ORGANIC COMPOUNDS, NATURAL AND SYNTHETIC POLYMERS USING IN STOMATOLOGY

1. Polymers. Classification.
2. Polymerization reactions: free radical, cationic and anionic polymerization.
3. Free radical mechanism of acrylates and methacrylates polymerization.
4. Modern restore materials of photo- and chemical hardening on base Bis-GMA, NTG-GMA, HEMA, PMDM, UDMA.
5. Low-molecular components, using in adhesive systems for improvement for sticking of filling materials to the tooth tissues (enamel and dentine).
6. Natural polysaccharides – alginic acids and waxes in base of dental impression materials.

POLYMERS.

A **polymer** is a large molecule (**macromolecule**) that consists of a number of smaller repeating units made from molecules called monomers.

Macromolecules are broadly categorized by size:

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

Polymers may contain many thousand of monomer units within the polymer molecule and certain natural macromolecules contain millions of repeat units.

There are two types of polymers in origin:

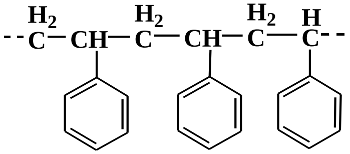
1. natural;

2. synthetic.

- Natural polymers affect our life in the biochemical processes. Proteins are important part of the structure of all animals, and enzymes catalyze the chemical processes that make bodies function. Cellulose is the structural material of plants, and starches are the energy storage medium for plants. Both RNA and DNA are polymers of individual nucleic acids.

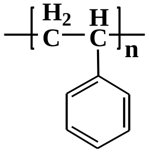
STRUCTURAL CHARACTERISTICS OF POLYMERS. CLASSIFICATION.

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



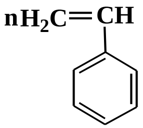
Polystyrene

Repeating unit



Polystyrene

Monomer



Styrene

I. 1. In a **homopolymer** all the repeating units are identical

$$nA \longrightarrow ---A-A-A-A-A-A-A-A--- \quad \text{or} \quad A_n$$

An example of homopolymer is polystyrene.

2. A **copolymer** contains more then one type of monomer unit. There are three types of copolymers:

1. Alternating copolymer

$$nA + nB \longrightarrow ---A-B-A-B-A-B-A-B---$$

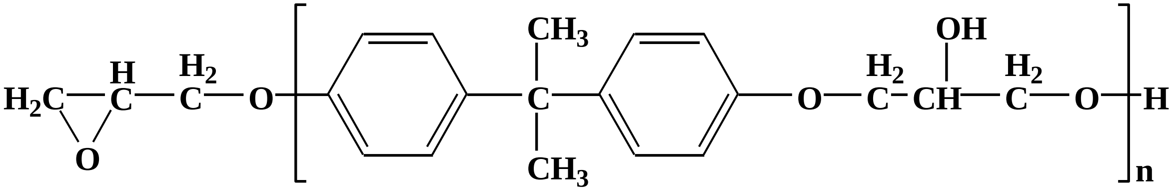
2. Block copolymer

$$mA + nB \longrightarrow ---A-A-A-A-A---B-B-B---$$

3. Random copolymer

$$mA + nB \longrightarrow ---A-B-B-B-A-A-B-B---$$

An example of copolymer is ***dian epoxy resin***



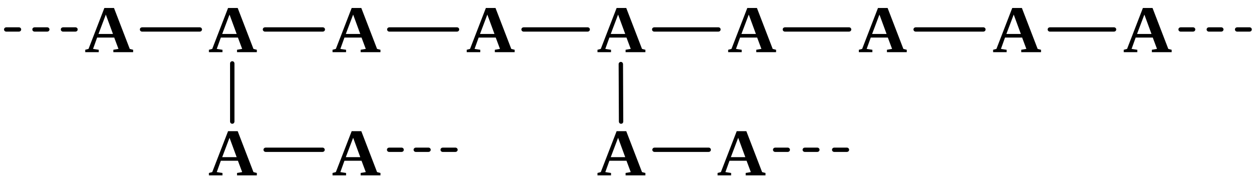
CLASSIFICATION OF POLYMERS.

II. Structural classification:

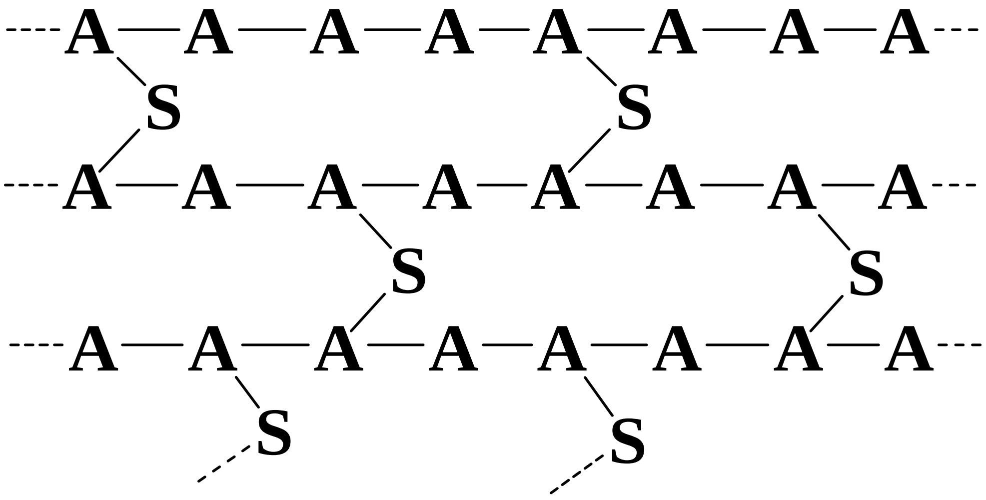
1. A linear polymer is a molecule with a series of connected repeating units.

----A—A—A—A—A—A—A—A---

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



3. Cross-linked polymers are linear polymer molecules joined by a branching connection.

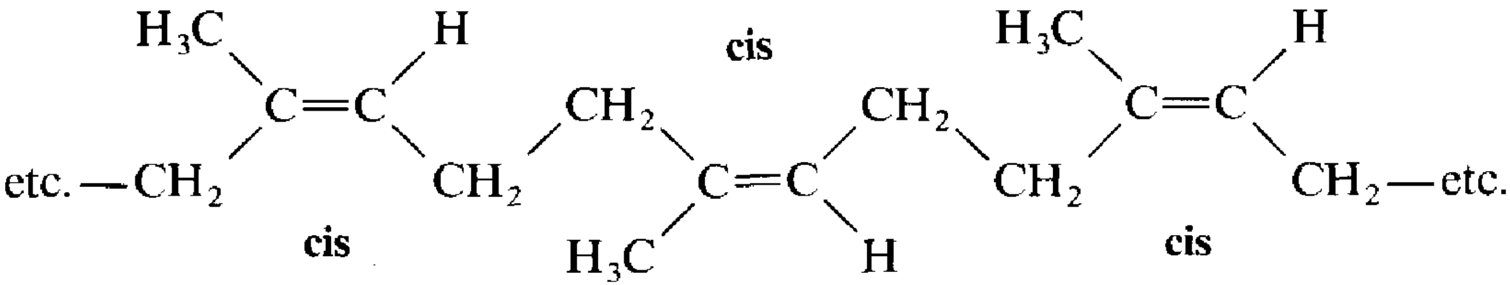


S is connected unit

CLASSIFICATION OF POLYMERS.

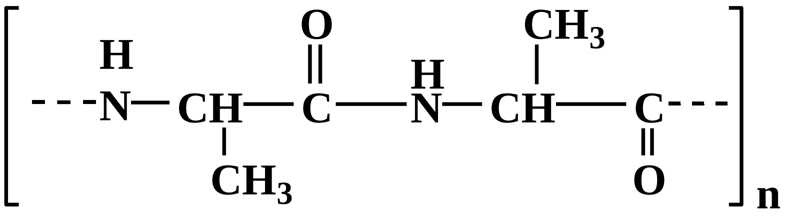
III. Classification of polymer on base nature of elements of main chain:

1. Homochain polymers (carbochain). The examples are **polystyrene and natural rubber**



Natural rubber
(*cis*-1,4-polyisoprene)

2. Heterochain polymers:

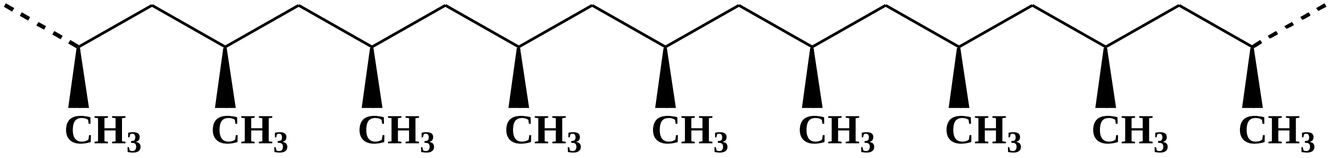


$$\left[---\overset{H}{N}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{CH_3}{\overset{|}{CH}}-\underset{O}{\underset{\|}{C}}--- \right]_n$$

PROTEIN

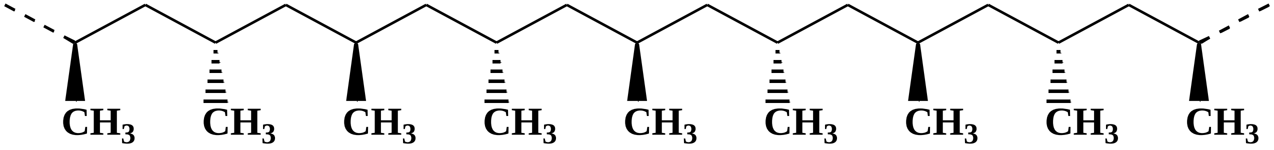
CLASSIFICATION OF POLYMERS ACCORDING TO STEREOISOMERISM

1. An **isotactic polymer** arranges all its substituents the same side of the polymer chain when you view the chain as a zig-zag structure.



