Polymerization
Synthetic polymers in dentistry

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Types of dental materials

- Metallic materials – denture frameworks, supraconstructions, implants, orthodontic brackets, wires, amalgams.

- Inorganic materials - cements, dental ceramics,gypsum products, investment materials.

- Organic (polymer-based) materials

Types of polymer materials in dentistry

- **Natural polymers** – guttapercha (obturation points), polysacharides agar, alginate (impression materials).
- **Synthetic polymers** – methacrylate-based polymers, silicone polymers, epoxies, etc.

WHY?

Easily modified to prepare **tailor-made materials with good mechanical** and **acceptable biologic properties**

Typical applications of polymer-based materials in dentistry

- Dentures (bases, artificial teeth, orthodontic appliences).
- Filling materials (composites, cements, adhesives).
- Root canal sealers (endodotics).
- Impression materials.
- Equipment (spatulas, measures, curing units, etc.).

What we are going to discuss?

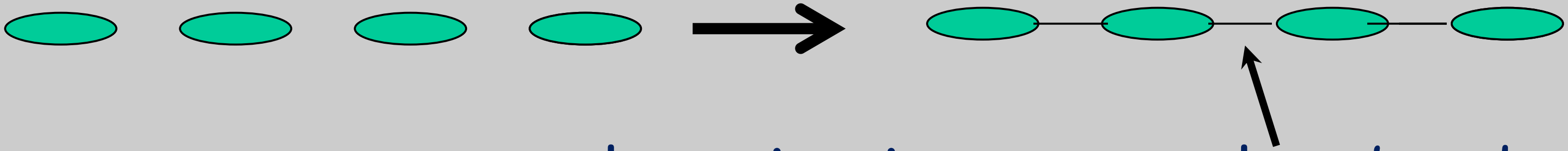
- Terms and definitions.
- Structure of polymer chains.
- Polymerization reactions.
- Methyl methacrylate polymers.
- Typical methacrylate monomers in dental materials.
- Other polymers used in prosthetic dentistry.

Definition

Polymer – a chemical compound composed of large molecules „MACROMOLECULES" formed by union of many „POLY" small repeating units „MER".

mono"MER" molecules

POLY"MER" chain, macromolecule



polymerization

covalent bond

Note:

In stomatology

Polymers = sometimes named resins

but:

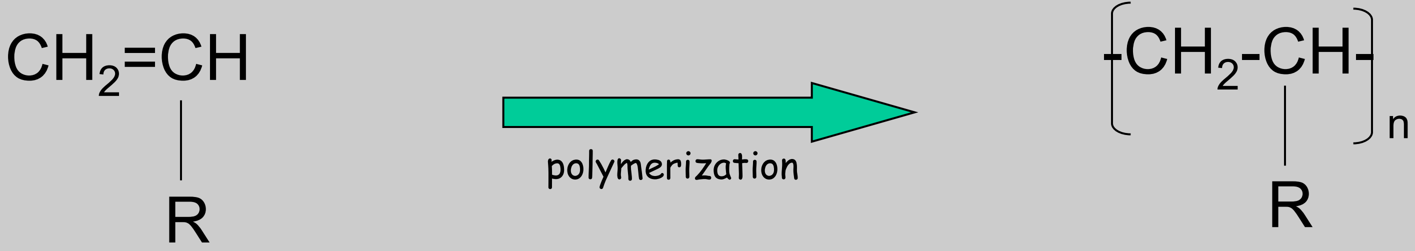
Some monomers – (dimethacrylates) are frequently mentioned also as resins, e.g. resin composites (instead of polymer composites used technical terminology)

What controls polymer properties?

1. Chemical composition and structure of monomer/s

Vinyl monomers

Structure of vinyl polymers

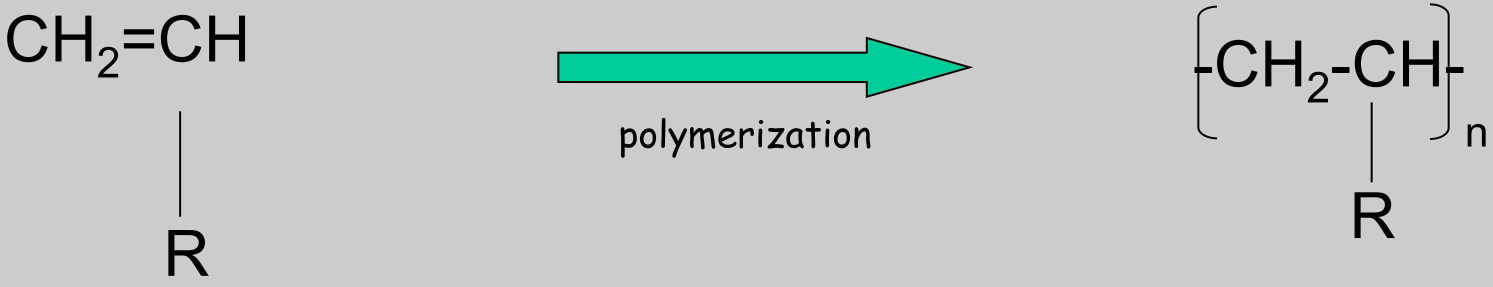


$$CH_2{=}\underset{\displaystyle R}{\underset{|}{CH}} \xrightarrow{\text{polymerization}} \left[CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}} \right]_n$$

Examples:

R = H: polyethylene – a hydrophobic, semicrystaline polymer

R = OH: poly(vinyl alcohol), a hydrophilic water soluble polymer with gelling properties due to H-bonds



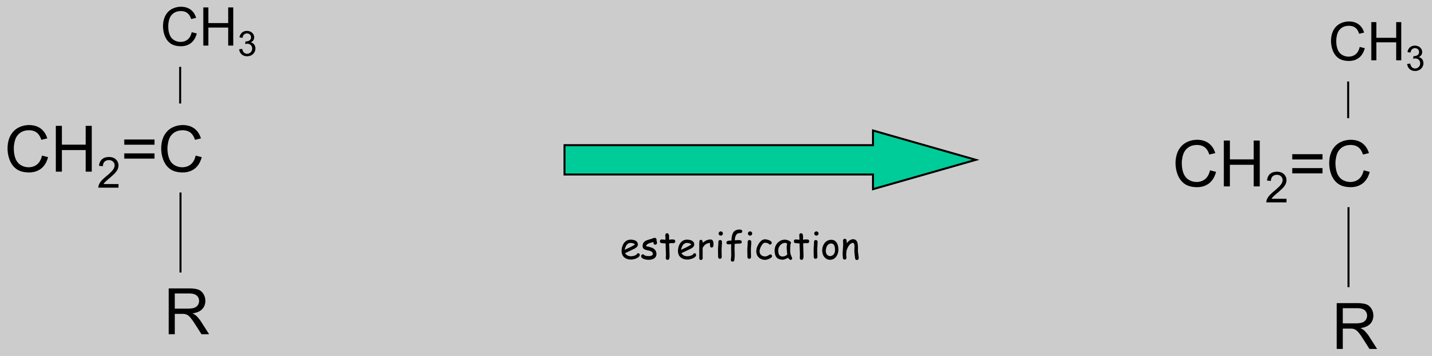
$$CH_2{=}\underset{\textstyle R}{\underset{|}{CH}} \xrightarrow[\text{polymerization}]{} \left[CH_2-\underset{\textstyle R}{\underset{|}{CH}}\right]_n$$

R = COOH – acrylic acid

Water soluble

R = COOH – polyacrylic acid

Water soluble



$$CH_2{=}\underset{\textstyle R}{\underset{|}{\overset{\textstyle CH_3}{\overset{|}{C}}}} \xrightarrow[\text{esterification}]{} CH_2{=}\underset{\textstyle R}{\underset{|}{\overset{\textstyle CH_3}{\overset{|}{C}}}}$$

R = COOH – methacrylic acid/**polymethacrylic acid**

Partly water soluble

R = $COOCH_3$ – methyl methacrylate/ **polymethylmethacrylate**

Insoluble in water

If one type or different monomers are linked together:

