost stopped when the end of macromolecular chain becomes acrylate residue due to formation of less stable secondary saturated carbon radical.

### 3.3.3.3. Polycarboxylate cements. Glass ionomers.

Since 1965 year other type of direct restorative filling materials - polycarboxylate cements was introduced. Unlike polyacrylate polymers polycarboxylates are water soluble and material has high adhesion to tooth tissues. Polycarboxylate cements were improved by invention of glass ionomers in 1970 year.

Glass-ionomers are water based self-adhesive restorative materials containing a reactive fluoroaluminosilicate glass filler and polymer or copolymer of carboxylic acid as the matrix. There are two types of glass ionomers: conventional glass ionomers and resin-modified glass ionomers.

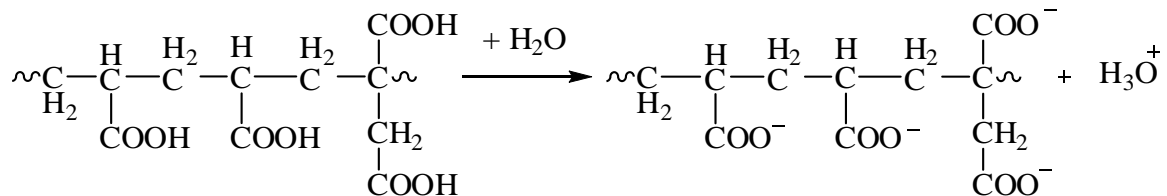
The **conventional glass ionomer** materials are supplied as two-part powder-liquid systems. The polymeric matrix of most glass ionomers is a copolymer of acrylic acid and itaconic acid or maleic acid.



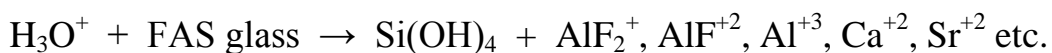
Polycarboxylic acids are water soluble and are supplied as a concentrated aqueous liquid. The working and setting characteristics of material are controlled by addition of tartaric acid. The powder is an acid-reactive comminuted fluoroaluminosilicate (FAS) glass contained ions such as calcium, strontium and lanthanum. Use of heavy metal ions makes the set material radiopaque to x-rays.

After mixing the powder and liquid an acid-base setting reaction begins between the polycarboxylic acid and FAS glass. An initial set is achieved within 3 to 4 minutes of mixing, however the ionic reaction continues for at least 24 hours or more and maturation is achieved much later.

In aqueous liquid carboxyl groups of polycarboxylic acid undergo partial ionization in water; so there is weak acidic of this liquid.

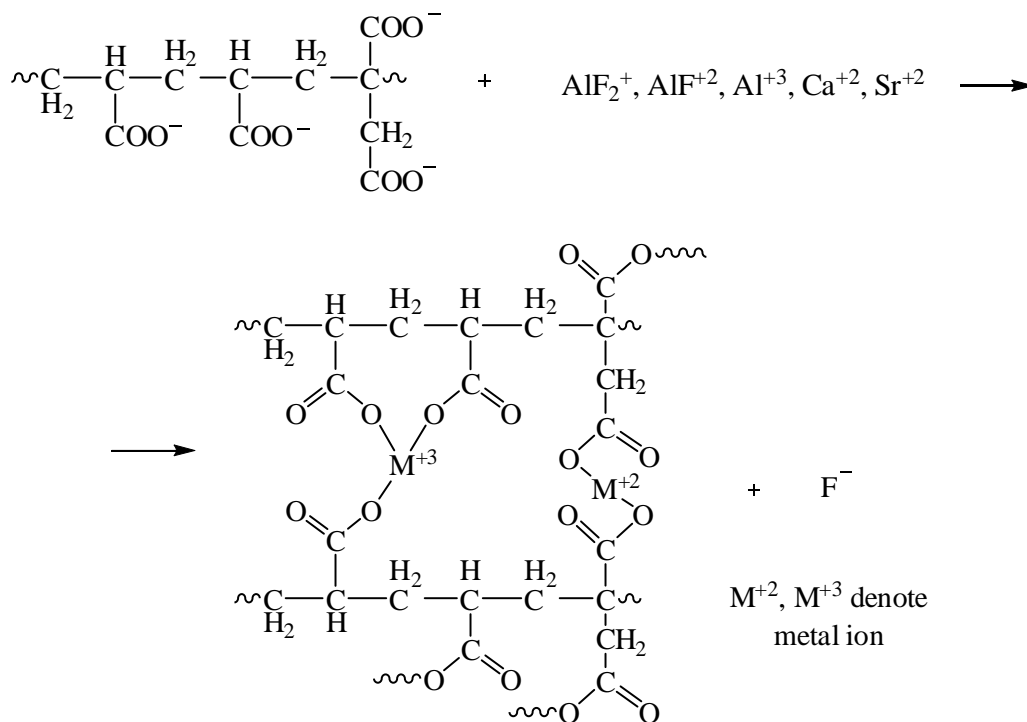


The hydrated proton attacks the surface of glass particles releasing calcium and aluminum ions.

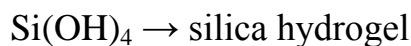


The carboxylate ions from the polymer react with these metallic ions to form a salt bridge resulting in gelation and setting. During the initial stage cal-

cium ions are more rapidly bound to the polyacrylate chains; binding to the aluminum ions occurs at a later stage. The strength of cement is built with time.



Silicic acid is initially formed when the glass breaks down, but it rapidly polymerizes to form silica hydrogel:

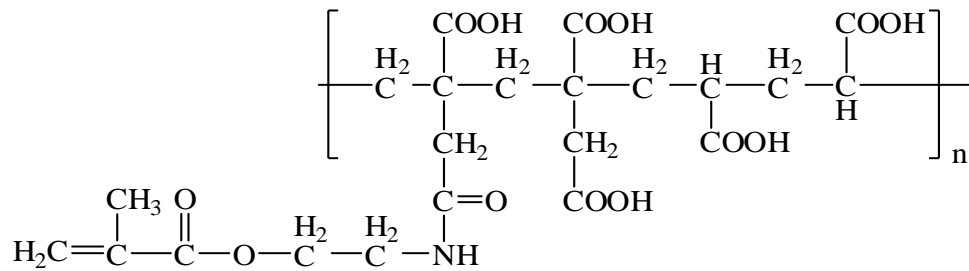


A very important result of the setting reaction is release of fluoride ions from the glass matrix. The fluoride release process is sustained and occurs over a long period of time.

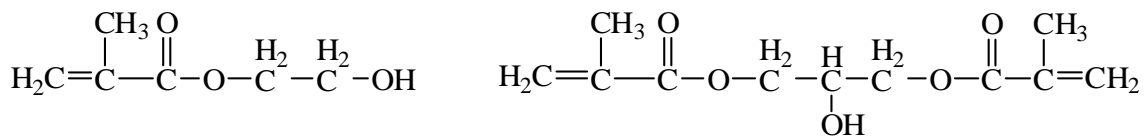
The set cement contains a hydrogel of calcium, aluminum and fluoroaluminum polyacrylates that involve the unreacted glass particles sheathed by a weakly bonded siliceous hydrogel layer. About 20% to 30% of the glass is dissolved in reaction. Smaller glass particles are completely dissolved and replaced by siliceous hydrogel particles with fluoride crystallites. The stability of matrix is provided by chain entanglement, weak ionic cross-linking and hydrogen bonding.