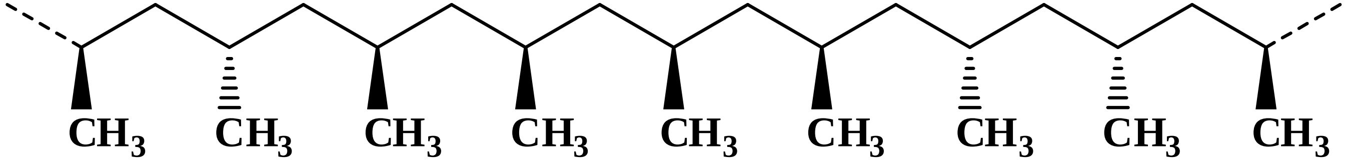
isotactic: methyl groups are all 1,3-*syn*

2. A **syndiotactic polymer** has its substituents 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

CLASSIFICATION OF POLYMERS.

Most polymers become plastic at high temperatures and can be cast into a desired shape.

According to the melting behavior polymers are classified to:

1. In **thermoplastics** the cycle of heating, melting and casting into shape can be repeated many times (indefinitely).

2. **Thermosetting plastics** (or thermosetting resins) can be heated and cast into shape only once; once a thermosetting polymer hes cooled in a particular shape, its shape cannot be altered by heating.

Most thermoplastics are linear, while thermosetting resins are usually two- or three-dimensional networks, cross-linked.

The molecular weight of the macromolecules obtained by polymerization of a monomer is characterized by **the degree of polymerization**, which is measure of **the average number of monomer units in each polymer molecule**. Reaction occuring with a high degree of polymerization give rise to high molecular weight polymers (high polymers). Polymerization reactions leading to macromolecules with relatively low molecular weights are designated as occuring with a low degree of polymerization.

The extent to which the monomer has been consumed is known as the **degree of conversion.**

TYPES OF POLYMERIZATION REACTIONS

There are two types of polymerization reaction mechanisms:

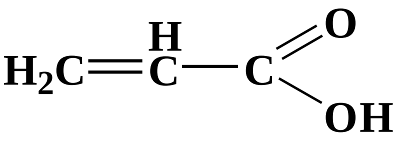
1. **Chain-growth polymerization (or addition polymerization).**
2. **Step-growth polymerization (or condensation polymerization).**

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

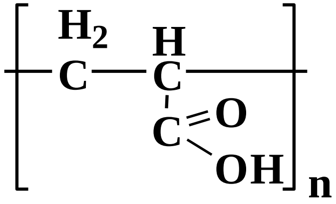
In **a step-growth polymerization** one monomer reacts with a repeating unit formed from a different monomers. Two or more monomers alternate reaction with the growing polymer chain. The monomer units are condensed into a polymer chain by substitution reaction with the elimination of one small molecule per monomer during each reaction that extends the growing polymer chain.

FILLING POLYMERS OF STOMATOLOGY. ACRYLATES and METACRYLATES.

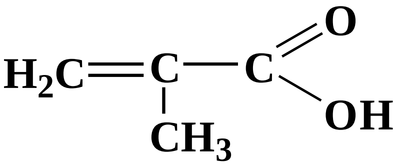
Monomers **Polymers**



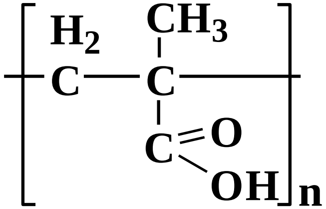
Acrylic acid



Poly(acrylic acid)

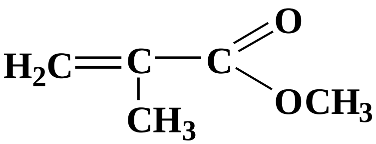


Methacrylic acid

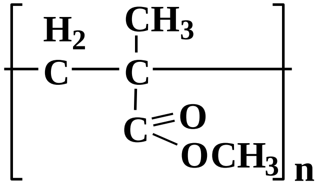


Poly(methacrylic acid)

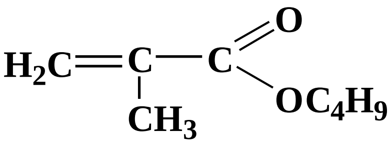
Monomers **Polymers**



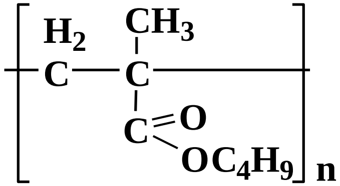
Methyl methacrylate



Poly(methyl methacrylate)



Butyl methacrylate



Poly(butyl methacrylate)

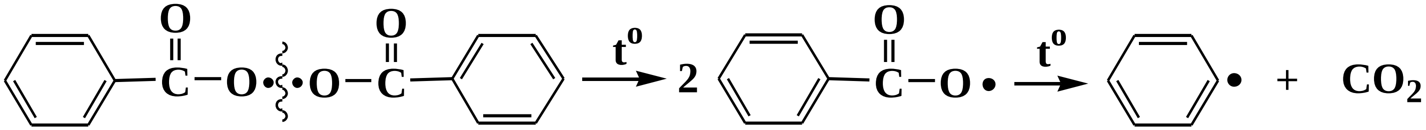
FREE RADICAL POLYMERIZATION

A radical polymerization follows three steps:

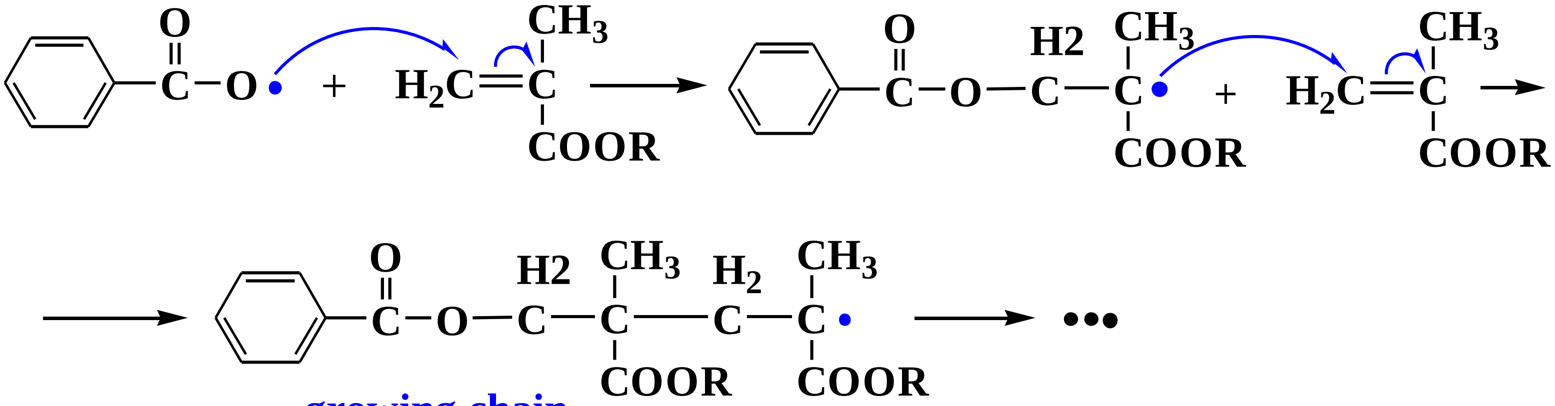
1. The initiation step.
2. The propagation step.
3. The termination step.

- Let’s consider the free radical addition reaction mechanism of chain-growth polymerization of filing material based on alkyl methacrylate.