One monomer - HOMOPOLYMERs

Two or three monomers - COPOLYMERs

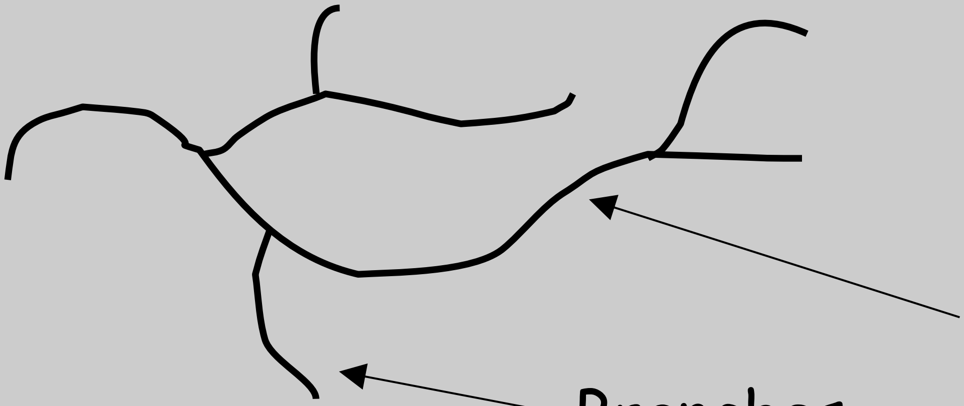
2. Topology of polymer chains

Linear polymers

(monomers with one double bond)

Nonlinear (branched) polymers

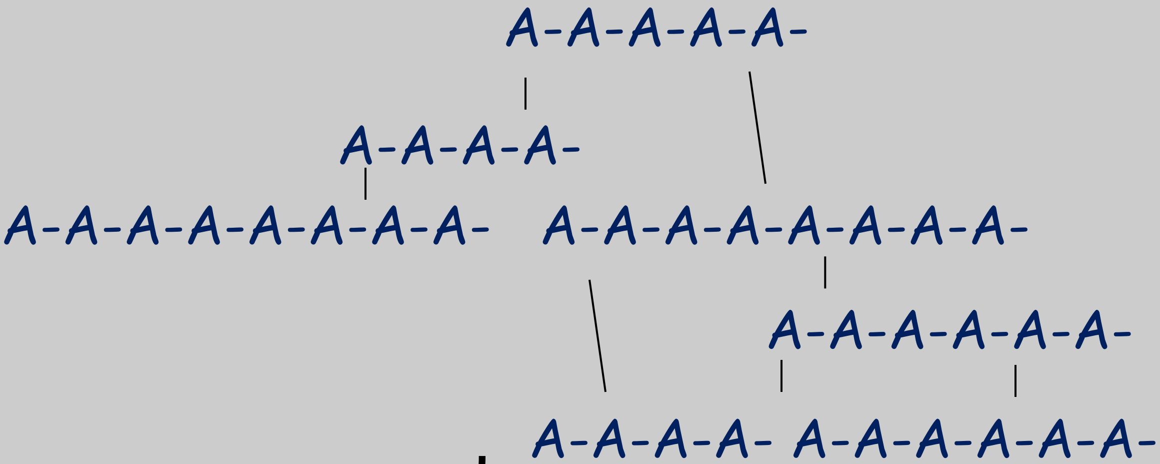
(monomers with two/more double bonds at their lower concentration)

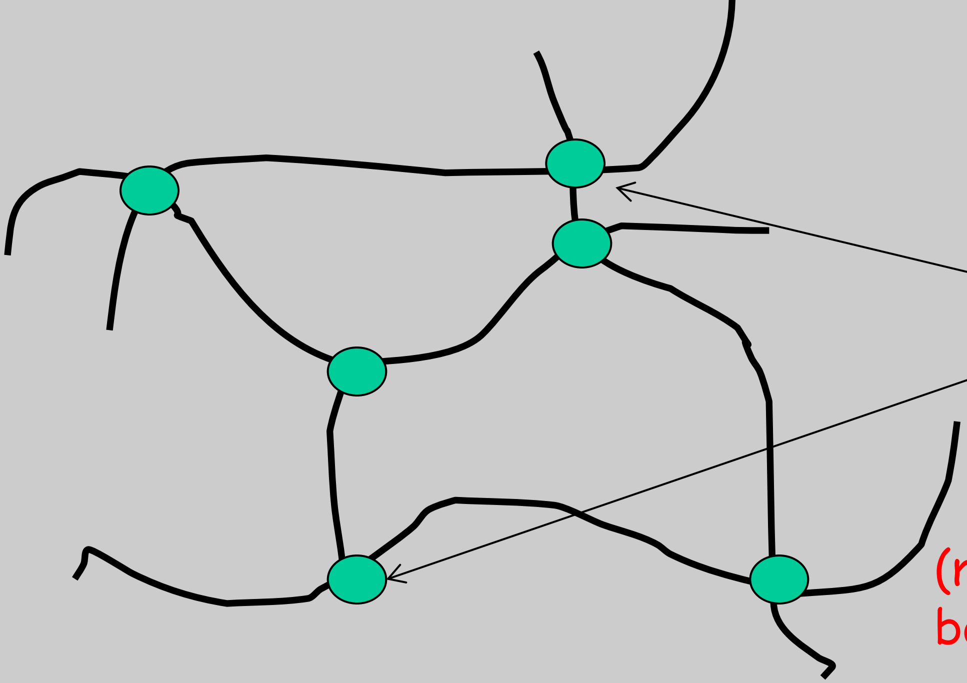


Polymer (linear) backbone

Branches

- Cross-linked polymer (polymer networks)





Cross-links (permanent conections between chains) **restrict motion of chains**

→ rigidity

(monomers with two/more double bonds at their higher concentration)

Cross-links strongly affect mechanical properties and thermal behaviour of polymers

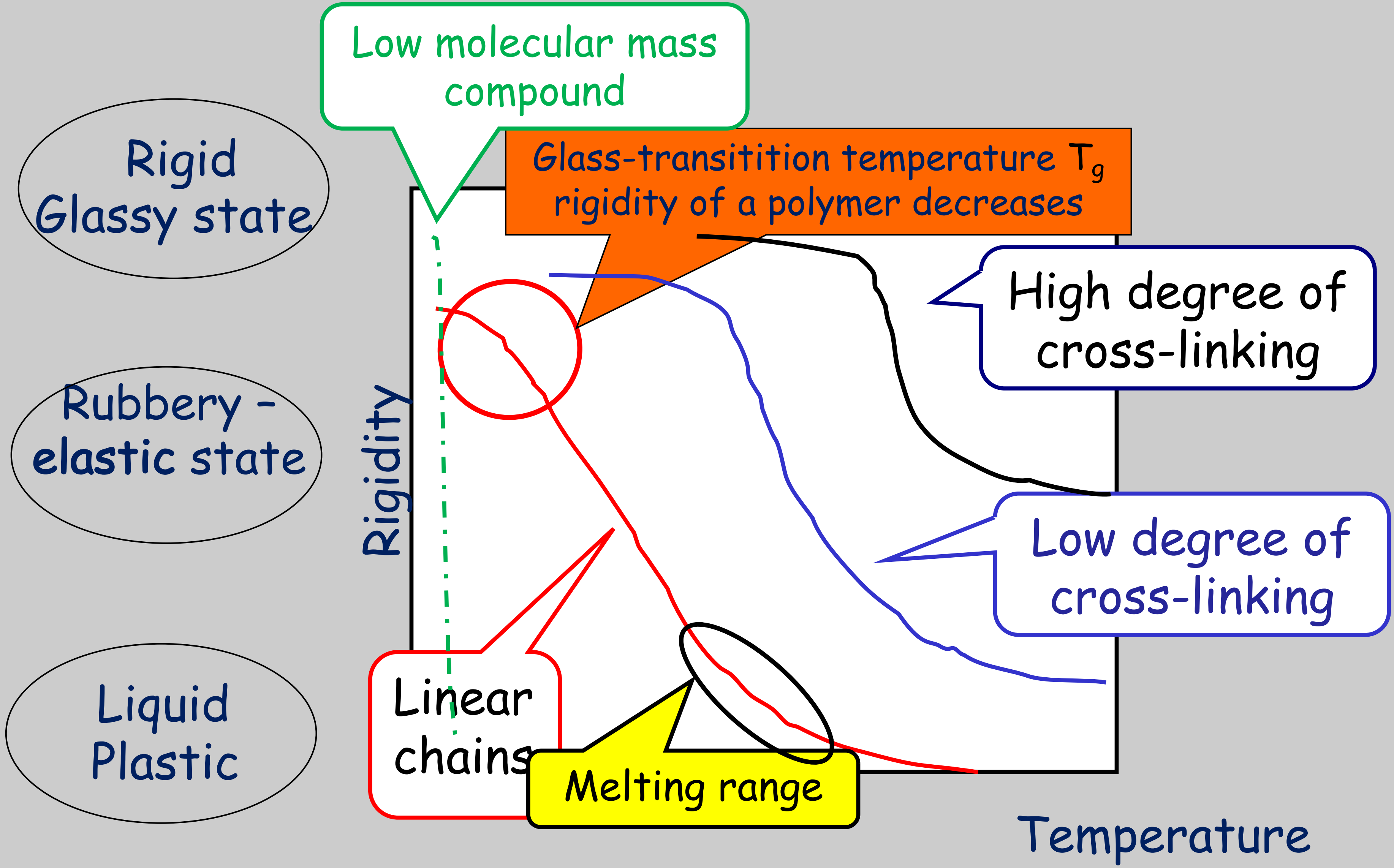
Linear or branched polymers - flow when heated, can be easily reshaped upon heating, usually soluble in organic solvents