The **resin-modified glass ionomer** system was introduced in late 1980s. It has a longer working time and quick setting time so that immediate finishing can take place. The resin-modified glass ionomers essential components are aqueous polycarboxylic acid and fluoroaluminosilicate glass. Additionally they contain some methacrylate component and free-radical initiator. There are two ways in which methacrylate components can be introduced. In the first type the

polycarboxylic acid polymer chain is modified with a pendent methacrylate group, for example:



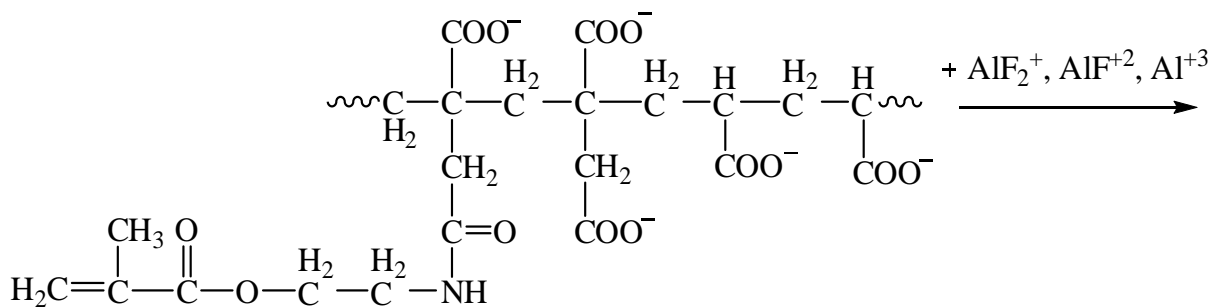
The liquid portion contains a water-miscible methacrylate monomer:



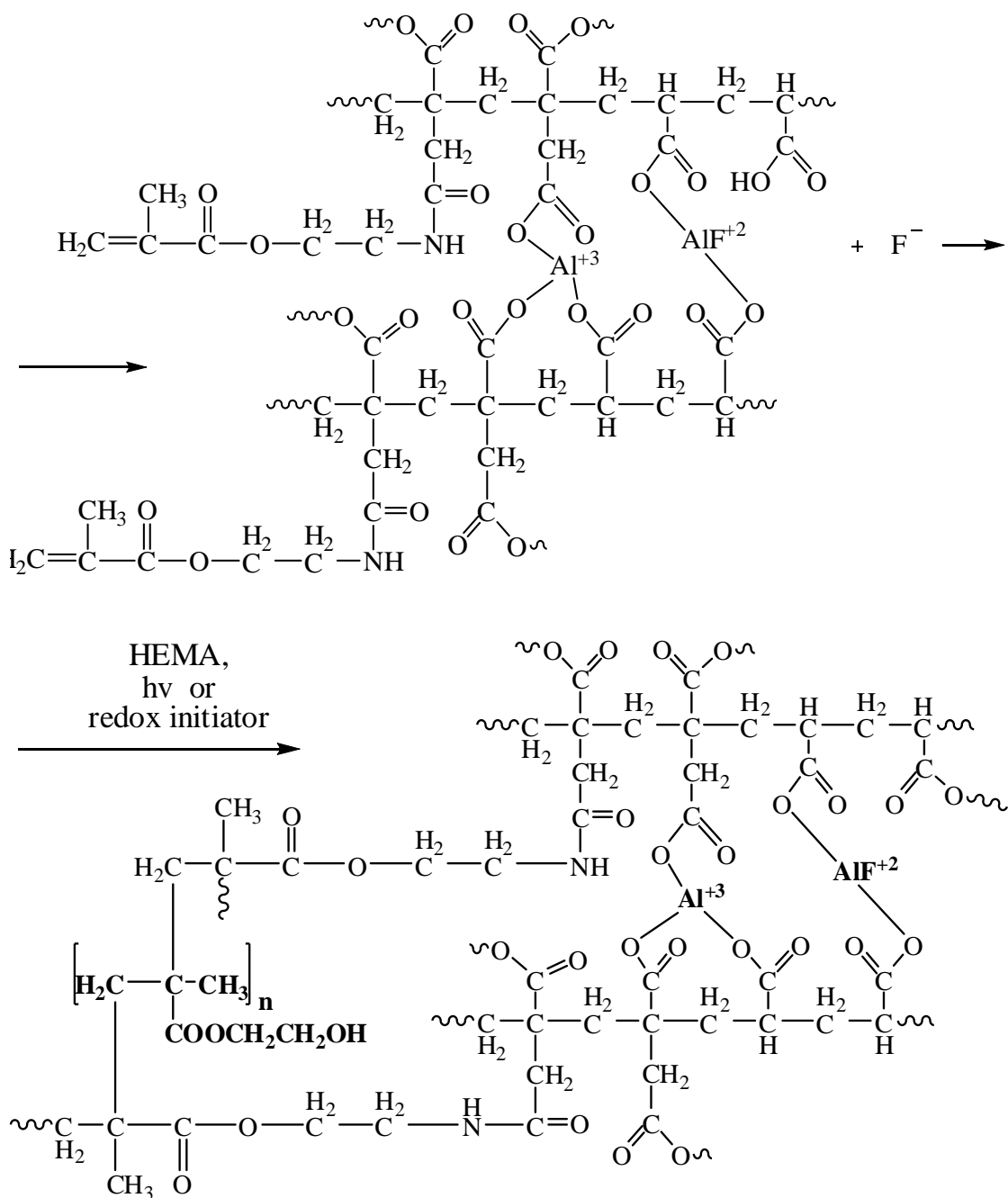
Hydroxyethylmethacrylate (HEMA). Glycerol dimethacrylate (GDMA).

In another type of resin-modified glass ionomer system the polymer is unmodified polycarboxylic acid. In this case the liquid has a mixture of hydrophilic methacrylate monomers and water. Generally the water content of these materials is lower and the monomer content is higher than for the first type. As a result these glass ionomers have the higher coefficient of thermal expansion. Free radical initiators are added to trigger the curing of methacrylate groups. To improve the manipulation and mechanical properties of material the FAS glass of both conventional and resin-modified glass ionomers the surface of glass are treated with an organic modifier.

Two distinct types of curing reactions take place in a light-cure glass ionomer: the traditional acid base glass ionomer cure and free-radical methacrylate polymerization.







Because the methacrylate reaction is a chain polymerization, it proceeds at several orders of magnitude higher rate than the acid-base reaction. In the system that is lower in water and higher in methacrylate components the extent of acid-base reaction is small because ionization of polycarboxylic acid is severely suppressed.

Using only photo-initiators for cross-linking of methacrylate groups requires curing of the resin-modified glass ionomer in layers due to a limited depth penetration of visible light. This is not disadvantage in applications where thin layers of materials are to be placed, for example, for lining or basing. But the need for incremental filling is not desirable for restorative and core build-up

application. To dissolve this problem the tri-cure glass ionomer system was proposed in materials “Vitrebond”, “Vitremer”(“3M”), “Fuji”(“GC”), “Iono-seal”(“VOCO”). The three curing reactions are the follows:

1. Acid-base glass ionomer reaction.
2. Light-activated polymerization.
3. Chemically activated polymerization.

Addition of self-cure redox initiators to photoinitiators provides the methacrylate polymerization in the absence of light. Reactions 1 and 3 take place spontaneously when the powder and liquid are mixed. Reaction 2 occurs only in light initiation.

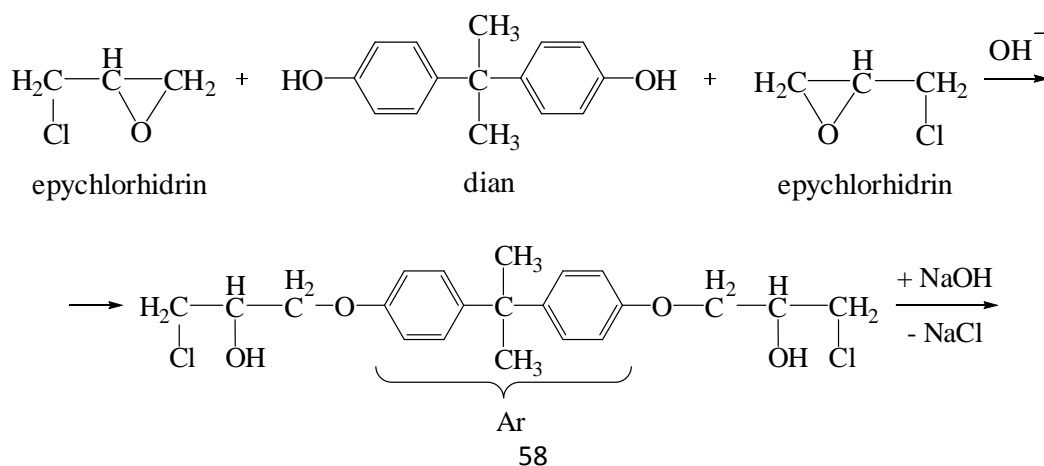
Clinical use of both conventional and resin-modified glass ionomers include a variety of restorative applications mainly in situations of high caries activity or where caries are likely to reoccur. The main clinical indications are for small lesions (long-term non-stress-bearing restorations and interim restoration in permanent teeth, the atraumatic restoration technique). They are used to make liners or bases and for a sandwiching, layering and stratification technique, in which a resin composite is bonded over a base of the glass ionomer.