1. Initiation step:



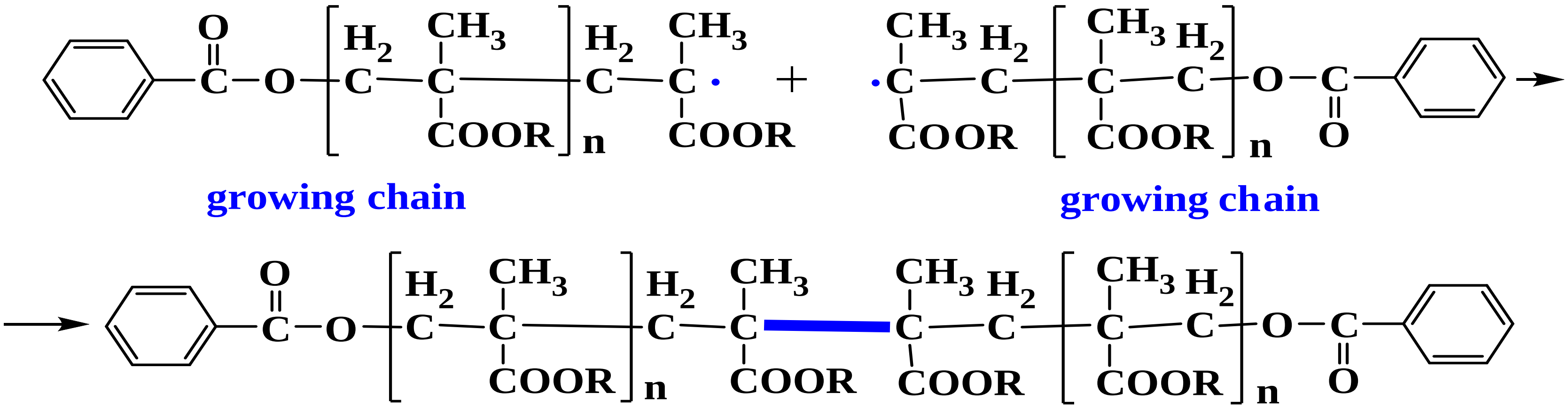
2. Propagation step:



FREE RADICAL POLYMERIZATION

3. Termination step:

a) Recombination of two growing chains free radicals.



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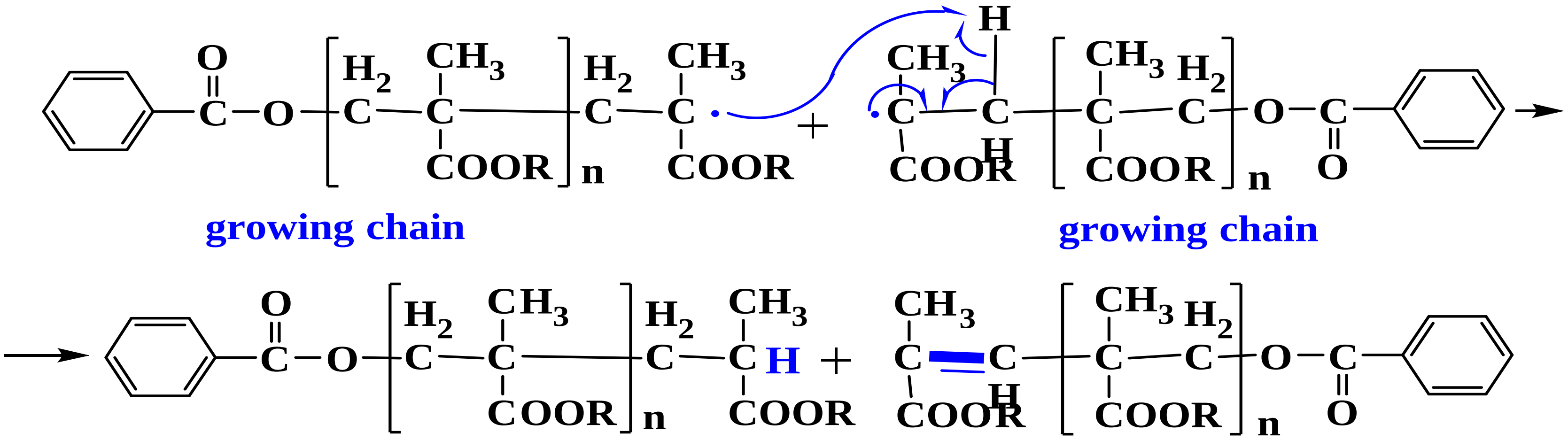
b) Disproportion of two growing chains free radicals.

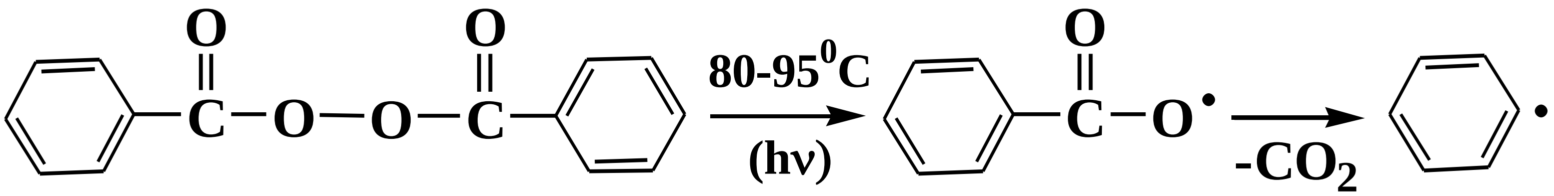


INITIATORS AND ACTIVATORS OF S_R POLYMERIZATION.

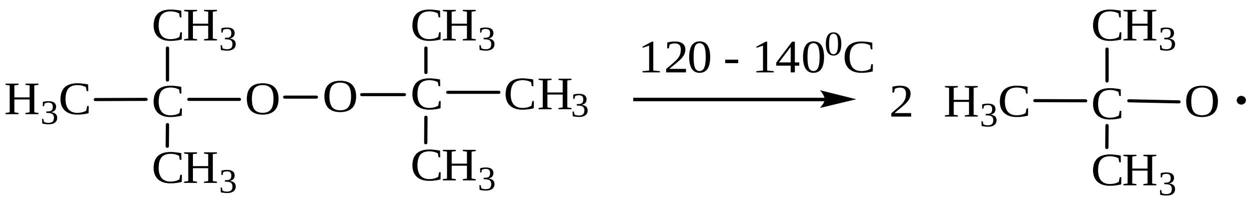
Free radicals are being formed by:

1. high temperature;
2. hard light;
3. irradiation;
4. initiators.

Initiators are compounds formed free radicals by easy breaking of weak covalent bonds like organic peroxides, such as benzoyl peroxide:

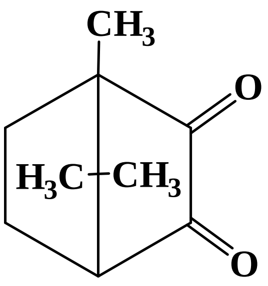


- Carphorquinone is initiator of light-cured polymerization.

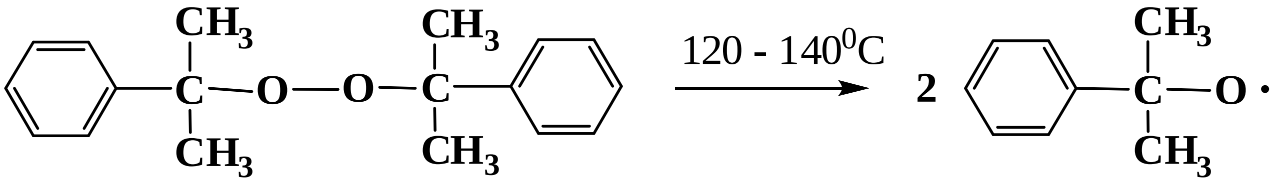


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{120\ -\ 140^0C} 2\ \ H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot$$

Tert-butyl peroxide



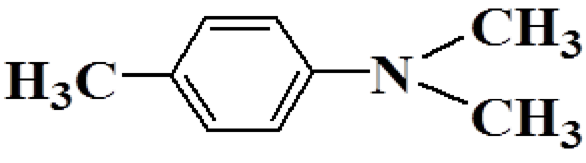
Camphorquinone



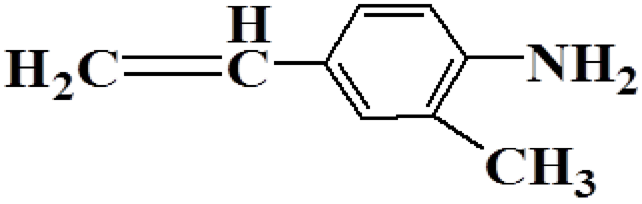
Dicumene peroxide

INITIATORS AND ACTIVATORS OF S_R POLYMERIZATION.