- **thermoplastic polymers**

Cross-linked polymers - they can not be reshaped on heating, do not melt, but decompose on heating, insoluble in organic liquids,

- **thermosetting polymers**

Thermal behaviour of polymers



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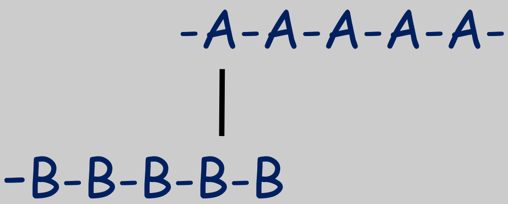
3. Monomer distribution in copolymers

A-B-A-B-B-B-A- *statistical (random)*

A-B-A-B-A-B-A- *alternating*

A-A-A-B-B-B-B-A-A- *block*

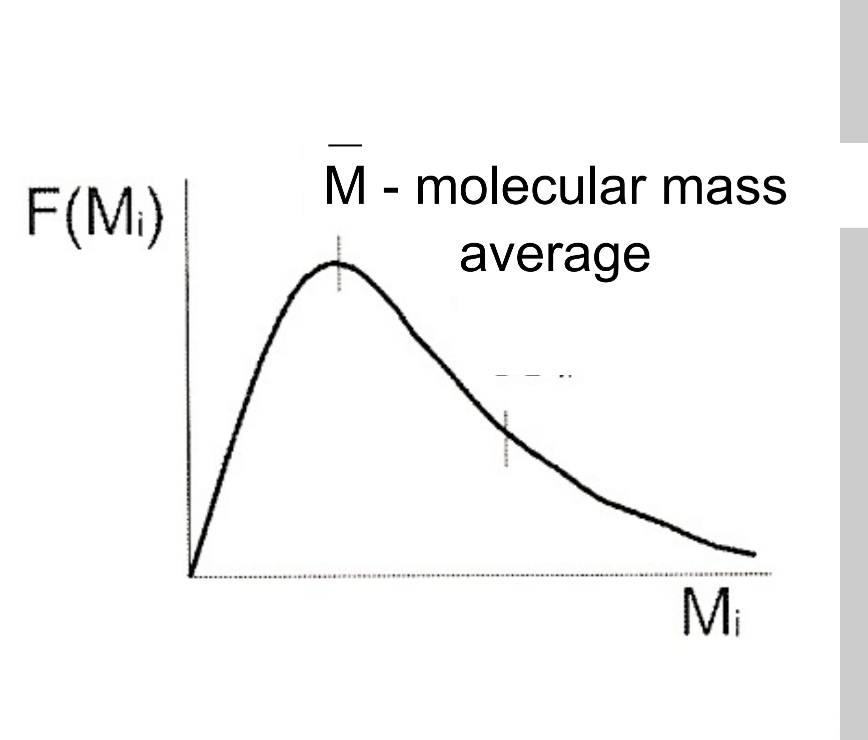

-A-A-A-A-A-
-B-B-B-B-B

graft/branched

4. Polymer molecular mass

Simple compounds – formed from identical molecules

Molecules of polymer – strongly differ (vary by many monomer units in macromolecules)



Polymers are characterized by **molecular mass/polymerization degree average**

Principal requirements on polymer materials in dentistry

1. Fast polymerization,

2. high molecular weight – (improved **mechanical properties**, e.g. strength, hardness, resistance to wear, oral cavity environment, etc.),

3. acceptable biologic properties - decreased **leachable** components.

Synthetic polymers

Prepared via polymerization reactions:

- **Chain-growth** (addition) **polymerization** most often free radical polymerization of monomers with **double bonds**.

- **Step-growth polymerization** (e.g. polycondenzation) of **di/more functional monomers**

  frequently with release of low molecular compounds (analogous reaction to low molecular weight compounds).

Types of chain-growth polymerizations:

- **Free radical polymerization** – active centre is a free radical (with an unpaired electron).
- **Cationic polymerization** – active centres bear positive charge.
- **Anionic polymerization** – active centres bear negative charge.

Free radical polymerization

Characteristics

- Starts from an active center (e.g free radical) only these molecules are capable to react.
- π-bond of monomer is converted to σ-bond in the polymer chain.
- Monomer molecules add sequentially to the end of a growing chain.
- Is very fast and exothermic.
- Produces high molecular mass polymers.
- Free-monomers are present.

Step-growth polymerization
used less often in dentistry

Types of step-growth polymerization

- Polycondensation
- Polyaddition

Step-growth polymerization

Characteristics

- Proceeds by conventional functional group reactions (condensation, addition).
- Needs at least 2 functional groups per reactant.
- Any monomer molecule has the „same" probability to react.
- After an elementary reaction – ability to grow remains.
- Polymers are formed more slowly than by free radical polymerization.

- The chain ends remain active.

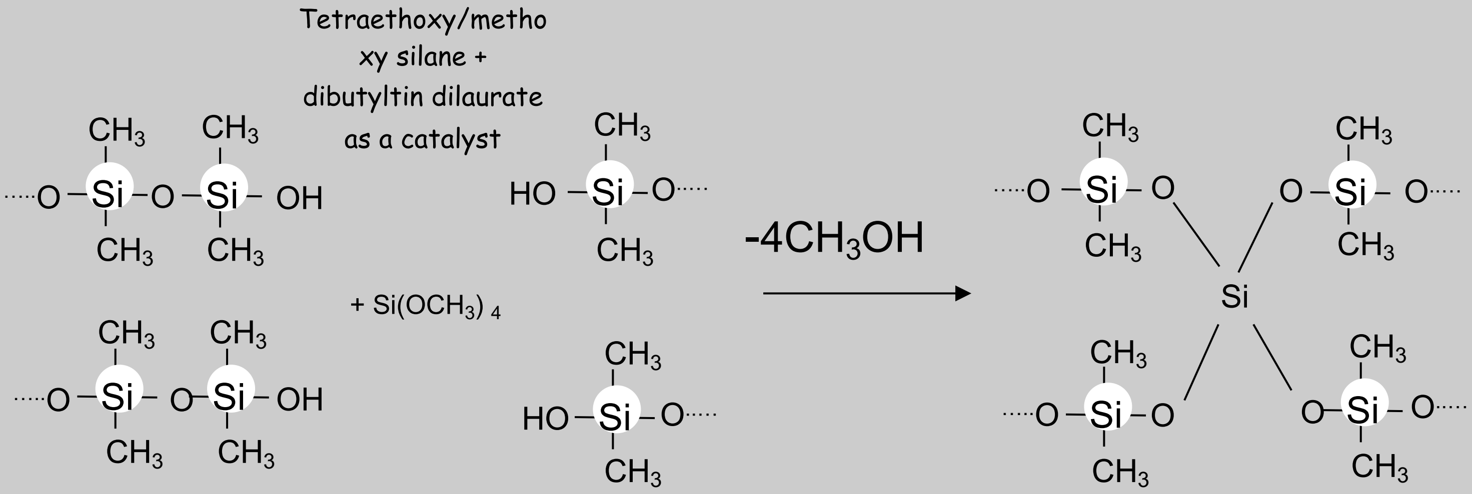
- Polymers are generally of lower molecular mass.

- Dimers, trimers or oligomers are present while concentration of free monomers **rapidly decreases.**

- A small molecular weight products are frequently released (polycondensation) – **inhibit polymerization**.