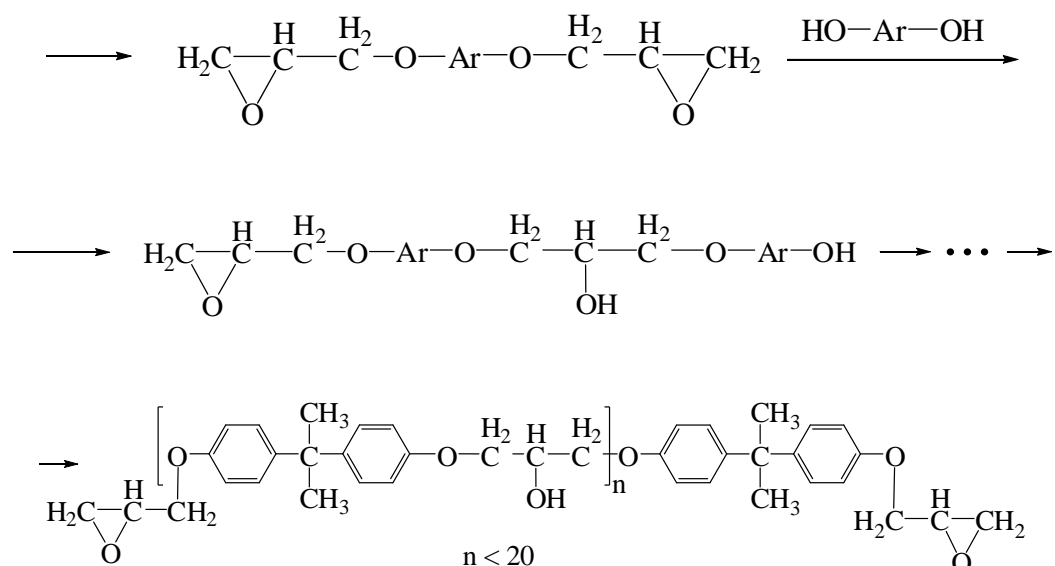
Glass ionomers have good clinical adhesion to tooth. The adhesion is mostly chemical and proceeds through the formation of bonds between carboxyl groups of polycarboxylic acid macromolecules in a restoration and calcium ions of tooth hydroxyapatite.

Important characteristic of glass ionomer materials is that they are a reservoir of fluoride ions. The fluoride is released by an ion-exchange mechanism from these materials over prolonged periods.

### 3.3.3. *Polymers on base epoxy resins.*

**Epoxy resins** are monomers, oligomers or polymers formed by the reaction between organic compounds contained epoxy group with acidic compounds like difunctional alcohols or phenols. Manufactured epoxy resins are product of polycondensation reaction between epichlorhydrine (3-chlor-1,2-epoxypropane) and bisphenol A or diane (2,2-di(4-hydroxyphenyl)propane) in an alkaline solution:

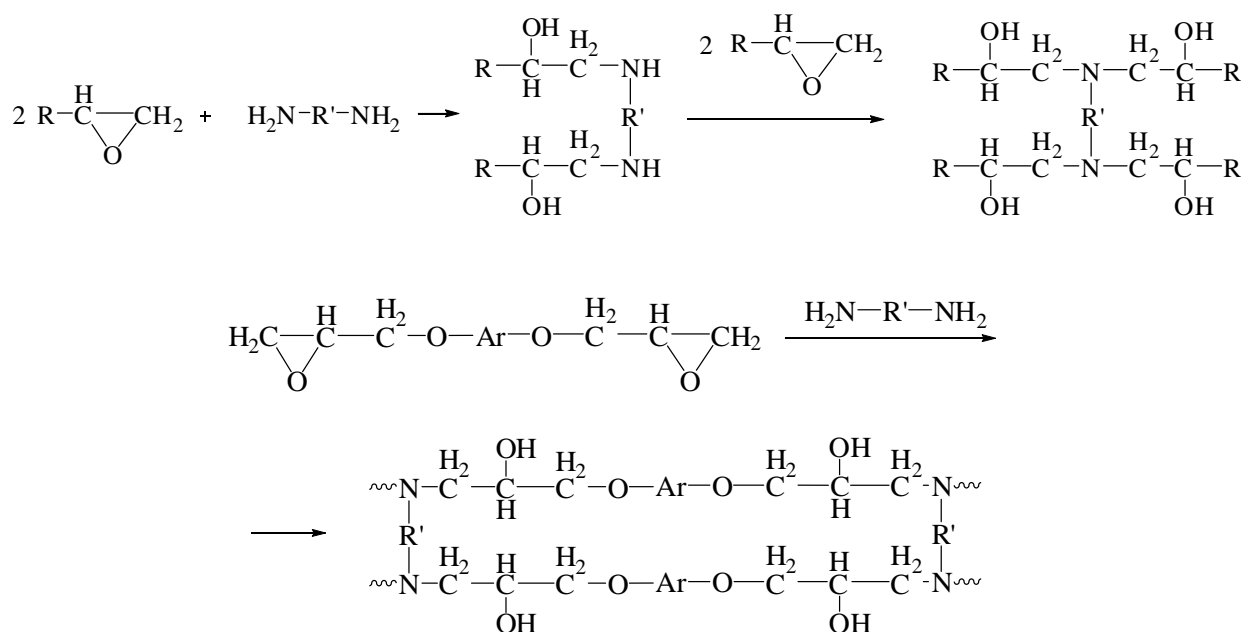




- Epoxy resins based on dian give materials the following useful properties:
1. High adhesion to polar materials like metals, glass, ceramic, dentine and enamel of tooth that provided by presence of polar hydroxyl and relatively flexible ether functional groups.
  2. High compressive strength and hardness that is provided by high concentration of rigid diphenylolpropane fragments contained aromatic rings in combination with group  $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$  that lead to relaxation of mechanical strains in a polymer macromolecule.
  3. Chemical and humid resistance explained by presence of high concentration of chemically stable aromatic fragments and resistant to hydrolysis ether functional groups.
  4. Low shrinkage in setting reaction because reduction of volume that occurs during opening of epoxy groups is less as compared with addition polymerization of acryl monomers.

Epoxy resin material sets by reaction that cross-links the oligomer molecules of epoxy resin to make three-dimensional network. Cross-linking reaction is carried out at room temperature (cold-cure) and takes place with the ending epoxy groups. Typically used cross-linking agents are primary and secondary di-, tri- and polyamines, for example, diethylentriamine  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  or polyethylenpolyamine  $\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_n-\text{H}$  ( $n=3-6$ ).

In a setting reaction initially linear polymers are formed. When molecular mass of polymer becomes relatively high cross-linking reactions occur to make finally set product. Cross-linking reaction takes place as nucleophilic substitution reaction with opening of epoxy cycle by nucleophilic attack of amino groups.



If the number of amino groups in the structure of cross-linking agent increases, the number of cross-linkages increases, the density and strength of set polymer material increases. The setting time depend on the number of active functional (amino) groups of cross-linking agent, the number of epoxy groups in an oligomer and viscosity of epoxy resin. The setting time of epoxy resin material is about 2 hours at room temperature. In heating epoxy resin materials set faster (during 2-3 minutes); however it is not comfortable in practice.

The epoxy resin restorative filling material, for example “Dentoxid”, is supplied as mixture of oligomers based on epychlorhydrine and bisphenol A (diane) in a tube, the powder (filling) and liquid diethylentriamine. More effective used cross-linking agents are ortho-oxyphenylmethylenethylenediamin and ortho-oxyphenylmethylenhexamethylenediamine. To improve mechanical properties epoxy resin restorative materials are filled with porcelain (“Dentoxid”) or quartz powder (“Epoxydan”).

## IV. MODERN RESTORATIVE MATERIALS. CHEMICAL CURED AND LIGHT CURED COMPOSITES.

### 4.1. OVERVIEW AND COMPOSITON OF COMPOSITES.

To improve clinical performance and mechanical properties of polymer restorative materials new materials called composites were developed in early 1960s. Dental **composites** are combination of two or more classes of materials: a polymer and ceramic. The polymer function as a matrix that binds ceramic particles and these ceramic particles are reinforcing materials. Polymer matrix composites are used to replace missing tooth structure and modify tooth color

and contour to enhancing esthetics. Resin composites are used as sealants, intracoronary and extracoronary restorations, provisional restorations, veneers, denture teeth, cements and core buildups.

