

Polymerization Synthetic polymers in dentistry

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Dental materials

- Metallic materials - denture frameworks, supraconstructions, implants, amalgams, orthodontic brackets, wires
- Inorganic materials - cements, ceramics, gypsum products, investment materials
- Organic (polymer-based) materials

Typical polymer-based materials used in dentistry

- Dentures (bases, artificial teeth, relining materials)
- Filling materials (composites, cements, adhesives)
- Obturation materials (endodontology)

- Impression materials

- Equipment (spatulas, measures, etc)

What is the lecture about?

- Terms and definitions
- Structure of polymer chains
- Polymerization reactions
- Methyl methacrylate polymers
- Typical dimethacrylate resins

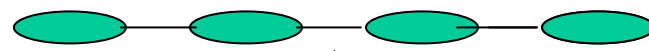
Definition

Polymer - a chemical compound consisting of giant 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 appointed as resins

but:

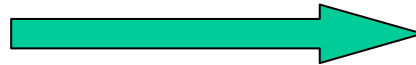
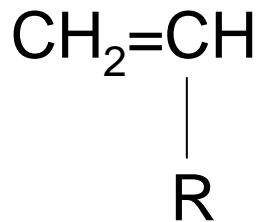
Some monomers – (dimethacrylates) are frequently appointed also as resins, e.g. resin composites

What controls polymer properties?

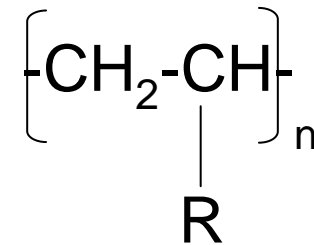
1. Chemical composition of polymers

monomer, its structure and composition

Vinyl monomers



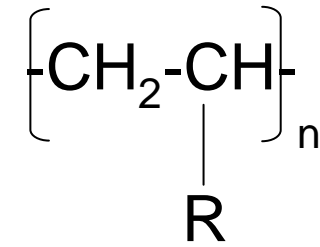
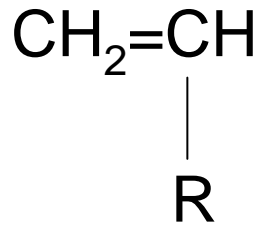
Structure of vinyl polymers



Examples:

R = H – polyethylene hydrophobic, semicrystalline polymers

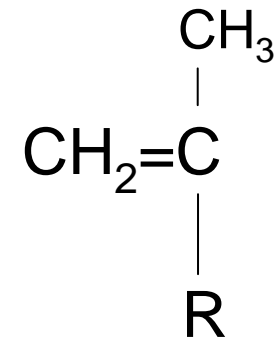
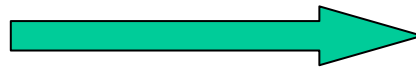
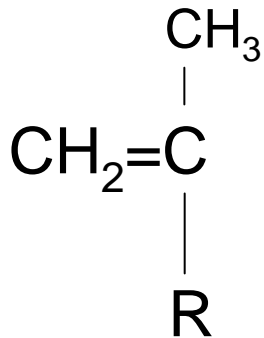
R = OH – poly(vinyl alcohol), hydrophilic water soluble polymer with gelling properties



R = COOH – acrylic acid

R = COOH – polyacrylic acid

Water soluble



R = COOH – methacrylic acid

R = COOCH₃ – methyl methacrylate

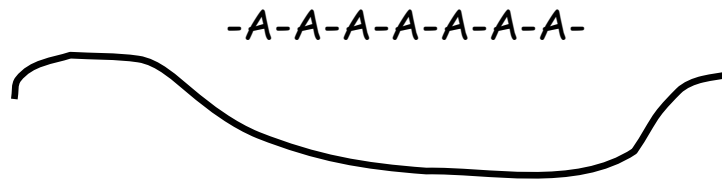
Less water soluble

If one or more monomers are linked together:

One monomer - HOMOPOLYMERS

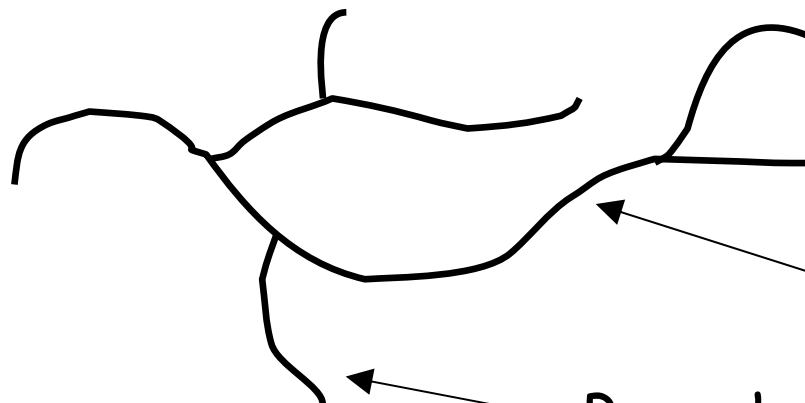
Two or three monomers - COPOLYMERS

2. Topology of polymer chains



Linear polymers

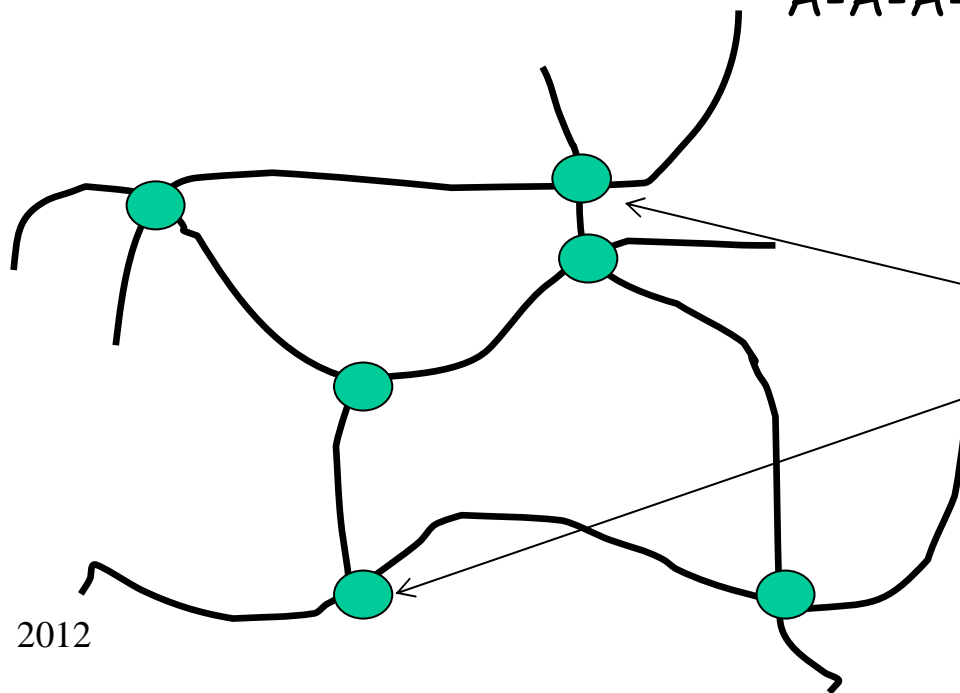
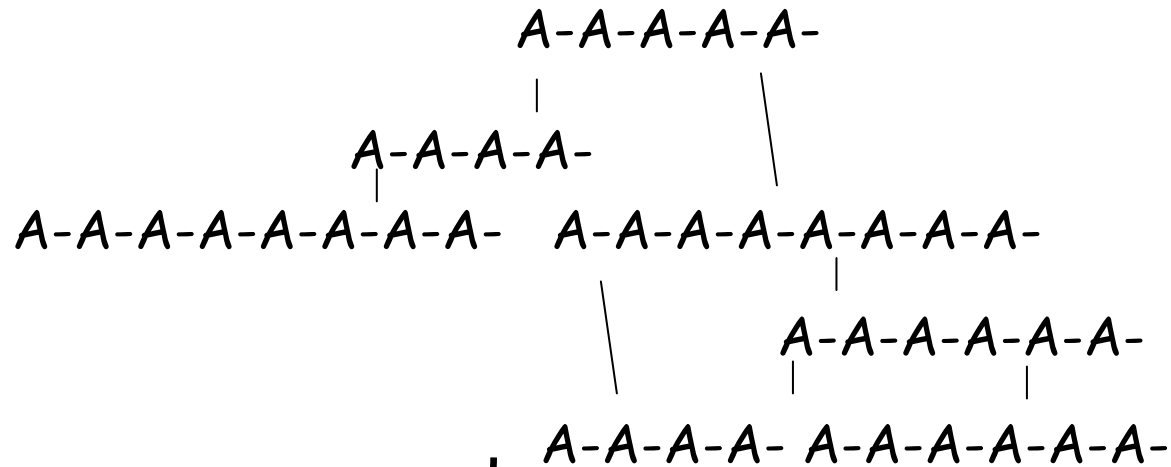
Nonlinear (branched) polymers