1. Polycondensation cross-linking

Setting reaction of C-silicone impression materials



Hydroxyterminated dimethylsiloxane prepolymers

2. Polyaddition

Setting reaction of A-silicone impression materials

$$CH_2{=}CH\text{-}Si(CH_3)_2O[(CH_3)_2SiO]_n\,Si(CH_3)_2\text{-}CH{=}CH_2$$

Vinyl terminated siloxane oligomer

Addition of -H on vinyl double bond

$$R_1R_2R_3SiH_x + CH_2{=}CHR \xrightarrow[\text{Pt Catalyst}]{} R_1R_2R_3SiCH_2CH_2R$$

methylhydrosiloxane oligomers – a cross-linking agent

Free radical polymerization

mechanism

Stages of free radical polymerization

1. Initiation/induction – process starts

- Primary radical formation

$$\text{In - In} \xrightarrow{\qquad} \text{In}^{\cdot} + \text{In}^{\cdot}$$ (activation)

Initiator   Free radicals

- Addition of primary radical on the double bond of monomer

$$\text{In}^{\cdot} + \text{M} \xrightarrow{\qquad} \text{In-M}^{\cdot}$$ (an active center)

the chain growth starts

2. Propagation - addition of monomer molecules to the active center → a polymer chain is growing

$$\text{In-M}^{\cdot} \quad + \quad \text{M} \longrightarrow \text{In-M-M}^{\cdot}$$

$$\text{In-M-M}^{\cdot} \quad + \quad \text{M} \longrightarrow \text{In-M-M-M}^{\cdot}$$

$$\text{In-M-M-M}^{\cdot} \quad + \quad y\text{M} \longrightarrow \text{In-M-M-M-.. M}_y^{\cdot}$$

3. Termination – the growing chain is stopped

- Radical coupling/recombination (most common)

$$\text{In-M}_x^{\cdot} + {}^{\cdot}\text{M}_y\text{-In} \longrightarrow \text{In-M}_x\text{-M}_y\text{-In}$$

- Chain transfer – an active centre is split off from the growing chain with a special molecule, terminating the chain growth and starting a new chain – control of molecular mass.

1. Original chain terminates

$$-M\text{-}M\text{-}M^{\cdot} \quad + \quad \underset{\text{Chain transfer agent}}{XB} \longrightarrow -M\text{-}M\text{-}M\text{-}X \quad + \quad \underset{\text{a new active radical}}{B^{\cdot}}$$

2. New chain growth starts

$$B^{\cdot} \quad + \quad \underset{\text{monomer}}{M} \longrightarrow \underset{\text{a new chain starts}}{BM^{\cdot}}$$

Special cases of chain transfer reactions:

A **retarder** is a substance that reacts with a growing chain forming **less reactive** radical $B^{\cdot}$ and thus making polymerization rate „**slow**“.

An **inhibitor** is a substance that reacts with an active radical to form **stable** compound unable addition to monomer - completely **stops** "inhibits" polymerization.

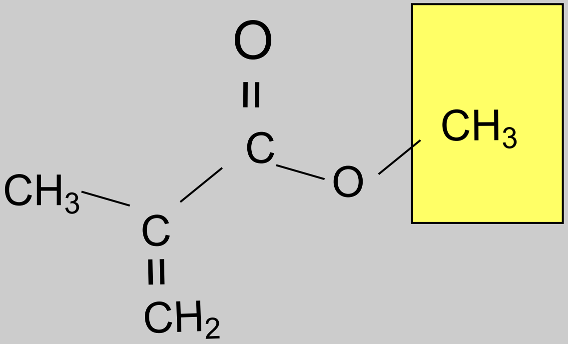
The most important polymerization route in dentistry is <u>**free radical polymerization**</u> of methacrylate monomers:

- Preparation of methacrylic polymers
  (dentures, artificial teeth, relininig materials, orthodontic appliences…).

- Setting reaction of dimethacrylate
  and other multifunctional based dental materials
  (composites, adhesive systems, glass-ionomer cements…).

Methyl methacrylate (MMA) polymers

Most frequently used group of polymers in prosthetic and orthodontic dentistry



methyl methacrylate (MMA)

Why? Because these materials can be easily **adopted** to individual purposes (dentures, teeth), **polymerization is fast** and the polymers are usually **well accepted** by the human body

Properties of MMA

- Colorless liquid
- Immisible with water but with organic solvents
- Melting point -48^{o}C
- Boiling point 100.3^{o}C
- Density 0.945 g/mL
- Heat of polymerization 54.3 kJ/mol (!! exothermic reaction !!)
- Irritant
- !! Flamable !!

Properties of poly(methyl methacrylate) - PMMA

- Transparency and high clarity,
- Compression strength 90 – 100 MPa,
- Very rigid - elastic modulus above 2.4 GPa,
- Water sorption up to app. 1.0 wt %,
- Temperature resistance T_g = 120 – 125°C,
- Soluble in organic solvents (MMA, aceton, toluene etc).

Density 1.19 g/cm^3 (causes **polymerization contraction /shrinkage app. 22 vol %)**

Main problem - how to overcome polymerization shrinkage ????

Leading to pronounced inaccuracy of dental reconstructions

- First applications in denture preparation was via compression moulding of molten PMMA (too expensive and complicated)

- 1936 – Kulzer: powder/liquid system

  Powder – PMMA prepolymer with residues of the initiator (dibenzoyl peroxide – DBP)

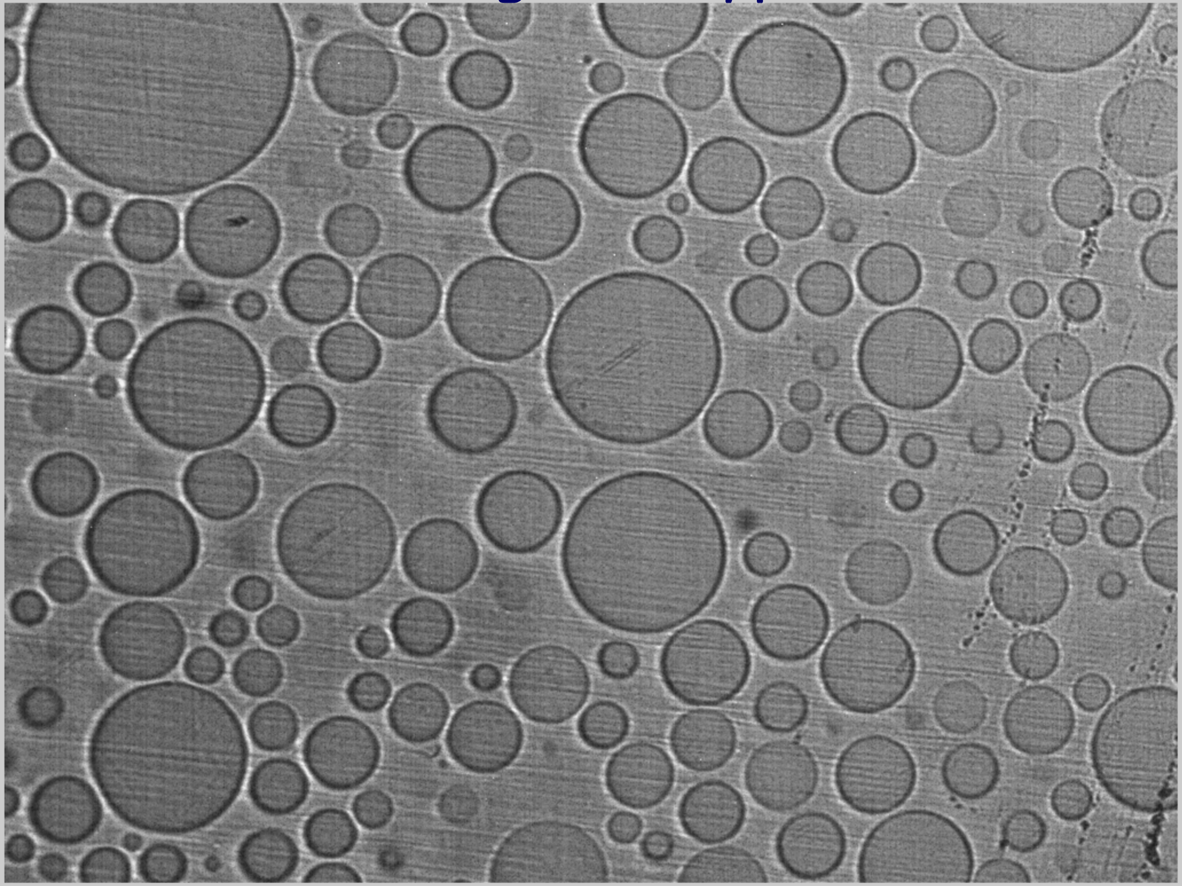
  Liquid – MMA monomer and additives

  - When mixed together a workable - plastic mass (dough) is formed and polymerized in individualy fabricated mould

  - Decreased polymerization shrinkage (app. 6 vol %) at powder/liquid ratio 3-2.6/1

PMMA prepolymer beads

Prepared by suspension polymerization in an aqueous media and using DBP type initiators



Average particle size 0.005-0.100 mm

Classification of methyl methacrylate polymers according to initiation reactions

- Heat activated (heat cured/heat curing) resins,

- Chemically activated (self cured/curing, cold curing, autopolymerizing, fast curing) resins.