In a composite the properties are intermediate between the two compositional materials and are not achievable with one material alone. Individual ceramic particles are not condensable or packable, but the addition of a polymer to bind them enables the composite to be used as a paste. Use of a polymer alone does not acquire sufficient stiffness and stability, which are properties contributed by ceramic particles. Resin composites have higher mechanical properties than acrylics and silicates; they are moderate in stiffness and hardness. Resin composites have lower thermal coefficient of expansion, lower dimensional change in setting and higher resistance to wear.

A resin composite consists of four major components:

1. organic polymer matrix;
2. inorganic filler particles;
3. coupling agent;
4. initiator - accelerator system.

The organic polymer matrix of most commercial composites is a cross-linked matrix of dimethacrylate monomers containing aromatic fragments. The double bonds on each end of such molecules undergo addition polymerization by free radical initiation.

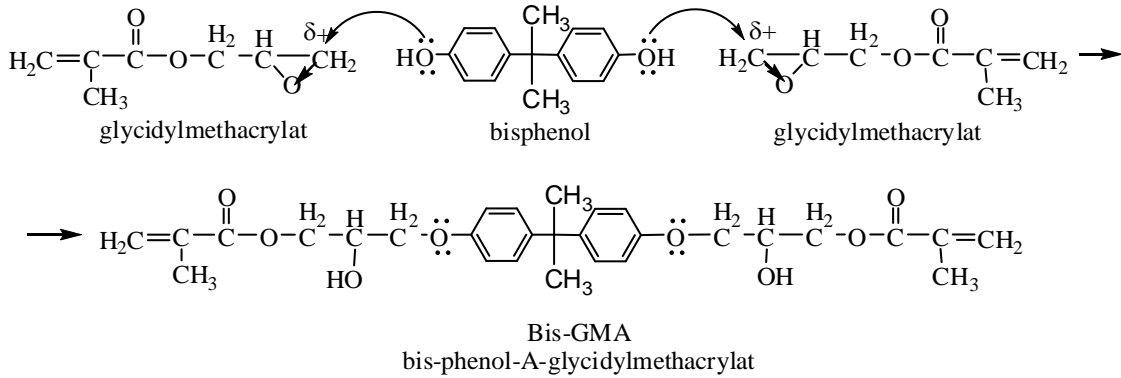
The dispersed inorganic filler particles contain one or more inorganic materials: finely ground quartz or glass, sol-gel-derived ceramics, microfine silica or more recently nanoparticles.

In dental resin composites coupling agents are used to enhance the adhesion between ceramic particles and polymer matrix, thereby increasing its wear resistance and long-term surface integrity. The typical coupling agent, an organosilane, forms covalent bonds between inorganic and organic phases of the composite.

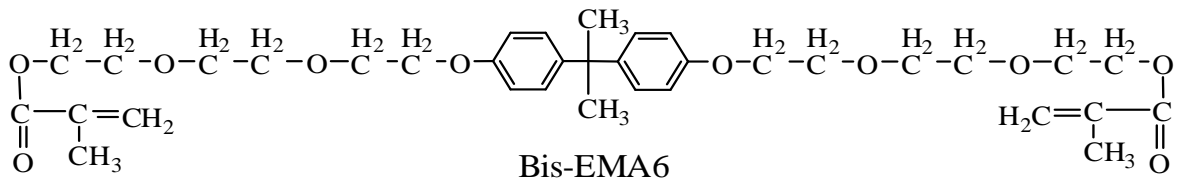
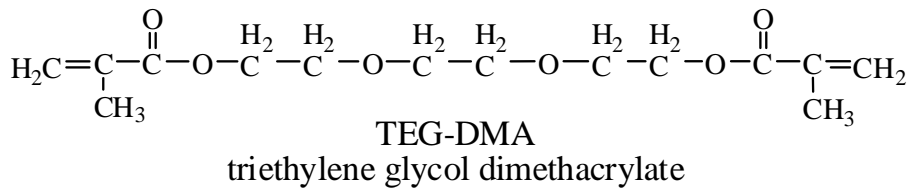
The initiator - accelerator system begins polymerization and cross-links the material into a hardened mass. The polymerization reaction can be triggered by typical light-activation, self-curing (chemical activation) and dual curing (chemical and light-curing).

#### **4.2. HIGH MOLECULAR MONOMERS OF THE MATRIX OF MODERN RESTORATIVE COMPOSITE MATERIALS.**

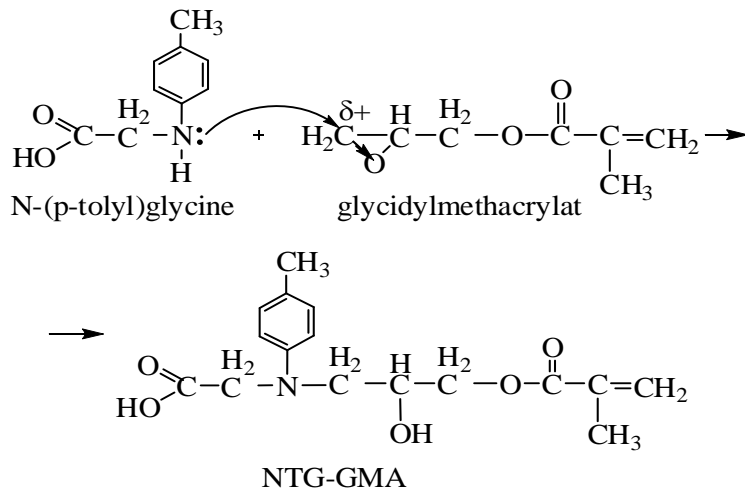
The monomers used for the resin matrix of restorative composite materials are mainly dimethacrylate compounds. The most common dimethacrylate monomer is adduct Bis-GMA (2,2-bis[4(2-hydroxy-3-methacryloxypropoxy)phenyl] propane or bis-phenol-A-glycidyl methacrylate). Adduct Bis-GMA is synthesized by the reaction of 2,2-di(4-hydroxyphenyl) propane (bis-phenol A or dian) with glycidyl methacrylate.



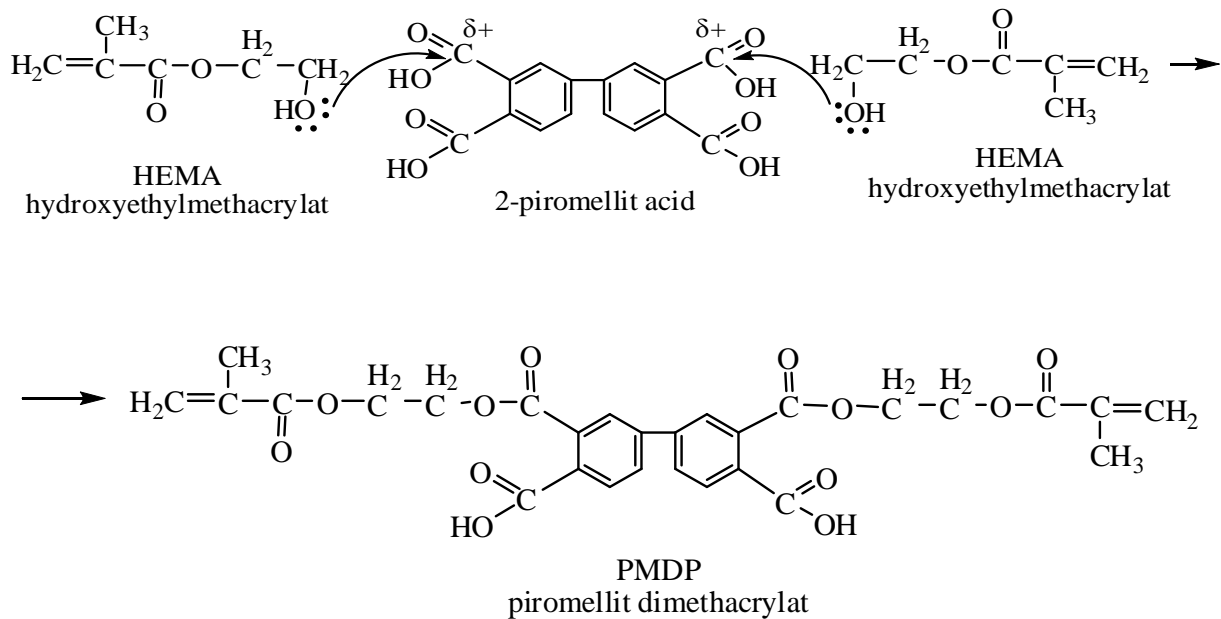
The use of aromatic groups affords a good match of refractive index with radiopaque glasses and thus provides better overall optical properties of composites. The viscosity of the monomer Bis-GMA is rather high, so diluents must be added. A clinical consistency can be reached by compounding of the resin mixture with the filler. Low-molecular-weight compounds with dysfunctional carbon double bonds and high distance between methacrylate groups, for example, triethylene glycol dimethacrylate (TEG-DMA) or Bis-EMA6 are added by manufacturers to reduce and control the viscosity.