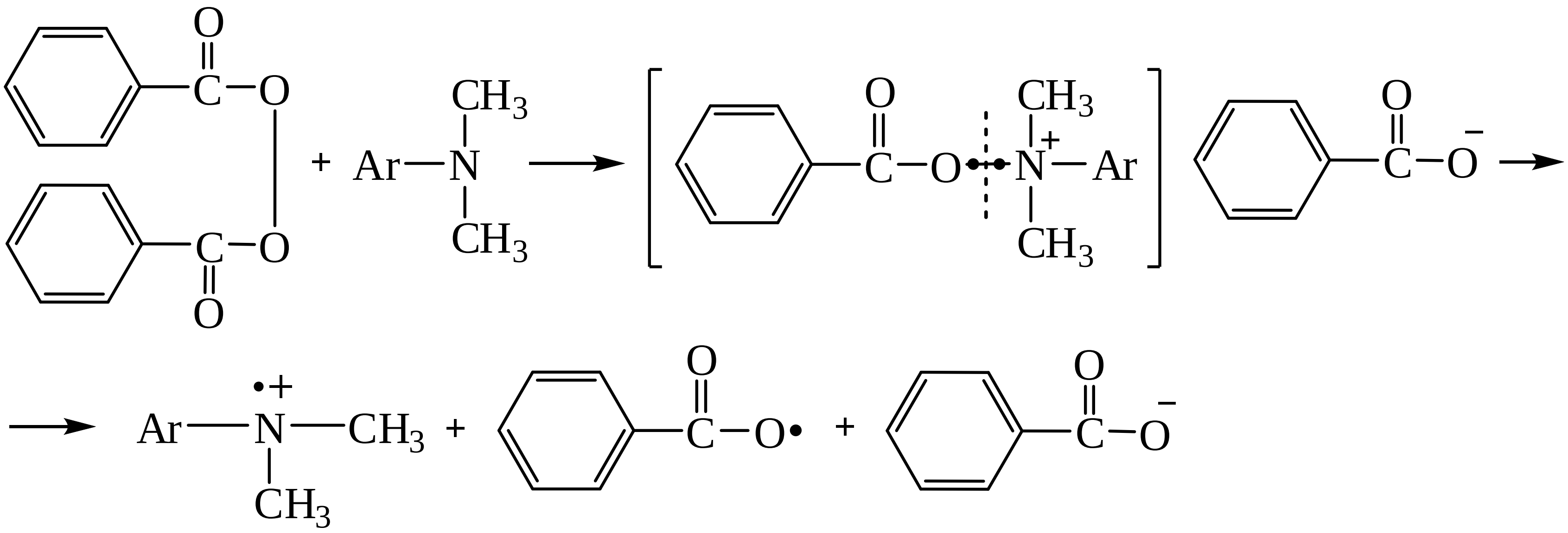
- **Activators** are compounds, which make free radical from initiators at room temperature, like $FeSO_4$, N,N-dimethyl-p-toluidine:



N,N-dimethyl-p-toluidine

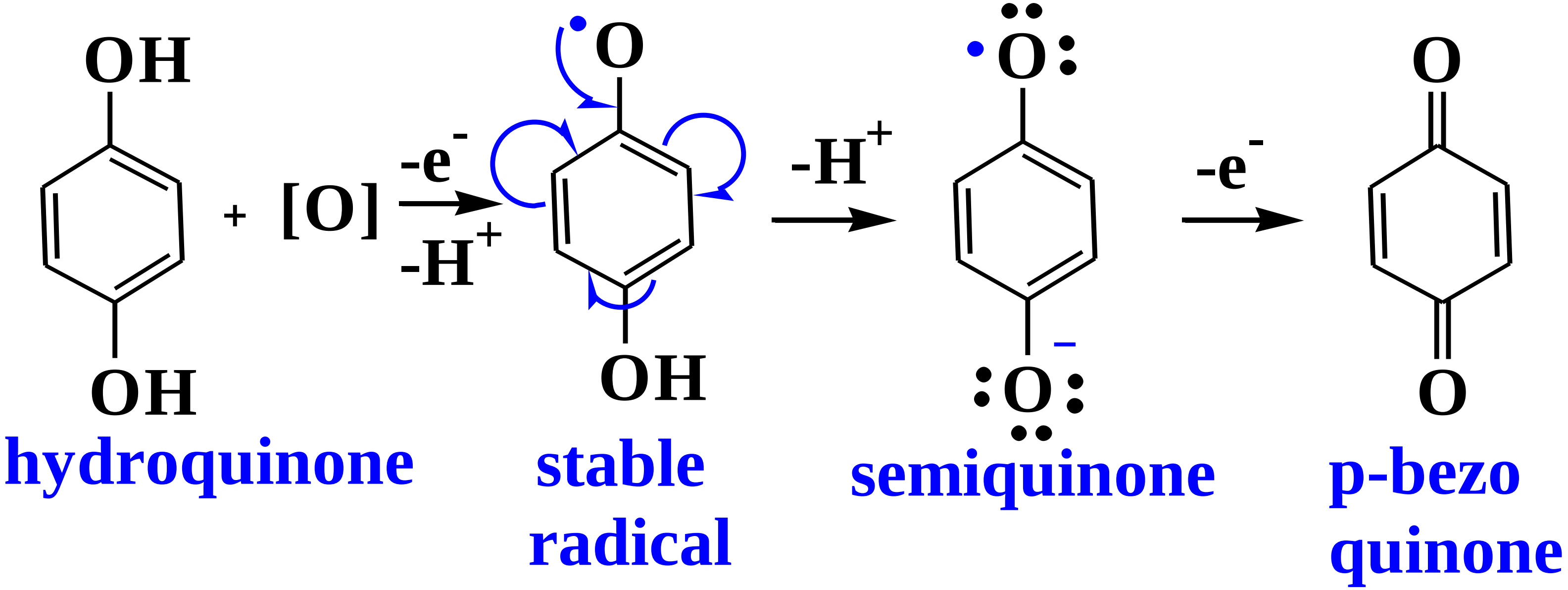


4-vinyl-2-methyl-aniline



INHIBITORS OF S_R POLYMERIZATION.

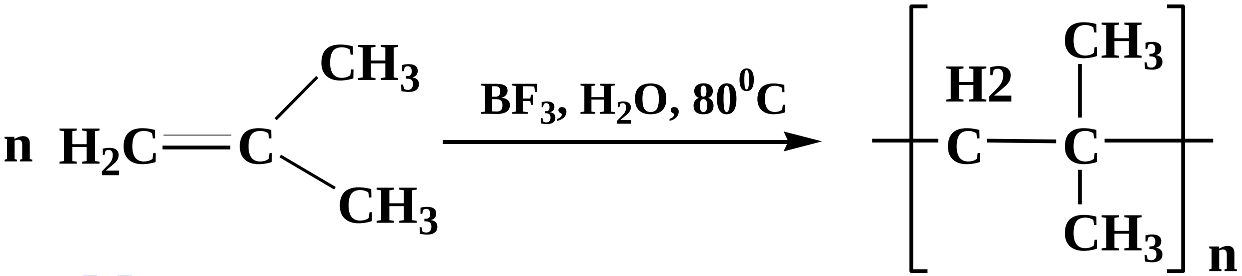
- **Inhibitors** are compounds formed stable free radicals and stopped polymerization, when monomers are stored. An inhibitor is some chemical species, either a molecule or radical, that is particularly reactive with a radical. Examples of inhibitors are phenols, benzoquinones:



CATIONIC POLYMERIZATION

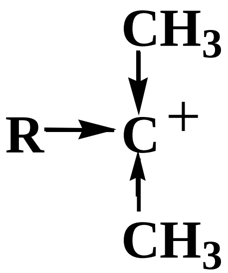
The chain reaction polymerization of electron-rich alkenes such as styrene and isobutylene, all of which will react with en electrophile to give a relatively stable cationic intermediate, can be carried out under conditions where the chain carrier is a carbocation rather than a free radical. Like free radical polymerization, cationic polymerization must be initiated. The most common initiators are protonic acids (H_2SO_4) or Lewis acids (BF_3 and $TiCl_4$). The electrophilic addition to each alkene monomer occurs with Markovnikov rule, and the ease of polymerization parallels the stability of the intermediate carbocation formed.

- **Example is cationic polymerization of polyisobutylene:**



Monomers: isobutylene

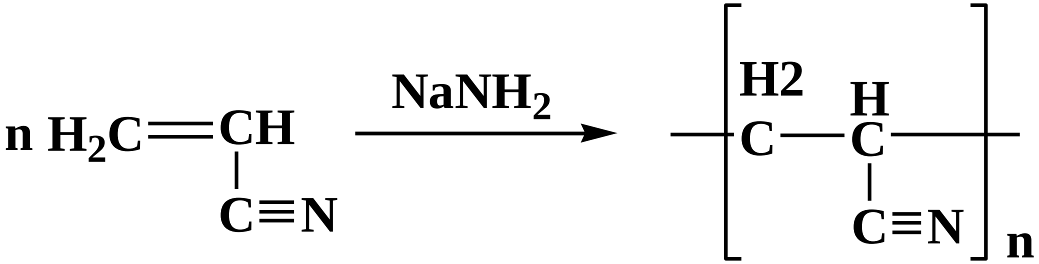
Polyisobutylene



Stable tertiary carbocation

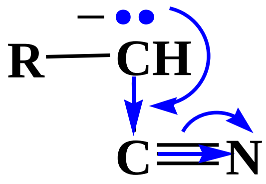
ANIONIC POLYMERIZATION.