Polymer (linear) backbone

Branches

- Cross-linked polymer (**polymer networks**)



Cross-links (permanent connections between chains restricting motion of chains → rigidity)

Temporary cross-links entanglements

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- *graft/branched*

|

-B-B-B-B-B

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

Linear or branched polymers - flow when heated, can be easily reshaped upon heating - **thermoplastic polymers**

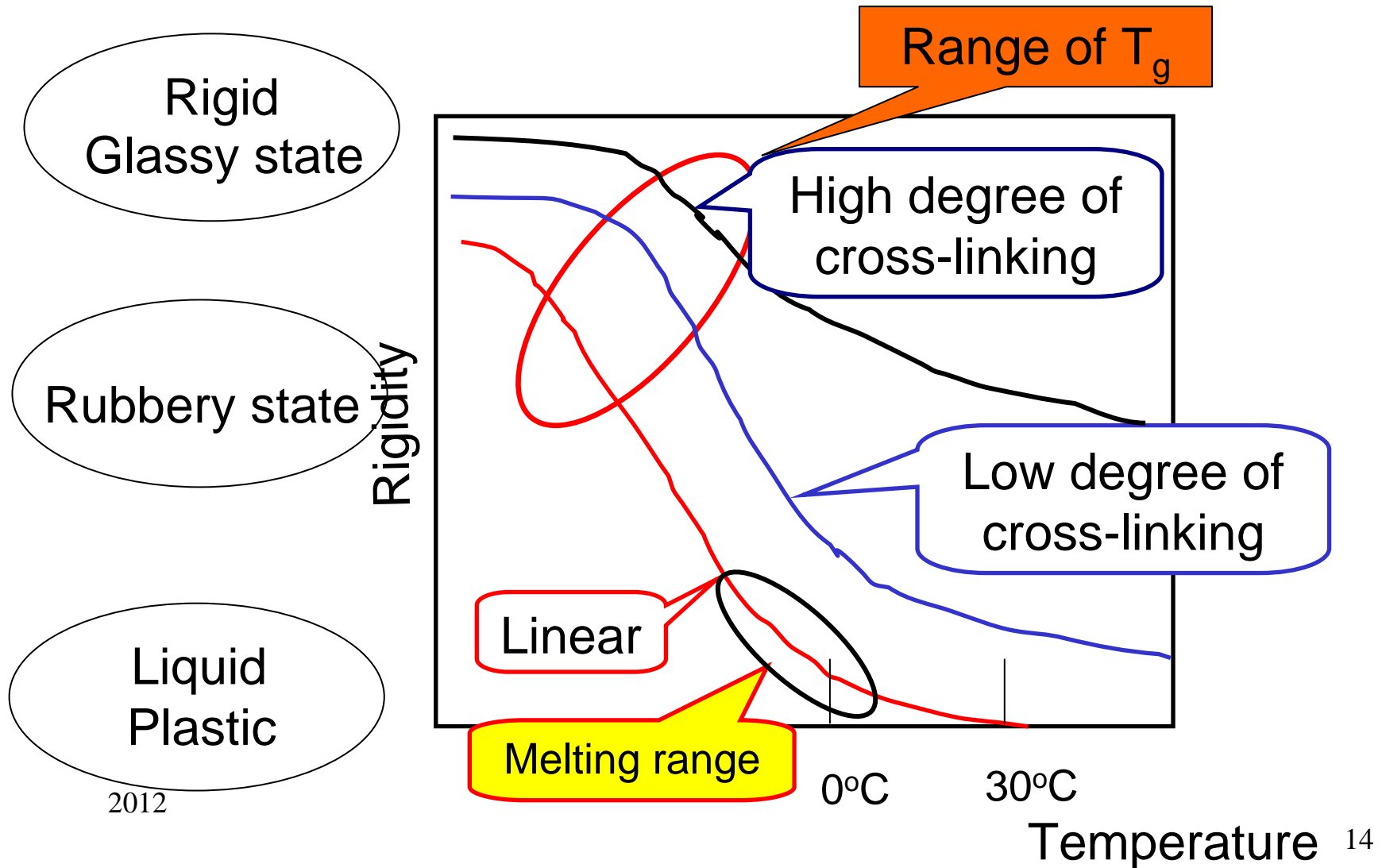
(usually soluble in organic solvents)