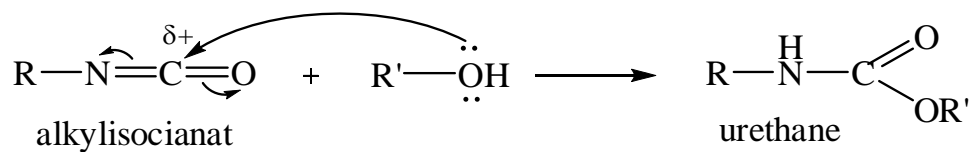
The main component of other modern light activated composites is NTG-GMA that is product of N-(para-tolyl)glycine condensation with glycidil methacrylate:



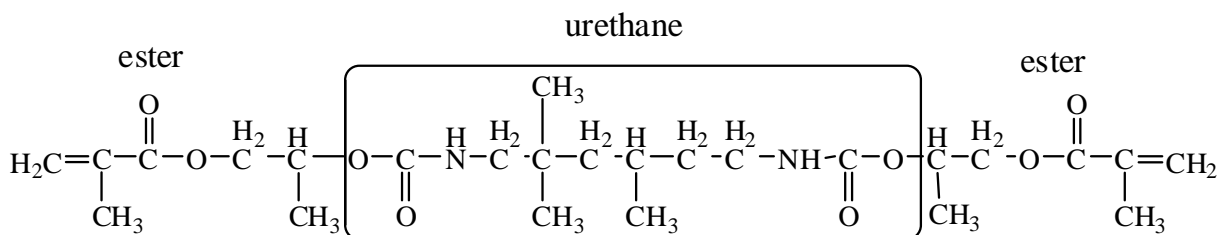
Other monomer of light activated composite matrix is product of esterification (S<sub>N</sub>) between hydroxyethylmethacrylate (HEMA) with 2-piromellit acid.



The monomer for the resin composite matrix is urethane dimethacrylate (UDMA). The general scheme of urethane formation reaction is the following:



For example 2,2,4-trimethylhexamethylen-bis-(2-carbamoyloxyisopropyl)-dimethacrylat:



2,2,4-trimethylhexamethylen-bis-(2-carbamoyloxyisopropyl)dimethacrylat

The relatively high distance between the methacrylate groups results in lower cross-link density and increases the stiffness of monomers. It reduces the volumetric shrinkage and polymerization stress of composites.

#### 4.3. FILLERS AND CLASSIFICATION OF COMPOSITES.

Fillers make up a major portion by volume or weight of the composites. The fillers reinforce the resin matrix, provide the appropriate degree of translucency and control the volume shrinkage of the composite during polymerization.

Dental composites are classified by the particle size, shape and the particle-size distribution of the fillers to the following:

1. **Macrofills** – these contain large spherical or irregular shaped particles of average filler diameter of 20 to 30  $\mu\text{m}$ .

2. **Hybride composites** are two types of fillers that are blended together: fine particles of size 2-4  $\mu\text{m}$  and 5% -15% of microfine particles of size 0.04-0.2  $\mu\text{m}$ .

3. **Microfine composites** – these consist of the fine particles of a lower particle size 0.04 to 0.2  $\mu\text{m}$  that are blended with microfine particles.

4. **Nanocomposites:**

a) **Nanofills** contain nanometer sized particles (1-100 nm). Larger particles are not present. Nanofills contains two types of nanoparticles:

- **Nanomers** that are essentially monodisperse nonaggregatives and nonagglomerated particles of silica and zirconia.

- **Nanoclusters** that are made by lightly sintering nanomeric oxides to form clusters of a controlled particle size distribution.

b) **Nano hybrid composites** – these consist of large particles (0.4 to 5 microns) with added nanometer sized particles.

The fine particles for fillers are traditionally obtained by grinding minerals such as glass (e.g. borosilicate glass, lithium or barium aluminum silicate glass, strontium or zinc glass), quartz or ceramic materials and have irregular shapes. The presence of heavy-metal oxides - barium or zinc - in a most glasses provides radiopacity for visualization in x-rays exposition.

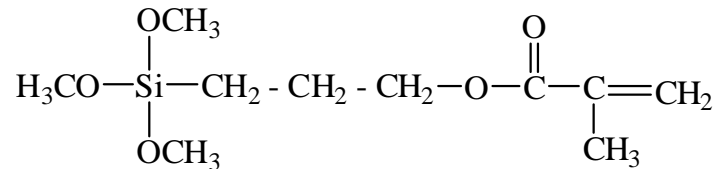
The latest advancement in composite technology is the use of nanotechnology in development of filler to produce structures in range of 1 to 100 nanometers (nm). The size of nanomeric particles is below that of visible light (400-800 nm), this provides the opportunity of creating highly translucent materials. Addition of pigments and shades may produce the color of restoration that is maximally the same as natural tooth tissues and have gloss like natural enamel. The sizes of smallest nanoparticles are almost closed to the size of polymer molecules, thus they can form a molecular scale interaction with the host resin matrix. As a result nanocomposites almost don't have polymerization shrinkage.

Manufacturers create also another type of nanoparticles - nanoclusters. Nanoclusters are made by lightly sintering silica sol or nanomeric oxides of silica and zirconia to form clusters of a controlled particle size distribution, usually ranging from 100 nm to submicron level. To improve properties of restorative materials nanomeric particles and nanoclusters are used in optimum combinations.

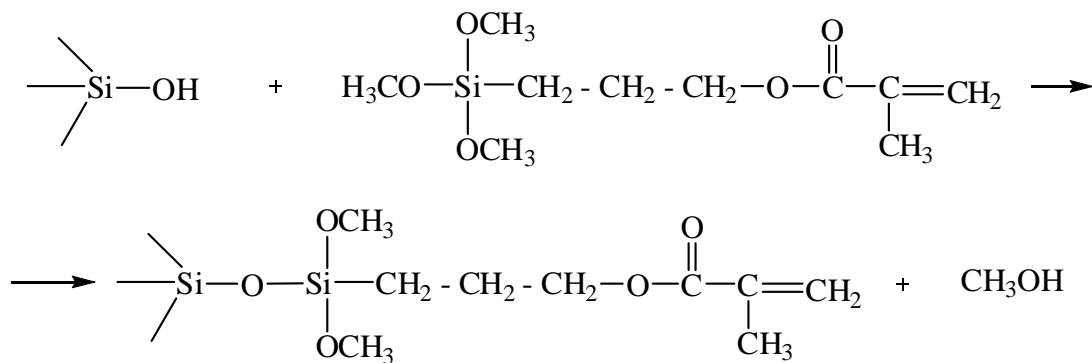


To have successful clinical performance with composites a good bond must form between inorganic filler particles and organic resin matrix during setting. There are two ways for it: using a coupling agent and formation of thin polymer film directly on the surface of filler particles.