Heat activated resins

(denture base resins, resins for artificial acrylic teeth, crown and bridge polymers)

Composition:

powder: PMMA prepolymer with dibenzoyl peroxide
(in the PMMA beads, 0.5 - 0.6 wt %)

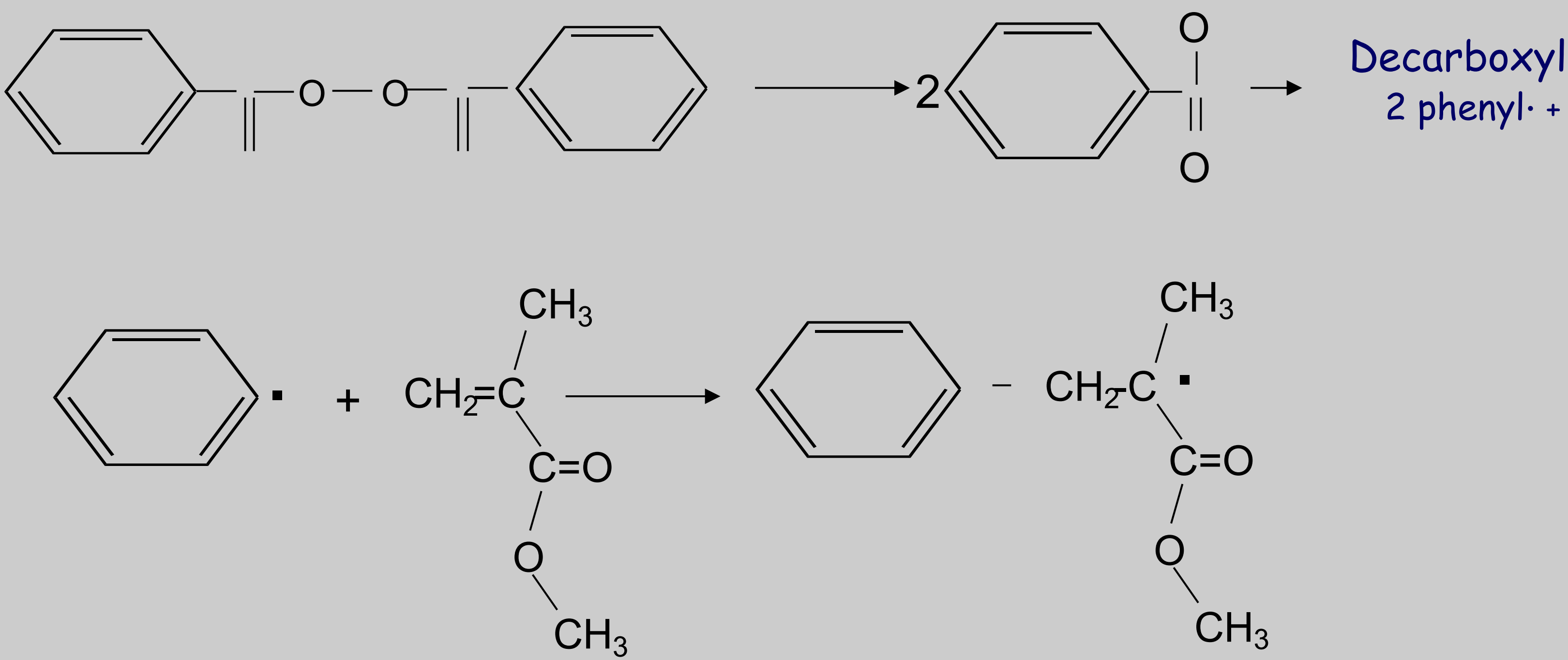
liquid: MMA, cross-linking agent (app. 1 - 6 wt %),

inhibitors, additives (plasticizers)

Volume mixing ratio (powder/liquid): 3-2.5/1.0

Polymerization scheme

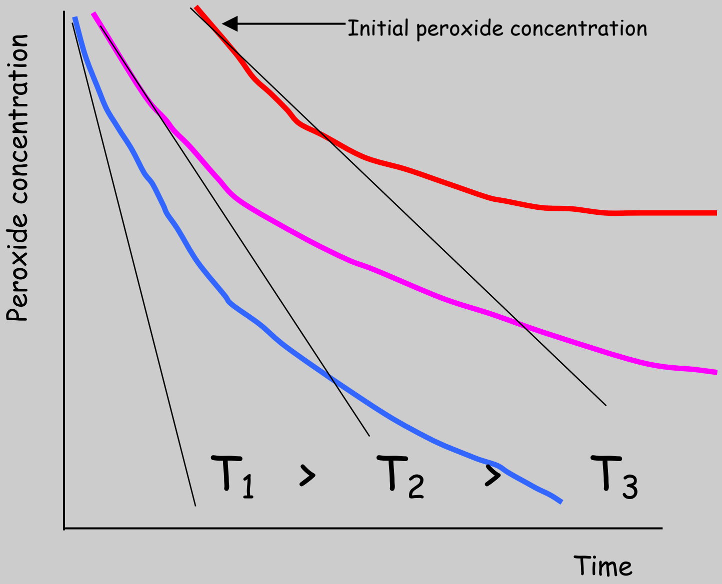
- Initiation
  - Thermal decomposition of residual dibenzoyl peroxide (DBP)



Benzoyloxy radical

Decarboxylation
2 phenyl· + CO_2

Thermal decomposition of DBP



$$C_t = C_o \cdot e^{-kt}$$

C_t = concentration of peroxide at time t

k = kinetic constant (slope)

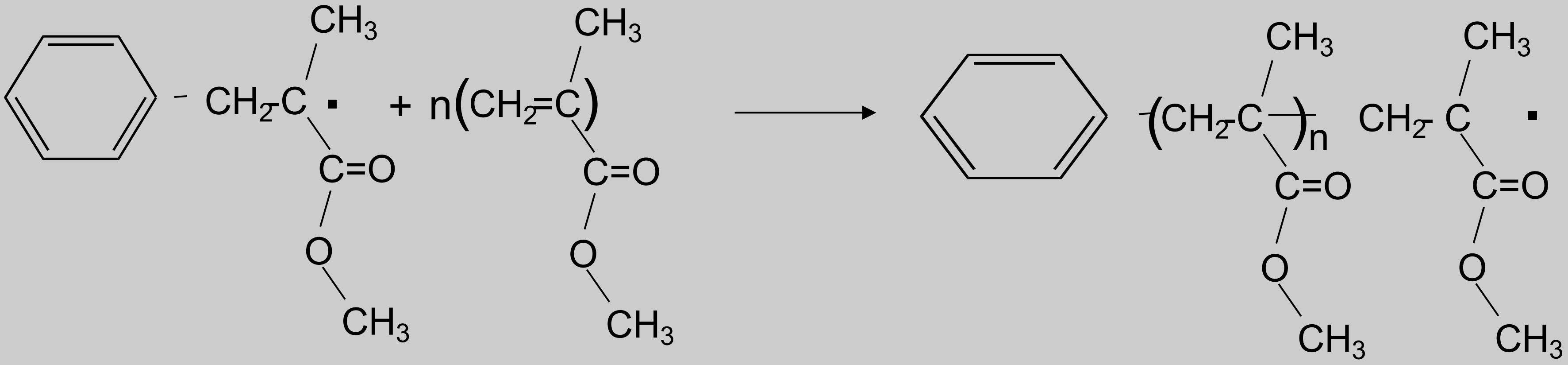
t = time

Effect of temperature

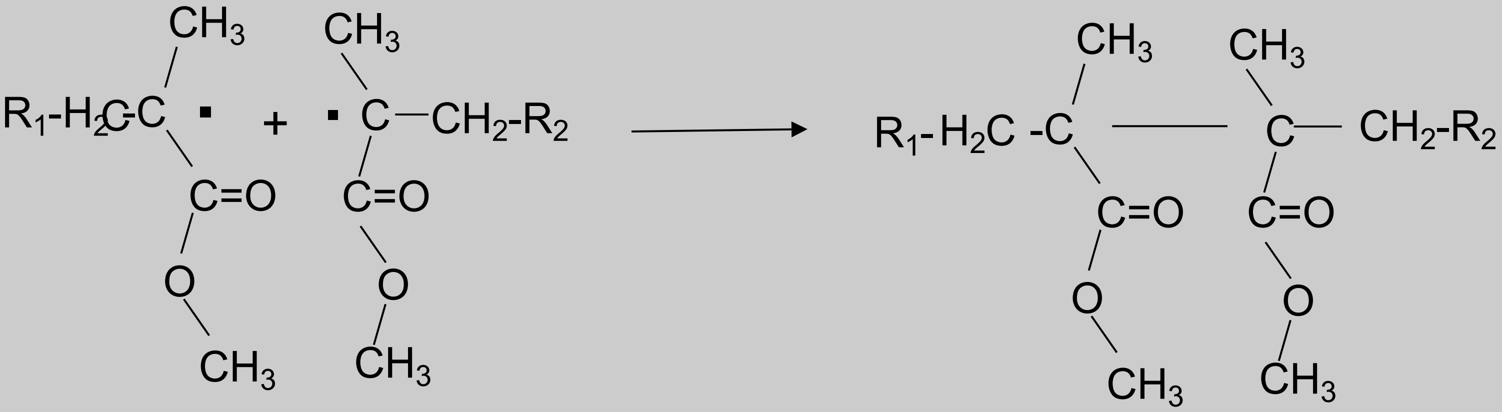
The temperature dependence of kinetic constant is given by the **Arhenius law:**