Cross-linked polymers - they can not be reshaped on heating, do not melt, but decompose on heating - **thermosetting polymers**

(insoluble in organic liquids)

Glass transition or softening temperature T_g

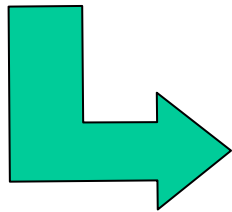
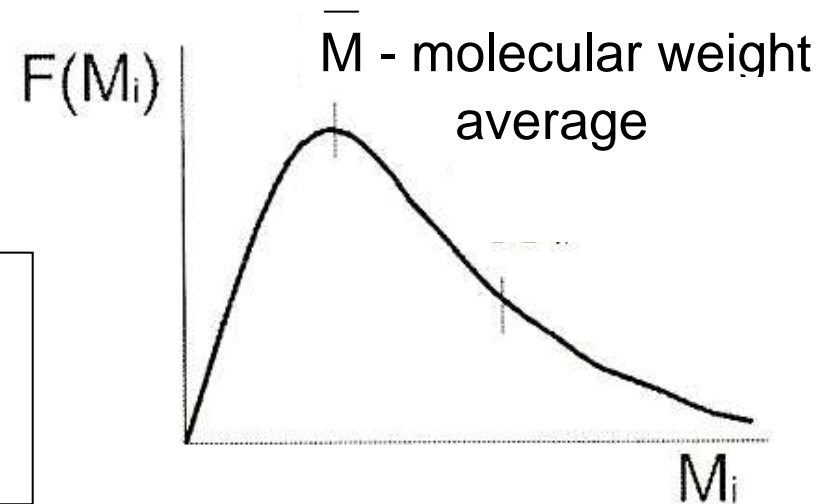
Temperature at which rigidity of a polymer decreases



4. Polymer molecular weight

Simple compounds -
composed of identical
molecules

Molecules of polymer -
strongly differ (vary by many
monomer units)



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

Synthetic polymers

Prepared via polymerization reactions:

- **Chain-growth** (addition) **polymerization**
usually free radical polymerization of monomers with double bonds
- **Step-growth polymerization** (e.g. polycondenzation) of **bifunctional 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
- Monomer molecules add sequentially to the end of a growing chain
- Is very fast and exothermic
- Produces high molecular weight polymers
- Free-monomers are present