- Alkenes are not normally susceptible to the addition of nucleophiles unless they are activated towards nucleophilic addition by the presence of an electron-accepting groups (-C_6H_5, -COOR, -CN, -NO_2).
- **Example is anionic polymerization of polyacrylonitrile:**



Monomers: acrylonitrile

Polyacrylonitrile

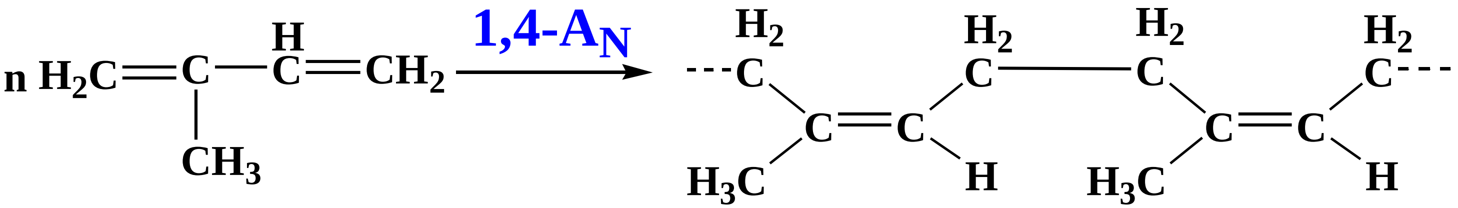


Stable carbanion

The anionic polymerization reaction continues until all the monomer is consumed, at this time the polymerization reaction ceases. It doesn’t have a termination reaction wile electrophile be added. 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 called “**alive**”. This characteristic 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.

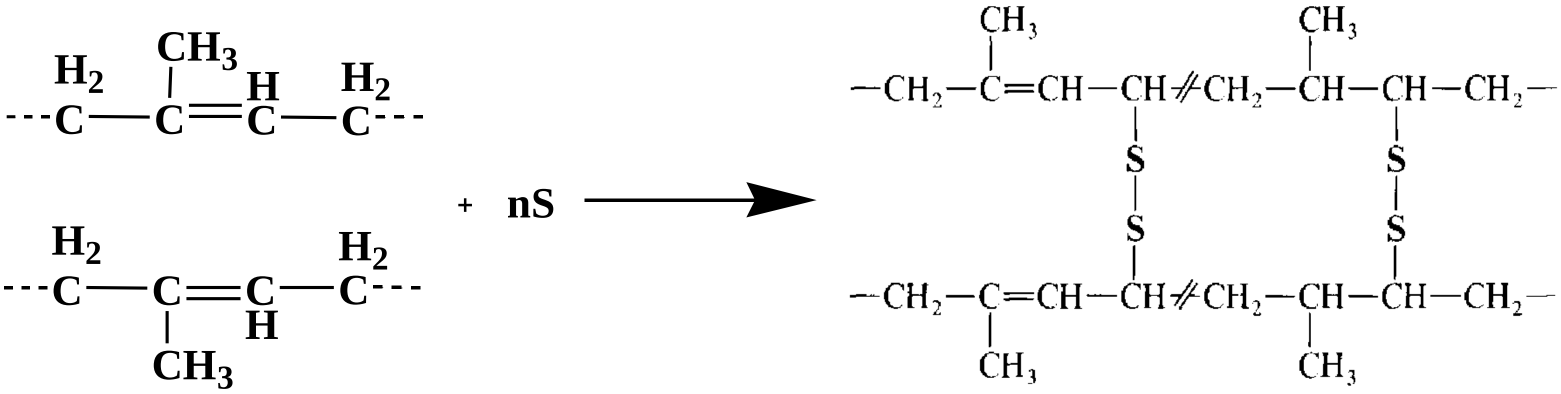
NATURAL RUBBER

Ziegler — Natta catalysts make possible anionic polymerization of isoprene and obtain a synthetic product that is identical with the rubber obtained from natural sources. Natural rubber can be viewed as a 1,4-addition polymer of isoprene.



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

Pure natural rubber is soft and tacky. To be useful, natural rubber has to be *vulcanized*. In vulcanization, natural rubber is heated with sulfur. A reaction takes place that produces cross-links between the cis-polyisoprene chains and makes the rubber much harder. Sulfur reacts both at the double bonds and at allylic hydrogen atoms.



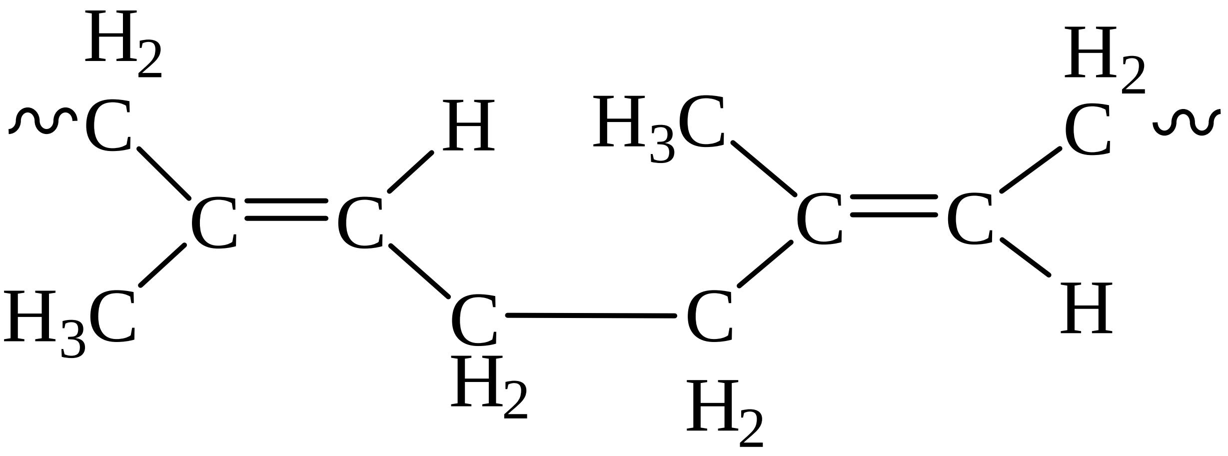
Vulcanized rubber

Natural rubber

MATERIALS FOR ROOT CANALS. GUTTA PERCHA

A related polymer, called gutta percha has a structure with trans double bonds and a much lower molecular weight of about 7 000.

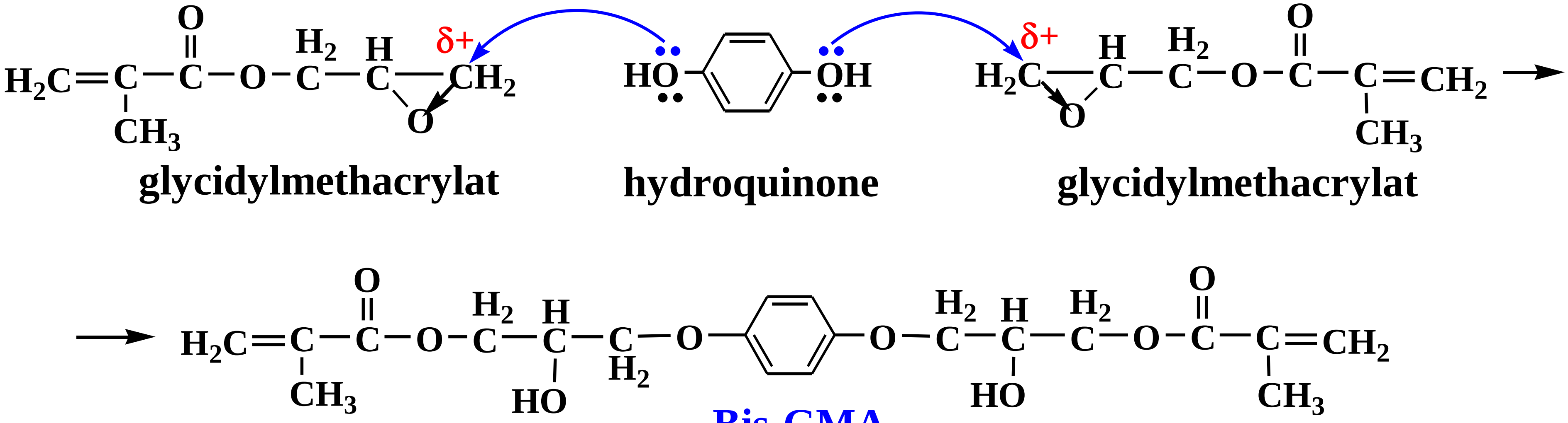
The physical properties of cis- and trans-isomers are different. molecules of gutta percha pack close together so it is more crystalline than rubber. In general, gutta percha is harder and less flexible than rubber. Dentists use these properties of gutta percha for filling of root canals.