The higher temperature – increased concentration of radicals (an increased rate of peroxide decomposition) and higher polymerization rate

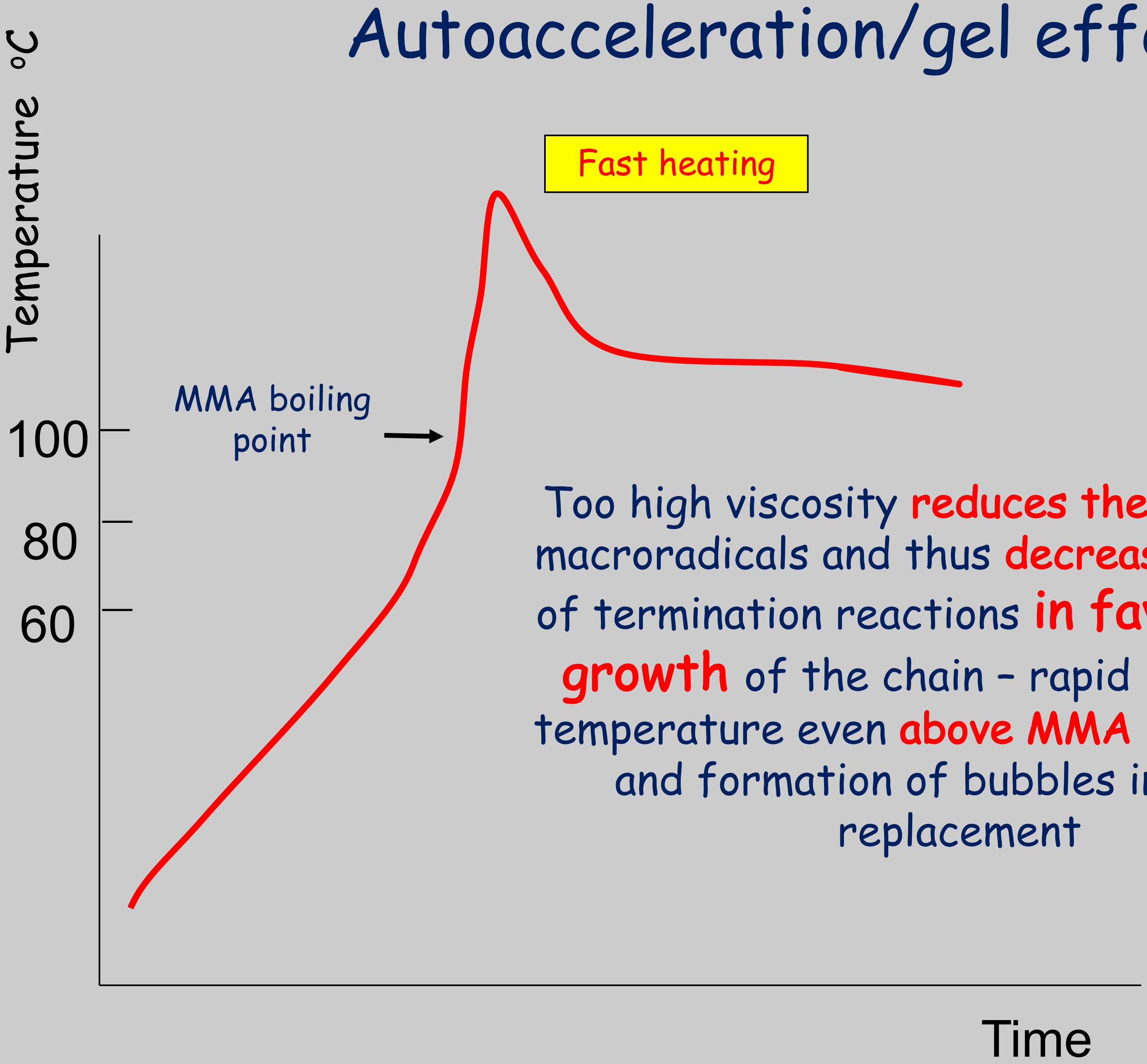
•Propagation



•Chain termination

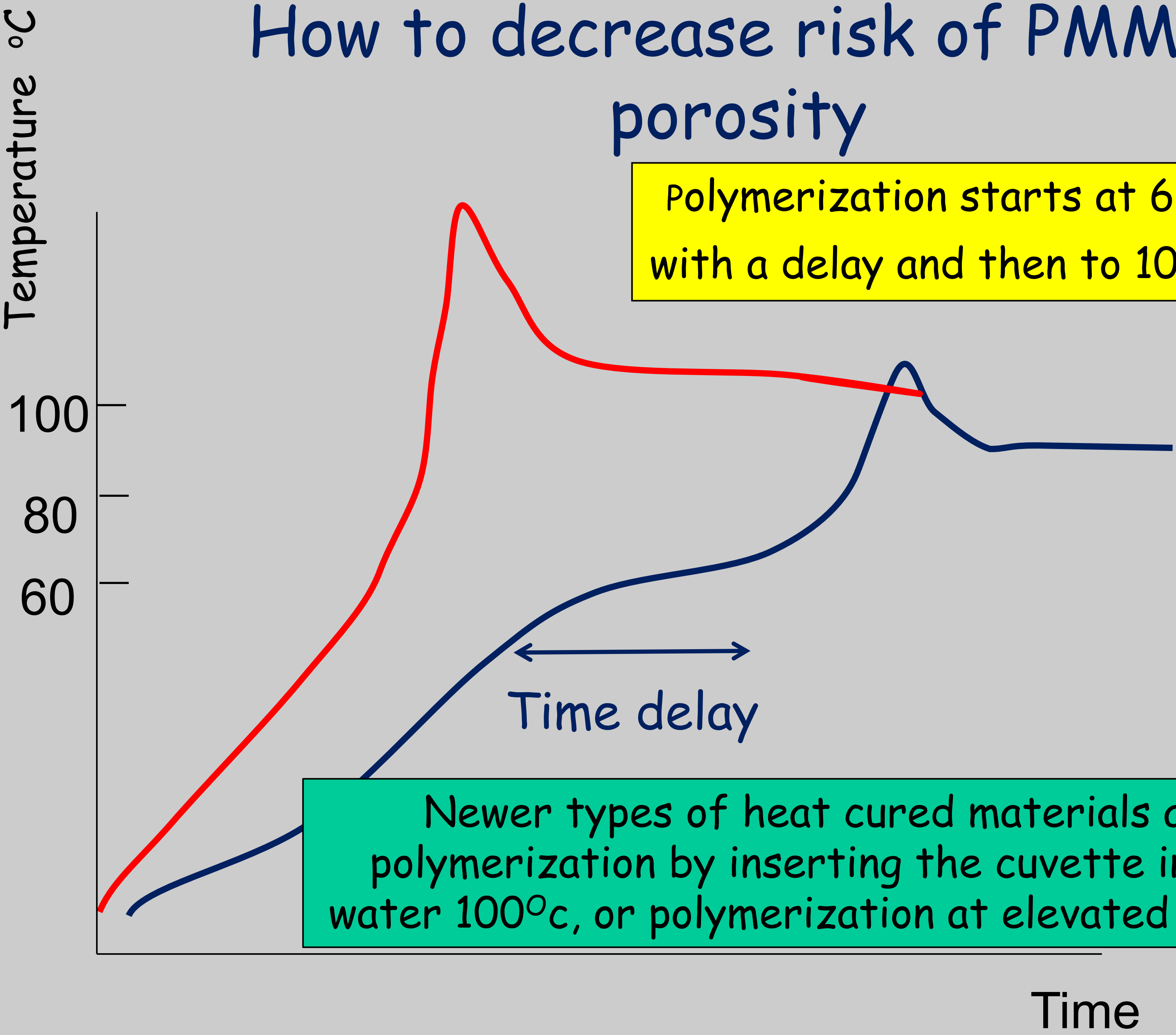


Autoacceleration/gel effect



Too high viscosity **reduces the mobility** of macroradicals and thus **decreases** the rate of termination reactions **in favor of the growth** of the chain – rapid increase in temperature even **above MMA boiling** point and formation of bubbles in PMMA replacement