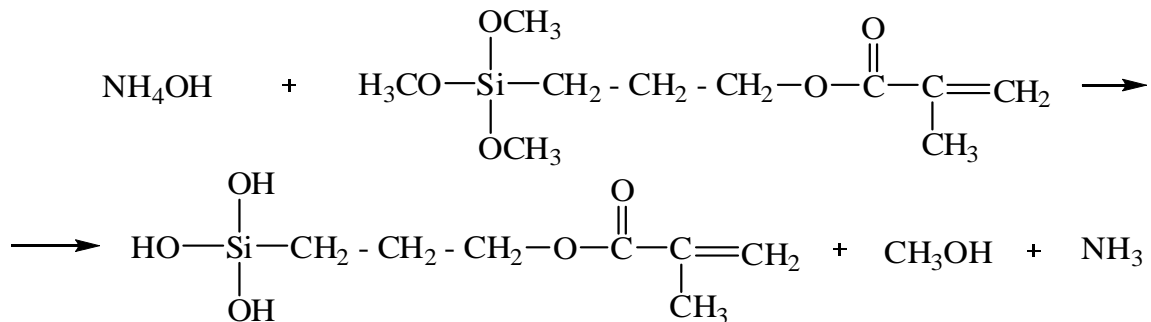
Coupling agent is difunctional compound containing functional group that can react with hydroxyl groups on a surface of filler (quartz, silane) and double bond that is involved to polymerization of matrix oligomers. A typical coupling agent is 3-methacryloxypropyltrimethoxysilane:

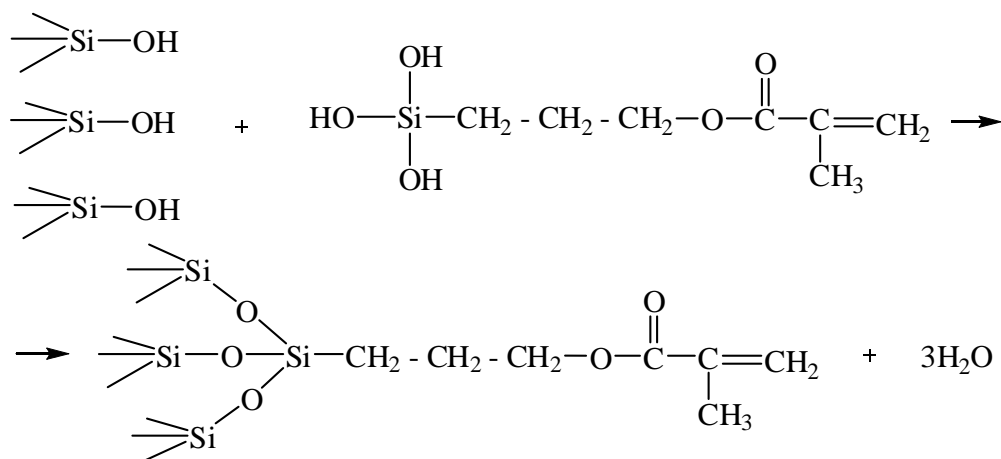


The surface of the filler is treated with a coupling agent during manufacturing the composite. In this process the methoxy group of coupling agent reacts with hydroxyl group on the surface of the filler particle, for example quartz, to form the bond  $-\text{Si}-\text{O}-\text{Si}-$ :

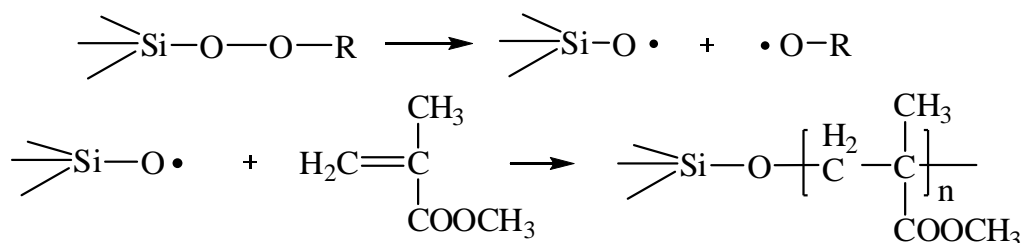


Sometimes the methoxy groups are hydrolyzed to generate hydroxyl groups through an acid or base catalyst, for example with ammonia solution:





In the second way the initiator of polymerization reaction is linked on the surface of the filler and polymerization reaction takes place directly on the surface of filler particle:



The reactions cause the formation of a very thin mono- or multilayer polymeric film on the surface of the filler with unreacted double bond. During the curing of the composite the double bond of the methacryloxy groups of the treated surface co-reacts with monomer or oligomer resins.

The treatment of the filler surface with coupling agent or initiator of polymerization forms an interfacial bridge that strongly binds the filler to the resin matrix. It enhances the mechanical properties of the composite and minimizes the plucking of the fillers from the matrix during clinical wear. The resulting interfacial phase provides a medium for stress distribution between adjacent particles and polymer matrix. It provides a hydrophobic environment that minimizes water absorption of the composite.

#### 4.4. PIGMENTS AND OTHER ADDITIVES.

Polyacrylates, poly(methyl acrylates) and nanocomposites are clear and translucent materials. Inorganic oxides in small amounts are usually added to polymer powder to provide shades. The most common pigments and shades are zinc oxide ZnO (1.2% - 15%) and titanium oxide TiO<sub>2</sub> (0.35% - 0.5%). Inorganic pigments – cadmium sulfide, iron oxides, mercury sulfide are used to color polymer beads when polymer is synthesized. Numerous shades are supplied ranging from very light shades to yellow and grey. Organic pigments are not

used because they are destroyed in presence of benzoyl peroxide. A UV absorber may be added to minimize color changes caused by oxidation.

Fluorescent agents are sometimes added to enhance the optical vitality of the composite and mimic the appearance of natural teeth. These are dyes that absorb light in ultraviolet and violet region (340-370 nm) of the electromagnetic spectrum and re-emit light in blue region (420-470 nm). Some disinfectants are added to the composite materials to prevent appearance and growing of microorganisms.

The light-cured composites are packaged in opaque, most often black, plastic syringes or unit-dose capsules (compules) that provides a delivery gun for direct intra-oral placement and lower risk of cross-infection. Self-cured and dual-cured materials are supplied in two syringes. Two pastes are mixed to initiate the chemical cure. It is advisable to store these materials in cool temperature to prolong their shelf-life.

## **V. ADHESION OF RESTORATIVE MATERIALS TO TOOTH TISSUES – ENAMEL AND DENTIN.**

The creation of a strong and durable bond of restorative material to the enamel and dentine of tooth is very important for formation of direct and cementation of indirect restorations. It protects the restoration's interface against penetration of bacteria causing secondary caries. It reduces the need for retentive areas in the penetration that would require removal of sound tooth structure. In some cases, bonding may help strengthen the remaining tooth structure.

In 1950s Dr. Michael Buonocore conceived the adhesion technique involved acid etching of enamel. Enamel is composed of hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  crystalline prisms and organic matrix contained polypeptides with molecular mass 500-1000 D.

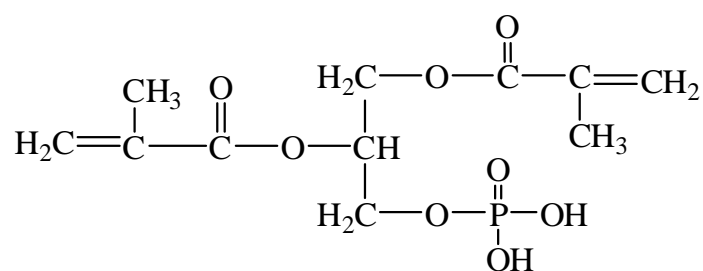
In modern direct restorative materials adhesion of dental material to the enamel and dentin is commonly micromechanical interlocking and secondary chemical bonds to collagen and residual hydroxyapatite. Etching of enamel and dentin with strong acid, commonly 37% orthophosphoric acid, dissolves hydroxyapatite crystals and removes part of the enamel rod and smear layer in several microns from the dentin surface. It results the microscopically rough surface of enamel and decalcified free collagen fibers on dentine surface. Etching of dentine also opens dentin tubules. The next step is application of primer. Primers are hydrophilic monomers, oligomers and polymers usually carried in a solvent that are acetone, ethanol or ethanol-water. The primer flows into the surface irregularities of etched enamel produced resin macrotags by penetrating the space surrounding the enamel prisms. The primer also flows into the opened dentin tubules and around the collagen fibers that were exposed when dentin was etched and form macrotags inside the surface dentin layer. The primer resin sets when an adhesive resin is applied on the next third step. Formation of tags in demine-

ralized surface of enamel and dentin provides sufficient micromechanical bonding between adhesive and tooth tissues.

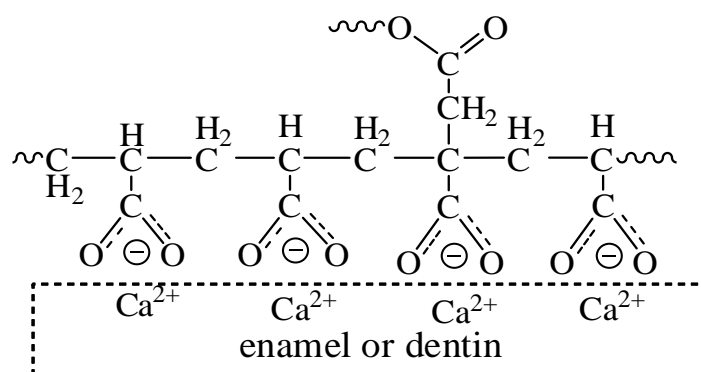


Some primers contain not only orthophosphoric acid, but also organic acids, for example maleic acid and maleic anhydride that gives maleic acid in hydrolysis.