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

MODERN RESTORATIVE COMPOSITE DENTAL MATERIALS. Bis-GMA.

The modern restorative dental composite materials are mixture of inorganic particles dispersed in binding organic matrix. The most composite materials have organic matrix based on monomer system **Bis-GMA**. It is product of condensation of glycidylmethacrylate with hydroquinone:



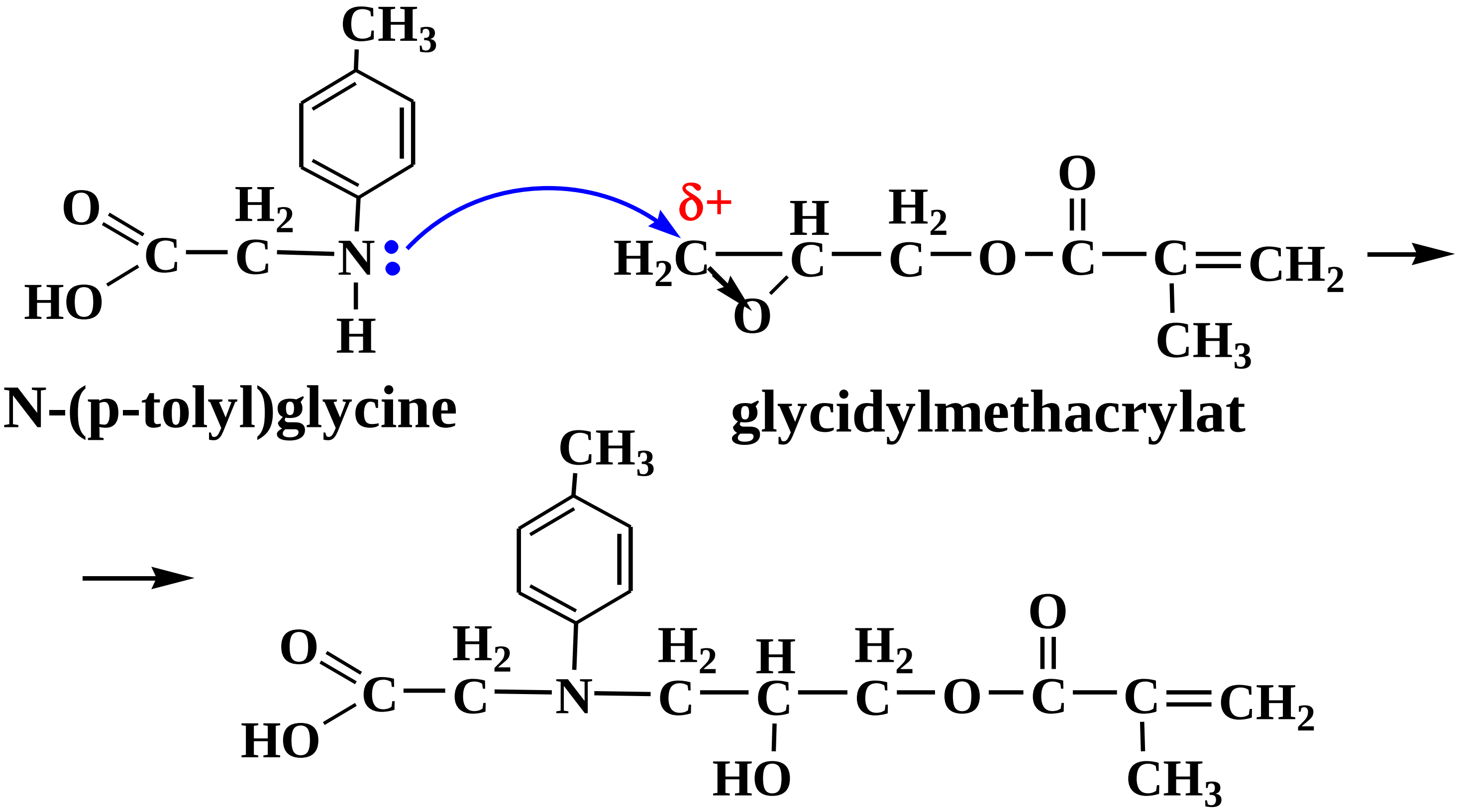
Bis-GMA

bis-phenol-A-glycidylmethacrylat

Bis-GMA system has high viscosity. So material requires diluent.

MODERN RESTORATIVE COMPOSITE DENTAL MATERIALS. NTG-GMA.

The main component of restorative dental materials of light-curing is **NTG-GMA** system. It is product of condensation of glycidylmethacrylate with N-(p-tolyl)glycine.



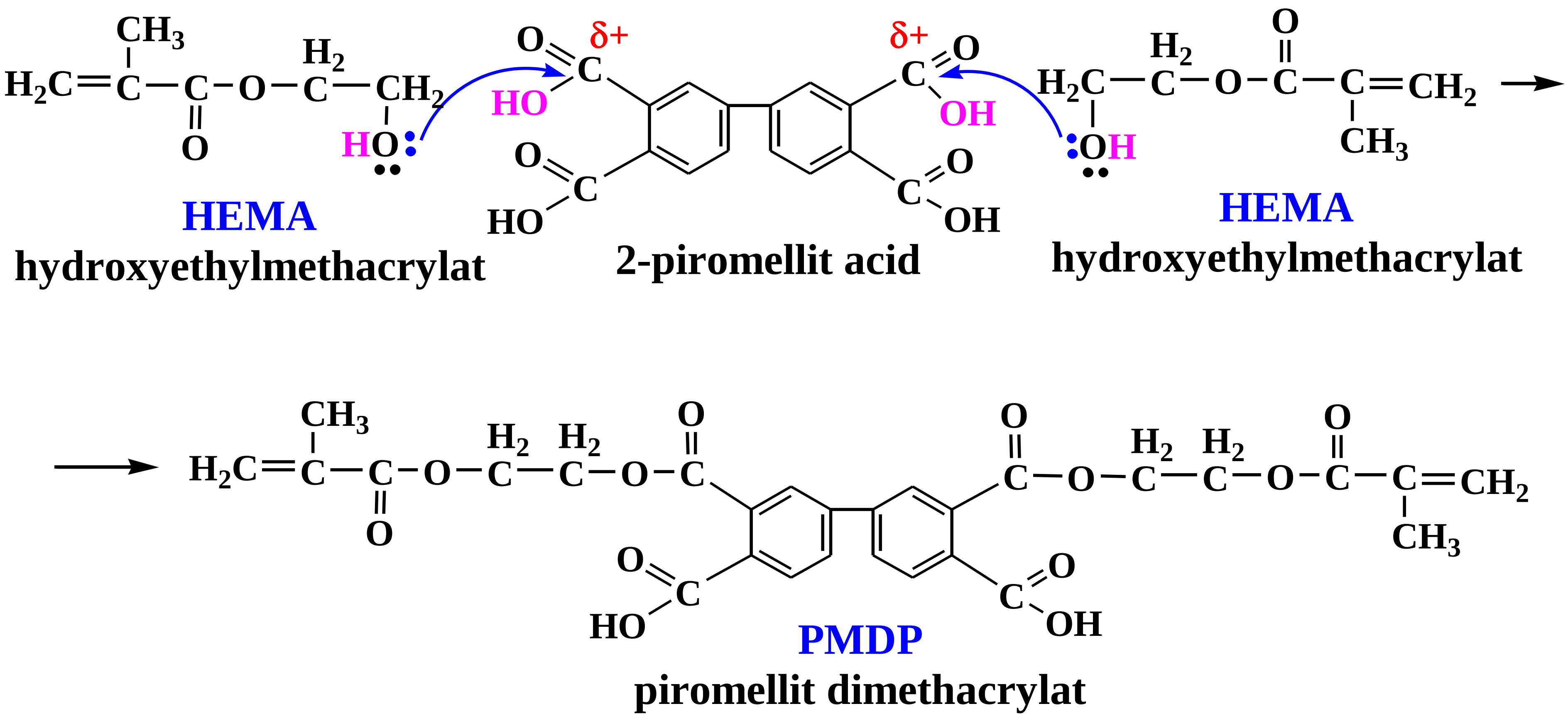
N-(p-tolyl)glycine

glycidylmethacrylat

NTG-GMA

MODERN RESTORATIVE COMPOSITE DENTAL MATERIALS. PMDM.

The another component of restorative dental materials of light-curing is **PMDM** system. It is product of condensation of hydroxyethylmethacrylate (**HEMA**) with 2-piromellit acid.