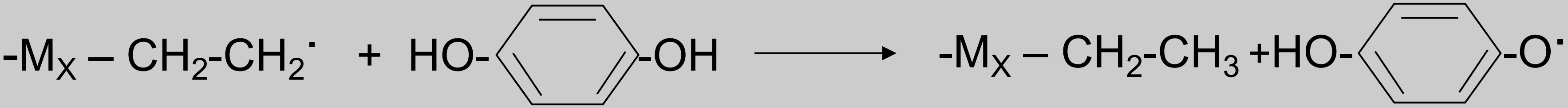
How to decrease risk of PMMA porosity



Polymerization starts at 60°C with a delay and then to 100°C

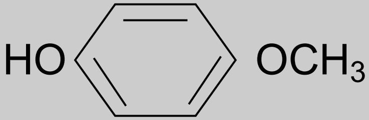
Newer types of heat cured materials allow polymerization by inserting the cuvette into the water 100°c, or polymerization at elevated pressure

Phenolic retarders/inhibitors

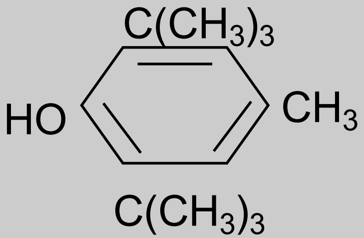


hydroquinone (HQ)

Stable hydroquinone radicals will not propagate and thus stops polymerization



methoxy phenol 4-MP, hydroquinone monomethyl ether, MEHQ



2,6-di-tertbutyl-4-methylphenol

(butylated hydroxytoluene - BHT)

1. Sterically hindered phenols BHT, 4-MP are less efficient than HQ but reduce colour change of polymers due to oxidation products of HQ.
2. Therefore synergetic mixtures HQ + 4-MP, 4-MP+BHT are now more frequently used.

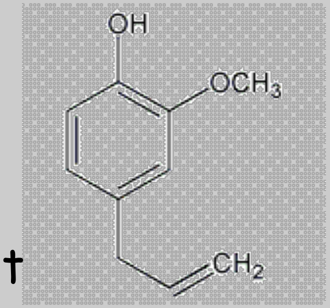
Why polymer inhibitors are added?

Usually 0.01 – 0.005 wt. %

1. To extend monomer shelf-life by preventing spontaneous polymerization
2. To prolonge the working time
3. To decrease sensitivity of monomers to ambient light (light cured composite materials)

Note

1. Eugenol = phenol (inhibits polymerisation)



Zinc oxide-eugenol cements-may negatively affect or stop setting of composite materials

4-Allyl-2-methoxyphenol

2. Oxygen inhibition

$$M_xI^{\cdot} + O_2 \longrightarrow M_xIOOH$$

Stable hydroperoxid

$\downarrow$

Oxygen-inhibited layer on the composite/adhesive surfaces

Chemically activated resins

(denture repair materials, relining materials, orthodontic appliences, pouring resins)

Composition:

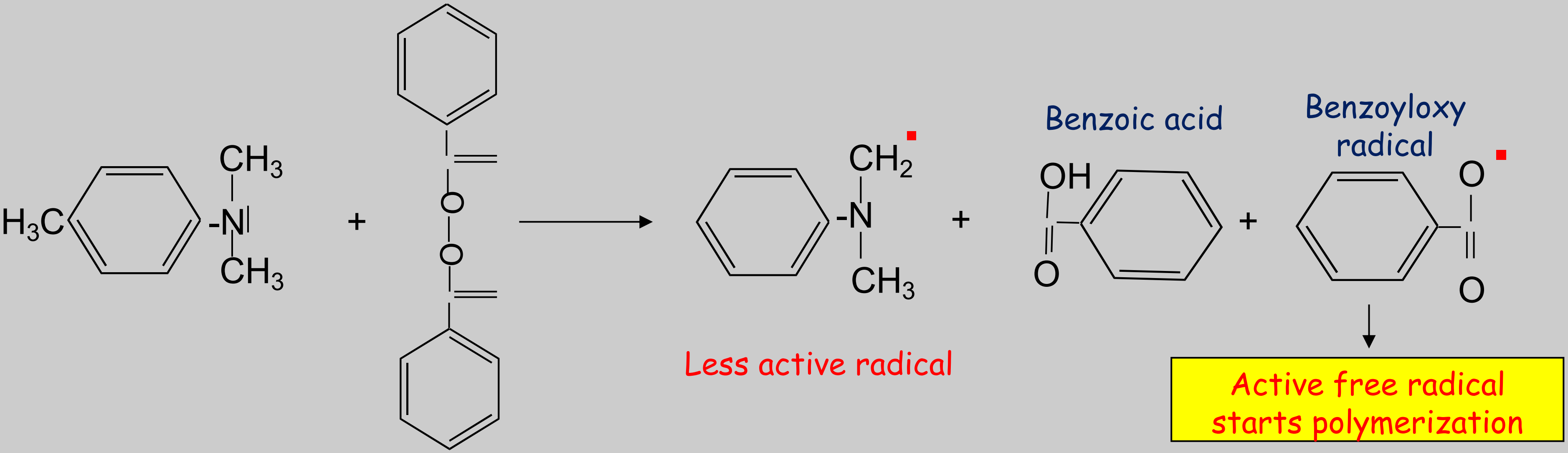
powder: PMMA prepolymer or copolymer (fine particle size), residual dibenzoyl peroxide in the PMMA beads, app. 0.5 - 0.6 wt %)

liquid: MMA, crosslinking agents, **acclerators** (1-4 wt%), inhibitors, UV absorbers

Acclerators

1. **Tercial aromatic amine**
2. Barbituric acid derivatives combined with aliphatic amine (lower color change) and Cu salts
3. Sodium p-toluene-sulfinate (for systems containing methacrylic acid)

Scheme of DBP decomposition accelerated by tertiary aromatic amine



Benzoic acid

Benzoyloxy radical

Less active radical

Active free radical starts polymerization

N,N-dimethyl-p-toluidine (DMPT); N,N-di(hydroxyethyl)-p-toluidine

<u>Compared to heat activated resins:</u>

- Lower molecular weight
- Higher amount of free monomers 3-5 wt %, heat activated app. up to 1 %
- Less color stability due to oxidation of aromatic amine accelerators – yellow/brown coloring

For dental applications PMMAs are often modified by:

Cross-linking

- improves hardness and stiffness,
- increases thermal resistance (polymers are easily finished - grinded and polished without melting),
- improves wear and solvent resistance but increases brittleness,
- increases crazing resistance (small cracks originating at the teeth-denture margin).

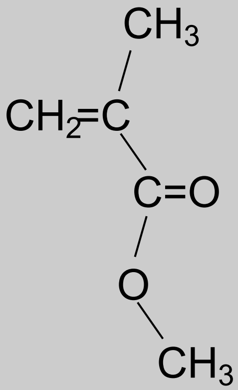
Copolymerization (e.g. with acrylic and methacrylic monomers, *butadiene*) mainly to avoid leaching of plasticizers

Long side substituent disturbs regular intermolecular order of a homopolymer – decrease in T_g

rigid

Methacrylate	Polymer Tg °C
methyl	125
ethyl	65
n-propyl	38
n-butyl	33

Soft, faster dissolution



(ethyl, propyl, butyl)

- decreases softening temperature
- improves fatique and impact resistance
- increases dissolution rate in MMA

Blending of various acrylic/methacrylic polymers

- increases rate of dissolution in MMA
- decreases softening temperature

Plasticizing

- to reduce stiffness and hardness,
- to prepare flexible polymers (acrylic relining materials)

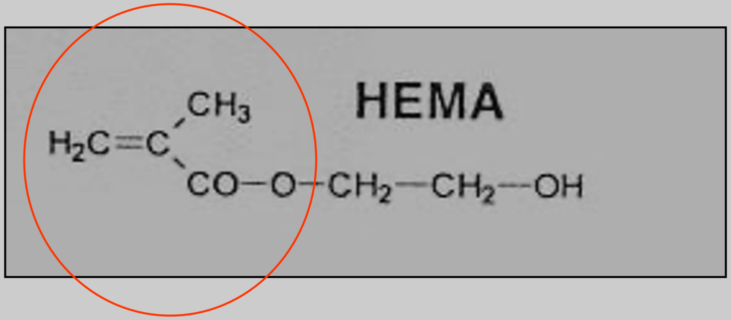
Plasticizers

high-boiling point compounds swell polymers (phatalates – dibutyl/dioctyl phtalates) – leachable potentially harmfull