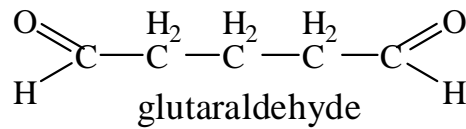
Chemical bonding is used for secondary bonding of adhesive material to the enamel and dentine. For example monomer dimethacrylate of glycerophosphoric acid contains phosphoric acid that forms bond to calcium ions of hydroxyapatite crystals and acrylic fragments that are involved to polymerization together with direct restorative materials.



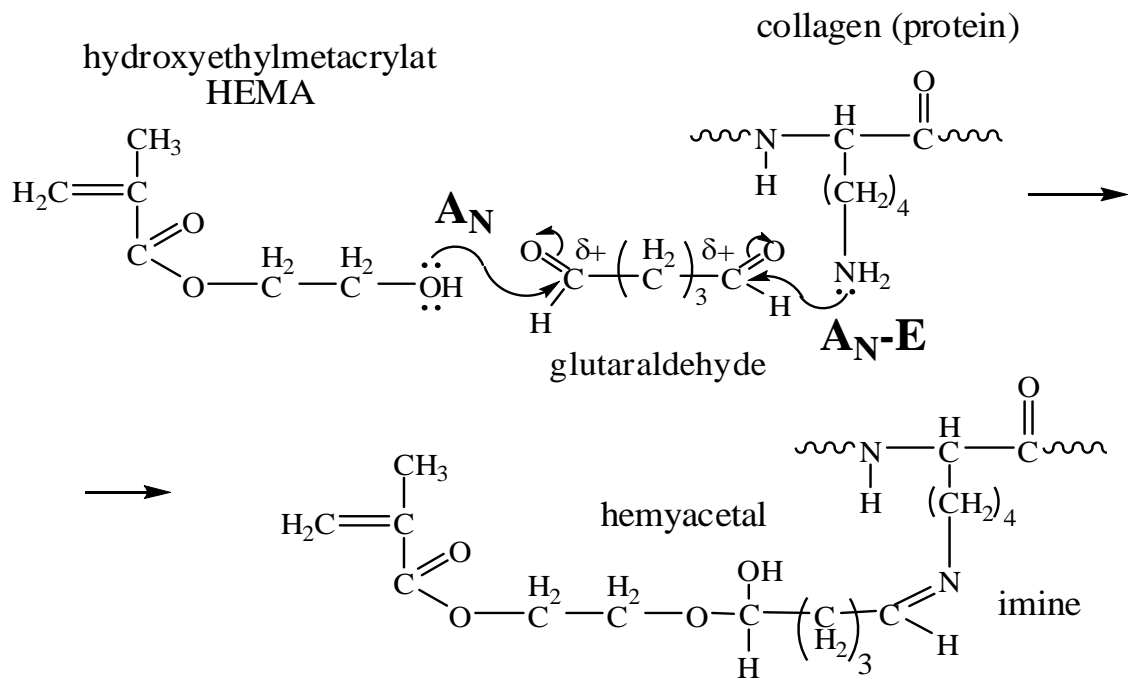
Glass ionomers are most popular materials for permanent cementation. The number of carboxylic groups along the macromolecular chain may form chelate bonding to calcium ions of enamel or dentin.



Adhesives often contain difunctional aldehydes, more commonly glutaraldehyde.

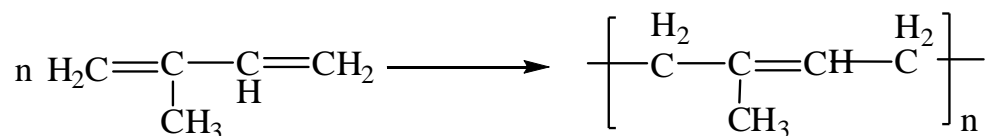


Difunctional aldehyde reacts with amino group of collagen and hydroxyl group of monomer, for example 2-hydroxyethyl methacrylate, simultaneously. One aldehyde group forms imine linkage (Schiff base) with amino group of lysine residue of collagen by  $A_N-E$  mechanism. Another aldehyde group forms primary hemiacetal group with hydroxyl group of 2-hydroxyethyl methacrylate by  $A_N$  mechanism or acetal.

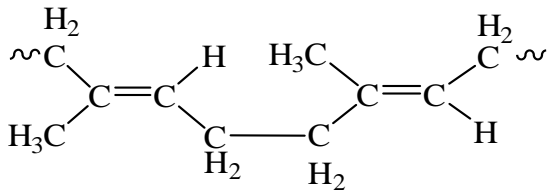


## VI. POLYISOPRENS: NATURAL RUBBER, GUTTA-PERCHA.

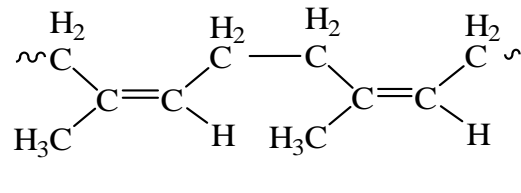
Polymerization of 2-methyl-1,3-butadiene (isoprene) in plants as a 1,4-addition can form two  $\pi$ -diastereoisomers.



*Cis*-poly isoprene is natural rubber; *trans*-poly isoprene is gutta-percha.



Gutta percha: *trans*-1,4-polyisoprene



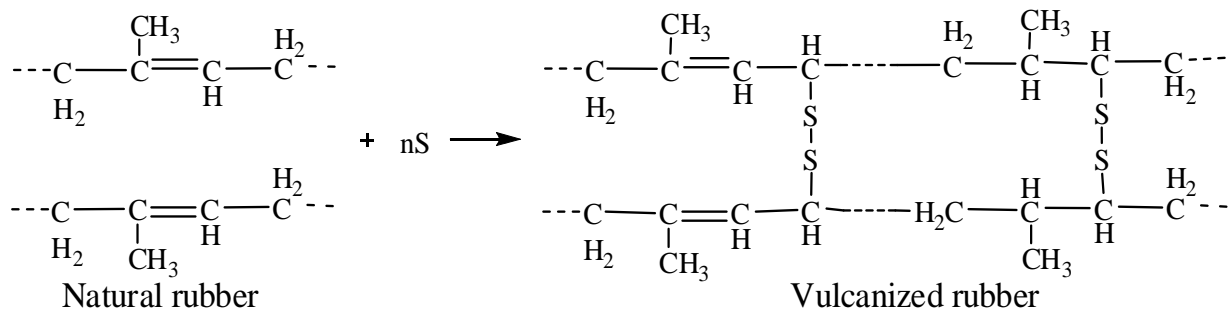
Natural rubber: *cis*-1,4-polyisoprene

Rubber is the most important and widely used natural polymer. The major source of commercial rubber is the *Hevea brasiliensis* tree originally found in Brazil and now it mostly grown in Southeast Asia. Natural rubber has a molecular weight ranging from 100 000 up to 1000 000.

Gutta-percha is found in trees of the genus *Dichopsis*, a tree native to Southeast Asia. Gutta-percha has much lower molecular weight - about 7 000.

The physical properties of *cis*- and *trans*-isomers are different. The *cis* arrangement of the double bonds in rubber prevents the rubber molecules from fitting into an ordered structure. Thus, rubber is an amorphous polymer. Because of the random coiling of its polymer chains, rubber stretches easily. When stretched, the rubber molecules are forced into a higher energy state. When the tension is released, rubber snaps back to its original random coiled state. On the other hand, molecules of gutta-percha pack close together so it is more crystalline than rubber. In general, gutta-percha is harder and less flexible than rubber. Both natural rubber and gutta-percha are thermoplastic. In hot water gutta-percha is soft; at room temperature it is hard. Dentists use these properties of gutta-percha for filling root canals in combination with an endodontic sealer.

Pure natural rubber is soft and tacky. To be useful, natural rubber has to be vulcanized by heating with sulfur.