HEMA
hydroxyethylmethacrylat

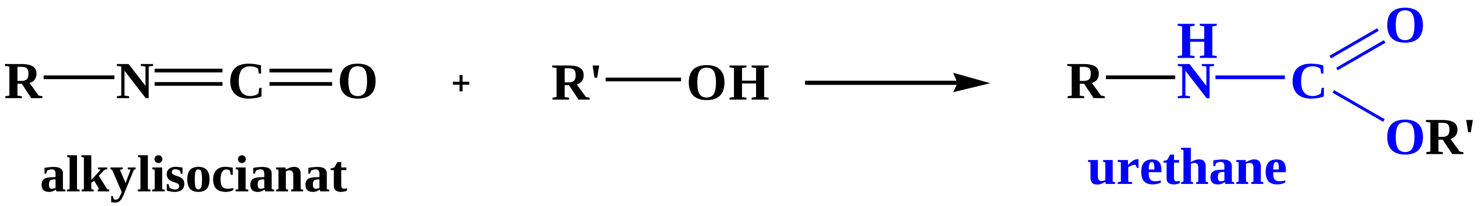
2-piromellit acid

HEMA
hydroxyethylmethacrylat

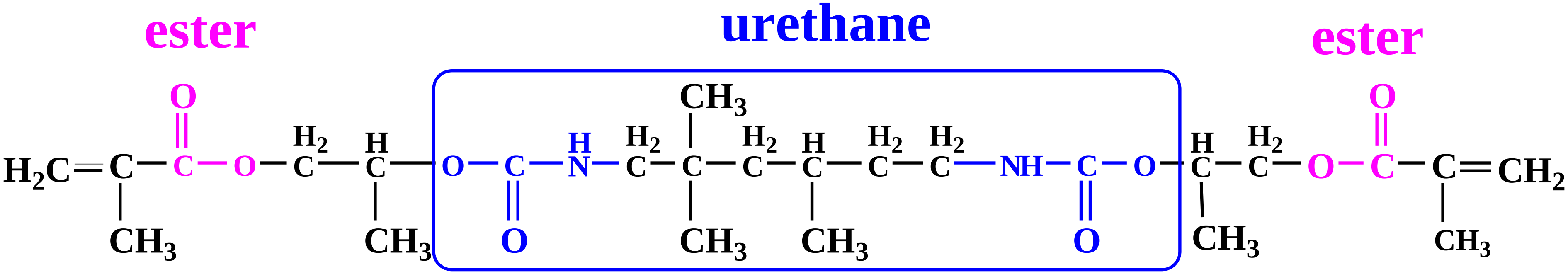
PMDP
piromellit dimethacrylat

MODERN RESTORATIVE COMPOSITE DENTAL MATERIALS. UDMA.

- ***Urethandimethacrylat (UDMA)*** is monomer of several dental materials. Restorative dental materials on base UDMA are very strong and lasting due to high molecular weight and long chain of this monomer.
- Scheme of urethane formation:



- For example:



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

ADHESION OF FILLING MATERIALS TO THE ENAMEL AND DENTINE TISSUES.

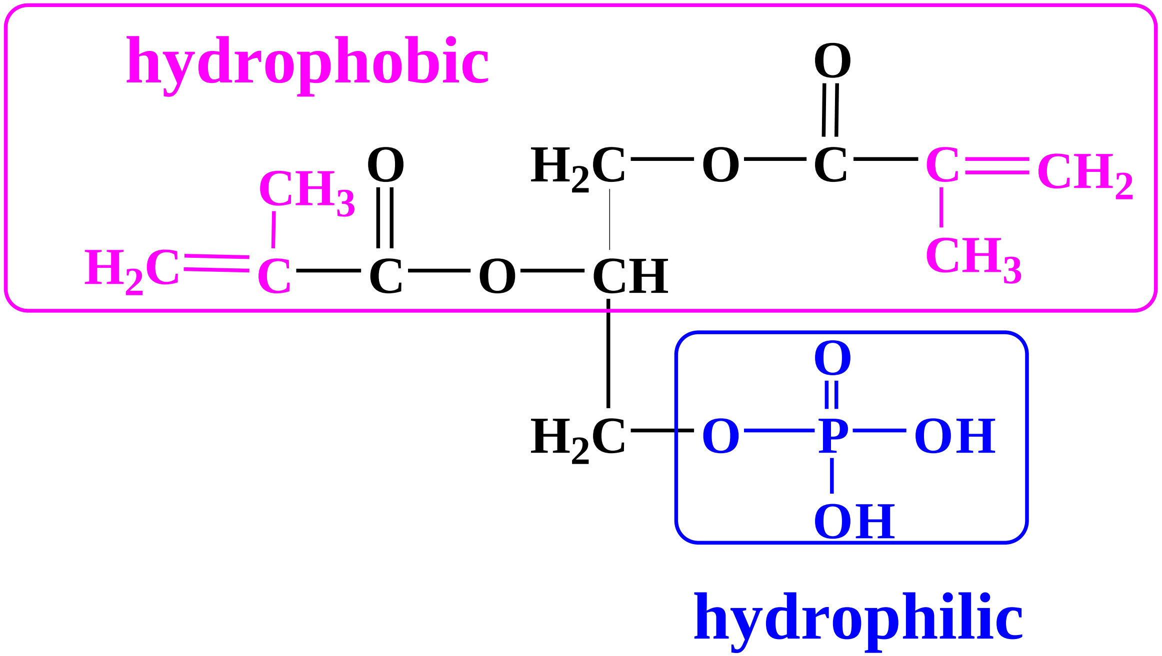
In the modern direct restorative materials adhesion of dental material to the enamel and dentin is commonly micromechanical interlocking and secondary chemical bonds to collagen and residual hydroxyapatite. Etching of enamel and dentin with strong acid, commonly 37% orthophosphoric acid, dissolve hydroxyapatite crystals ($Ca_{10}(PO_4)_6(OH)_2$) 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 collaged fibers that were exposed when dentin was etched and form macrotags inside the surface dentin layer. The primer resin sets. Formation of tags in demineralized surface of enamel and dentin provides sufficient micromechanical bonding between adhesive and tooth tissues.

ADHESION OF FILLING MATERIALS TO THE ENAMEL AND DENTINE TISSUES.

- For increasing of adhesion to the enamel and dentine tissues of tooth modern composite dental materials contain special adhesive –

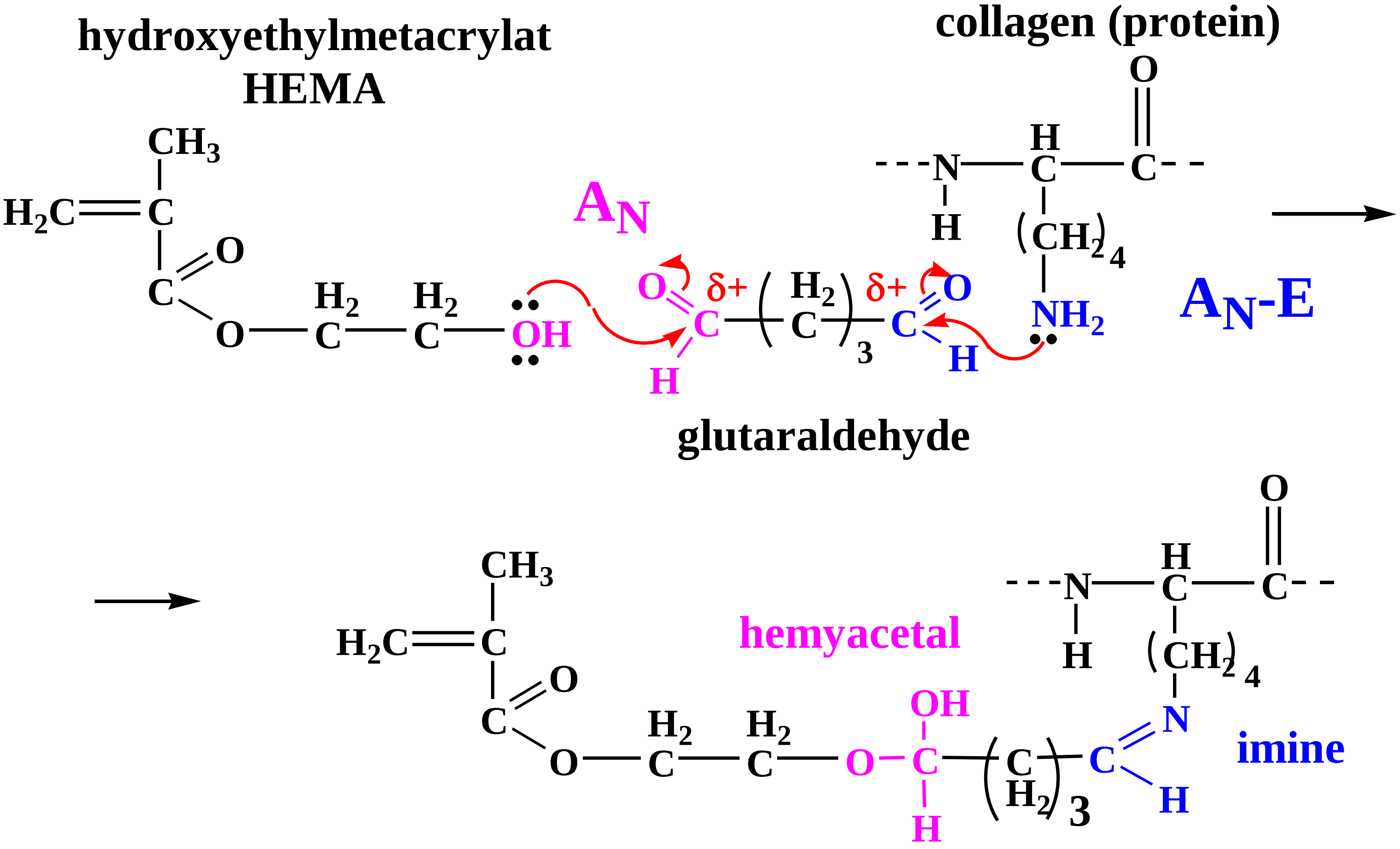
dimetacrylate of glycerophosphoric acid.