Currently – not frequently used

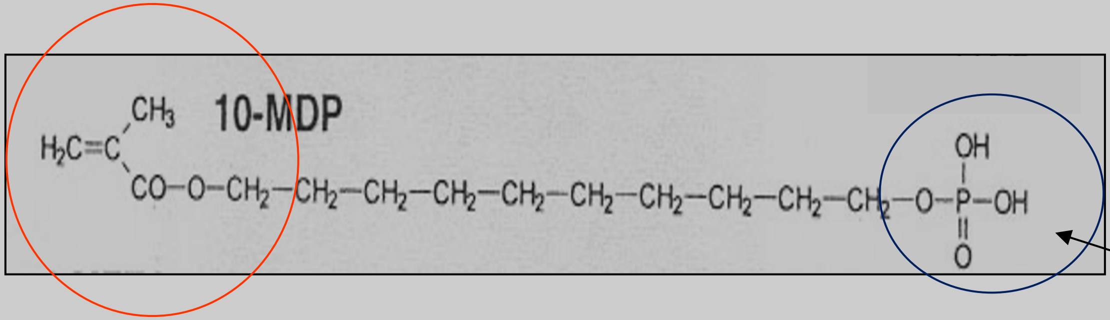
Polymerization of methacrylate/acrylate and other multifunctional monomers

Examples of monomers used in dental adhesives



HEMA

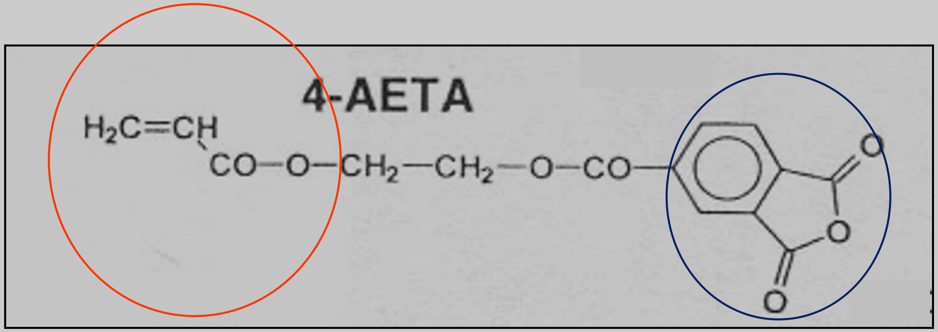
2-hydroxyethyl methacrylate



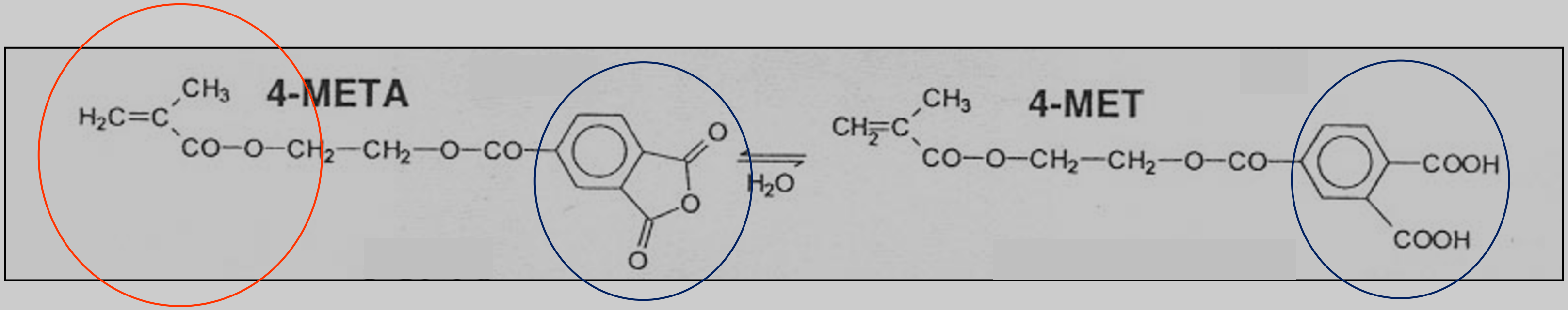
10-MDP

10-methacryoloyloxydecyl dihydrogenphosphate

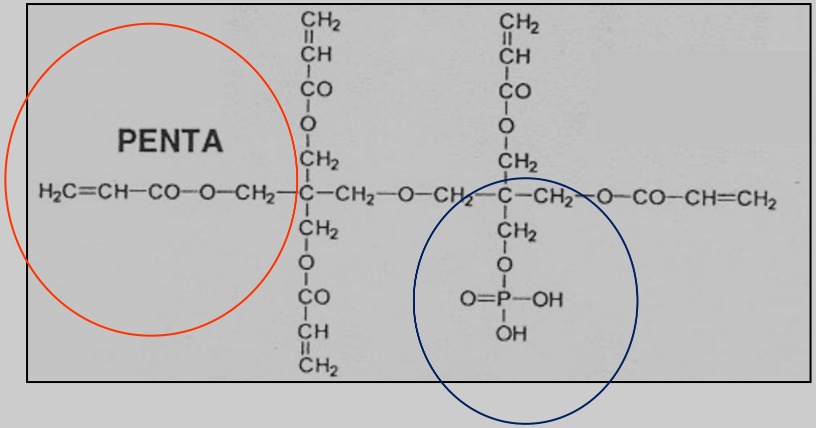
Acidic part of the adhesive molecule bonding to enamel and dentin



4-acryloxyethyl trimelitic acid anhydride



4-methacryloxyethyl trimelitic acid anhydride/acid



Dipentaerythritol **penta** acrylate monophosphate

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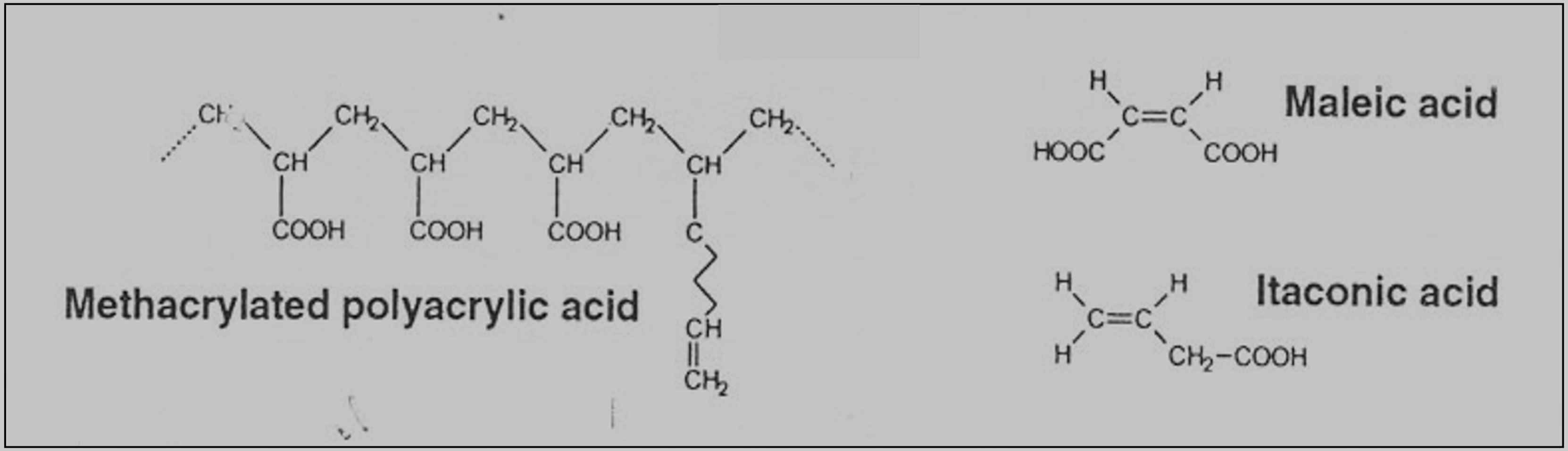
Multifunctional polymers and monomers

Similar principles of free radical polymerization as for monomers with a single MMA unit


Methacrylated polyacrylic acid

Maleic acid

Itaconic acid

Polyacrylic acid with pendant methacrylate groups used in hybrid glass-ionomer cements

Multifunctional monomers in composite formulation

Summary

1. Polymers, characterization, properties (molecular structure)
2. Chain-growth polymerization (free radical); step-growth (polycondenzation and polyaddition)
3. Phases of free radical polymerization
4. Properties of MMA, polymerization of PMMA
5. Inhibitors
6. Characteristics of heat, chemical and light activation systems
7. Dimethacrylate resins used in composite materials
8. Other monomers and polymers in dentistry

Literature:

- Craig RG., Powers JM., Wataha JC: Dental Materials, Properties and Manipulation, Mosby
- Powers JM., Sakagushi RL: Craig´s Restorative Dental Materials, Mosby
- Gladwin M., Bagby M.: Clinical Aspects of Dental Materials, Theory, Practice and Cases, Lippincott Williams/Williams
- Anusavice KJ.: Phillips´ Science of Dental Materials, Saunders

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