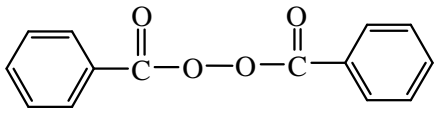
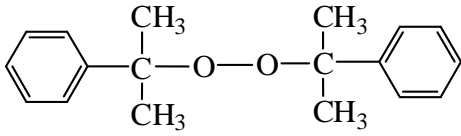
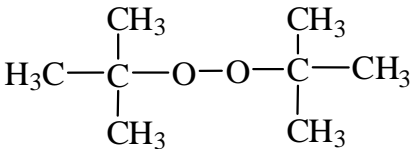
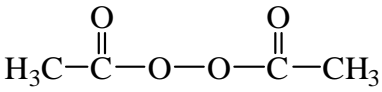
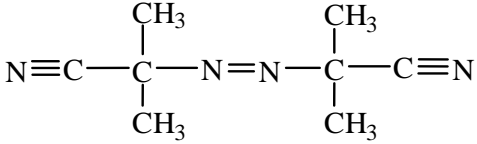


A reaction produces cross-links between the *cis*-polyisoprene chains and makes the rubber much harder. Sulfur reacts both at double bonds and at allylic hydrogen atoms. The vulcanized polymer becomes thermosetting; it is harder and more durable when the amount of sulfur is increased. At 30-32 % of sulfur mass much hard product called ebonite is formed. Ebonite with abrasion filling is used for fabrication of abrasion and polishing instruments in dentistry.

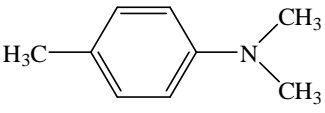
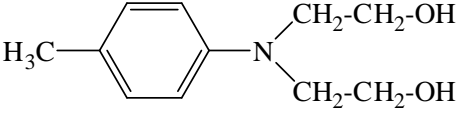
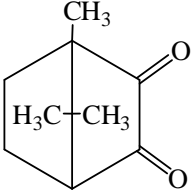
## REFERENCE MATERIALS

### I. Compounds – regulators of restorative dental materials polymerization reactions.

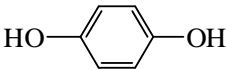
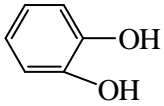
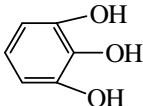
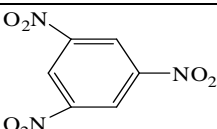
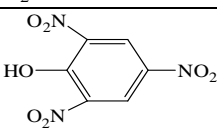
#### 1.1. Initiators.

Common name	Formula
Benzoyl peroxide	
Dicumene peroxide,	
Tert-butyl peroxide	
Acetyl peroxide	
Azo-bis-isobutyronitrile (AIBN)	

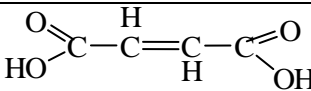
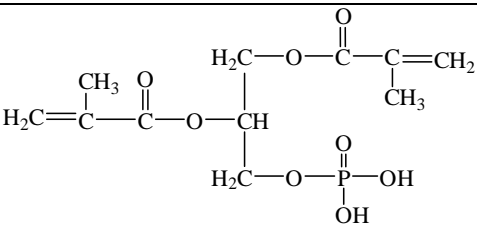
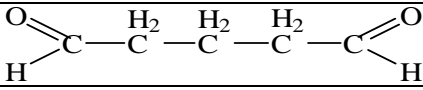
#### 1.2. Activators.

Common name	Formula
N,N-dimethyl-p-toluidine	
N,N-dihydroxyethyl-p-toluidine	
Camphorquinone (fotosensibilizator)	

### 1.3. Inhibitors.

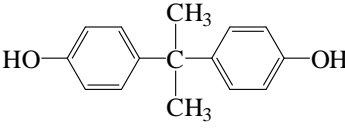
Common name	Formula
Hydroquinone	
Catechol	
Pyrogallol	
1,3,5-trinitrobenzene	
Picric acid	
Acetic acid salts	$\left[ \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \right] \text{Cu}^{2+}$
Salicylic acid salts	$\left[ \text{C}_6\text{H}_4(\text{OH})-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \right] \text{Cu}^{2+}$
Acrylic acid salts	$\left[ \text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \right] \text{Cu}^{2+}$
Methacrylic acid salts.	$\left[ \text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \right] \text{Cu}^{2+}$

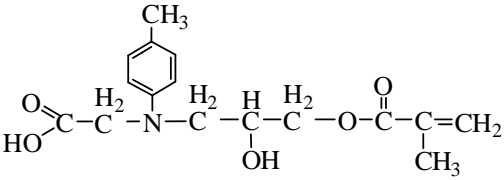
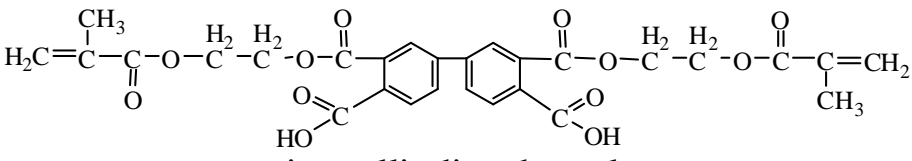
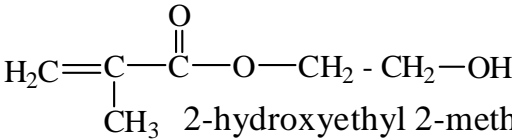
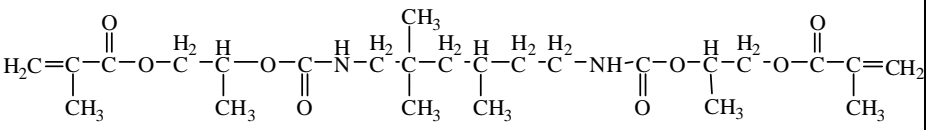
### II. Compounds used for adhesion of restorative materials to tooth tissues.

Common name	Formula
Maleic acid	
Dimethacrylate of glycerophosphoric acid	
Glutaraldehyde	
Polyethylenglycoldimethacrylat	$\left[ \text{H}_2\text{C}-\underset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{CH}_3}{\text{C}}-\text{H}_2 \right]_n$



### III. Monomers of dental polymers.

Common name	Formula, systematic name.
Acrylic acid	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{H} \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OH} \end{array}$ 2-propenoic acid
Methacrylic acid	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{CH}_3 \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OH} \end{array}$ 2-methyl-2-propenoic acid
Methyl acrylate	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{H} \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OCH}_3 \end{array}$ methyl 2-propenoate
Methyl methacrylate	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{CH}_3 \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OCH}_3 \end{array}$ Methyl 2-methyl-2-propenoate
Butyl methacrylate	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{CH}_3 \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OC}_4\text{H}_9 \end{array}$ Butyl 2-methyl-2-propenoate
Ethyl methacrylate	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C} \\ \quad   \quad \quad // \\ \quad \text{CH}_3 \quad \quad \text{O} \\ \quad \quad \quad \quad \backslash \\ \quad \quad \quad \quad \text{OC}_2\text{H}_5 \end{array}$ Ethyl 2-methyl-2-propenoate
Isoprene	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \\ \quad   \quad \quad   \\ \quad \text{CH}_3 \quad \quad \text{H} \end{array}$ 2-methyl-1,3-butadiene
Bisphenol A (di-ane)	 2,2-di(4-hydroxyphenyl)propane
Epychlorhydrine	$\begin{array}{c} \text{H}_2\text{C}-\text{C}-\text{CH}_2 \\ \quad   \quad \quad \backslash \\ \quad \text{Cl} \quad \quad \text{O} \end{array}$ 3-chlor-1,2-epoxypropane
Bis-GMA	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(=\text{O})-\text{O}-\text{C}(\text{H})(\text{OH})-\text{C}(\text{H}_2)-\ddot{\text{O}}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\ddot{\text{O}}-\text{C}(\text{H}_2)-\text{C}(\text{H})(\text{OH})-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$ bis-phenol-A-glycidylmethacrylat
TEG-DMA	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(=\text{O})-\text{O}-\text{C}(\text{H}_2)-\text{C}(\text{H}_2)-\text{O}-\text{C}(\text{H}_2)-\text{C}(\text{H}_2)-\text{O}-\text{C}(\text{H}_2)-\text{C}(\text{H}_2)-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$ triethylene glycol dimethacrylate

NTG-GMA	
PMDP	 <p style="text-align: center;">piromellit dimethacrylat</p>
HEMA (hydroxyethyl methacrylate)	 <p style="text-align: center;">2-hydroxyethyl 2-methyl-2-propenoate</p>
UDMA (urethane dimetacrylate)	 <p style="text-align: center;">2,2,4-trimethylhexamethylen-bis-(2-carbamoyloxyisopropyl)dimethacrylat</p>

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