- Hydrophilic part of molecule forms complex salt with calcium ions of dentine tissues. Hydrophobic part forms linkage to the dental organic polymer material.

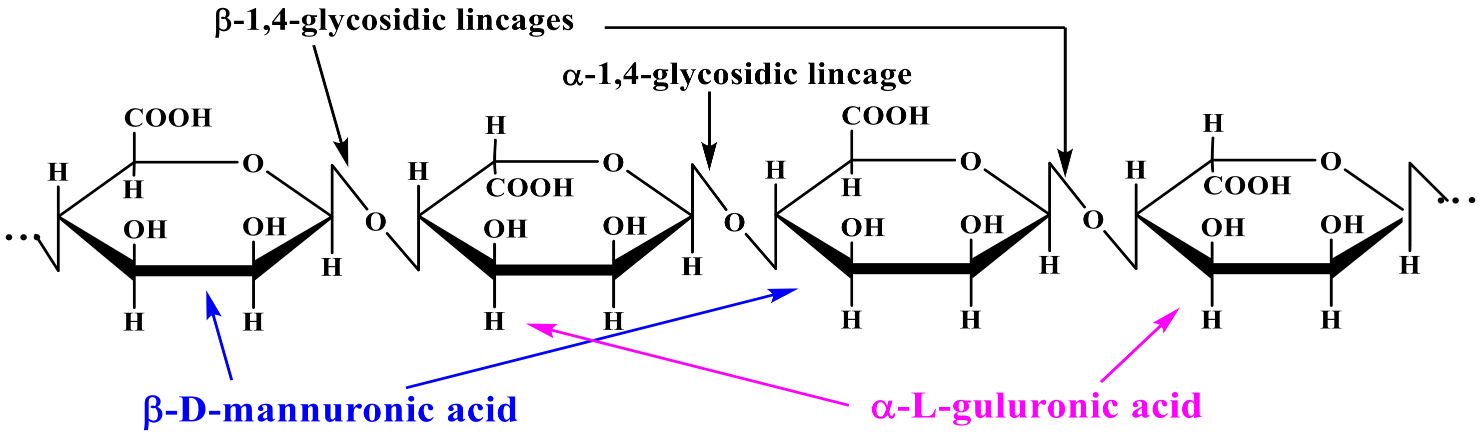
ADHESION OF FILLING MATERIALS TO THE TOOTH TISSUES.

Adhesive often contains dialdehydes (glutaraldehyde), acetone or paraform (poly-formaldehyde). Dialdehyde forms linkage between **hydroxyl groups** of monomer units of dental filling polymer material and **amino groups of** dentine collagen.

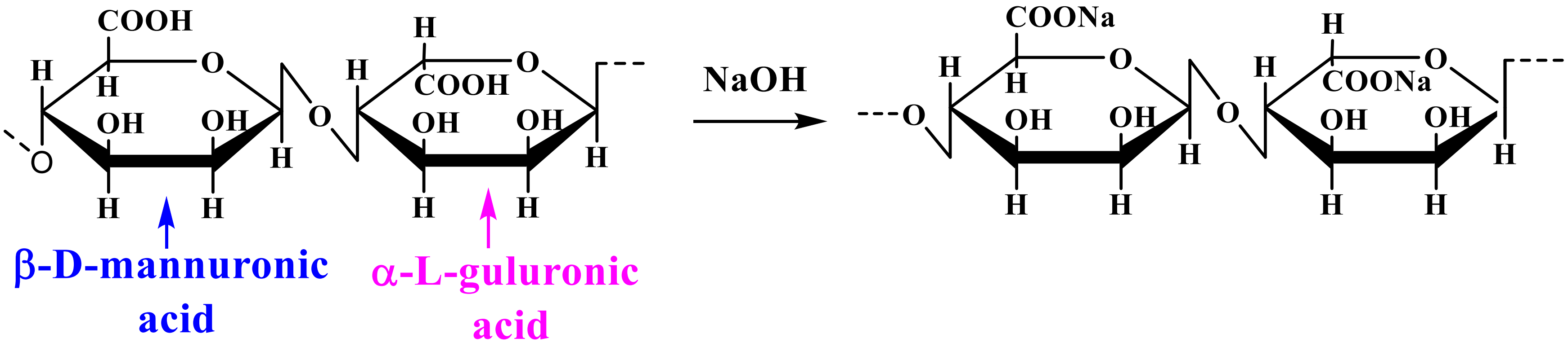


Vegetable heteropolysaccharides in base of dental elastomeric impression materials

- *-β-D-mannuronic acid-β-1,4-L-guluronic acid-α-1,4-*



➢Alginic acids are natural biopolymers of algae.The salts of alginic acids are alginates. Sodium alginats are extended molequles. Calcium alginats have cells structure.Alginats materials is used in stomatology **as non-reversible elastic hydrocolloid impression materials on base alginic acid salts**.



alginic acid

sodium alginat

Waxes in base of dental inelastic impression materials

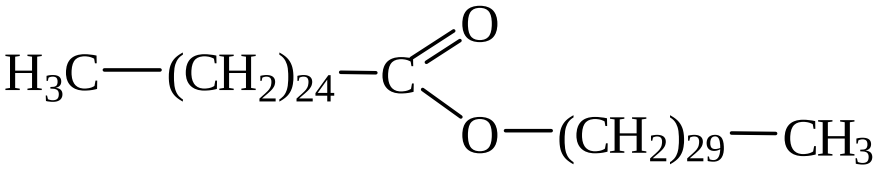
Saturated fatty acids of waxes.

Common name		Structural formula	Systematic name
Myristic acid	**C_{14}**	$CH_3(CH_2)_{12}COOH$	tetradecanoic acid
Palmitic acid	**C_{16}**	$CH_3(CH_2)_{14}COOH$	hexadecanoic acid
Stearic acid	**C_{18}**	$CH_3(CH_2)_{16}COOH$	octadecanoic acid
Lignoceric acid	**C_{24}**	$CH_3(CH_2)_{22}COOH$	tetracosanoic acid
Cerotinic acid	**C_{26}**	$CH_3(CH_2)_{24}COOH$	hexacosanoic acid

Saturated alcohols of waxes

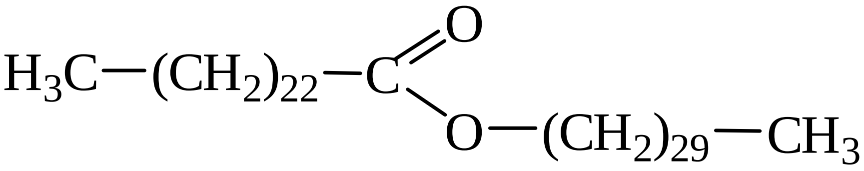
The common name		Structural formula	Systematic name
Cetyl alcohol	**C_{16}**	$CH_3(CH_2)_{14}CH_2OH$	1-hexadecanol
Stearyl alcohol	**C_{18}**	$CH_3(CH_2)_{16}CH_2OH$	1-octadecanol
Ceryl alcohol	**C_{26}**	$CH_3(CH_2)_{24}CH_2OH$	1-hexacosanol
Myricyl alcohol	**C_{30}** **C_{31}**	$CH_3(CH_2)_{28}CH_2OH$ $CH_3(CH_2)_{29}CH_2OH$	1-triacontanol 1-hentriacontanol

Waxes in base of dental inelastic impression materials



$H_3C-(CH_2)_{24}-C(=O)-O-(CH_2)_{29}-CH_3$

myricyl cerotate



$H_3C-(CH_2)_{22}-C(=O)-O-(CH_2)_{29}-CH_3$

myricyl lignocerate

Waxes are inelastic impression materials. Waxes 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. Wax is softened or melted and then formed into a desirable shape. Carnauba wax is used as additional component of wax mixtures to make them more hard and less plastic.

Carnauba wax contains also long carbon chain alcohols (10%); 1-octacosanol CH3-(CH2)27-OH and 1-heptacosanol CH3-(CH2)26-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 g/cm3, softening temperature 40-450C and melting point near 83-910C. Carnauba wax is used as additive of wax mixtures to make them harder, less plastic and to increase melting point.