Step-growth polymerization

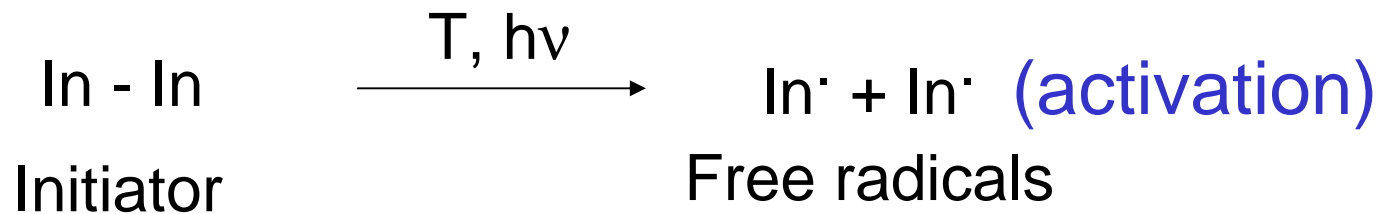
Characteristics

- 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
- Polymers are generally of lower molecular weight
- Dimers, trimers or oligomers are present (instead of free monomers)

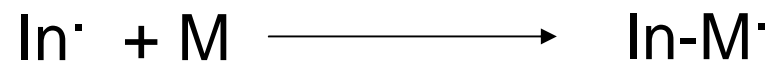
Stages of free radical polymerization

1. Initiation/induction - process starts

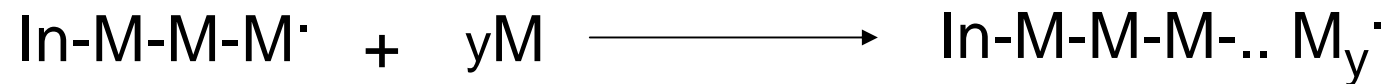
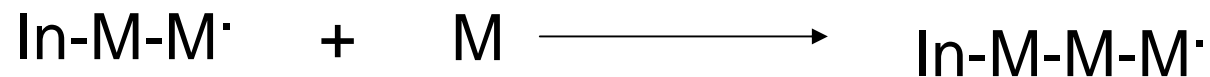
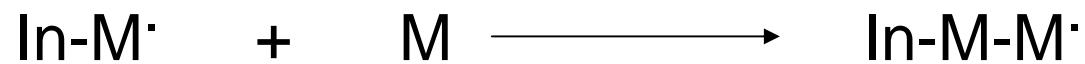
- Primary radical formation



- Addition of primary radical on the double bond of monomer

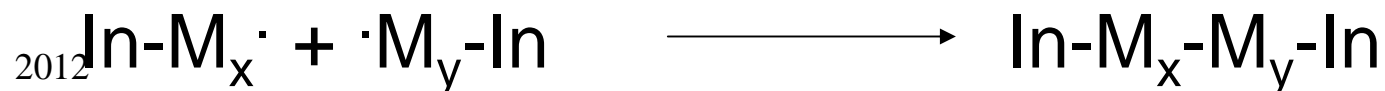


2. Propagation - the addition of monomer to the active center (free radical) to generate a new active center



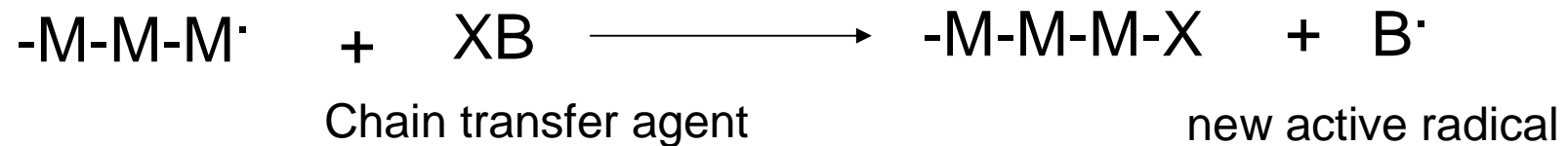
3. Termination - the growing chain is stopped

- Radical coupling/recombination (most common)



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

1. Original chain terminates



2. New chain growth starts



Special cases of chain transfer reactions:

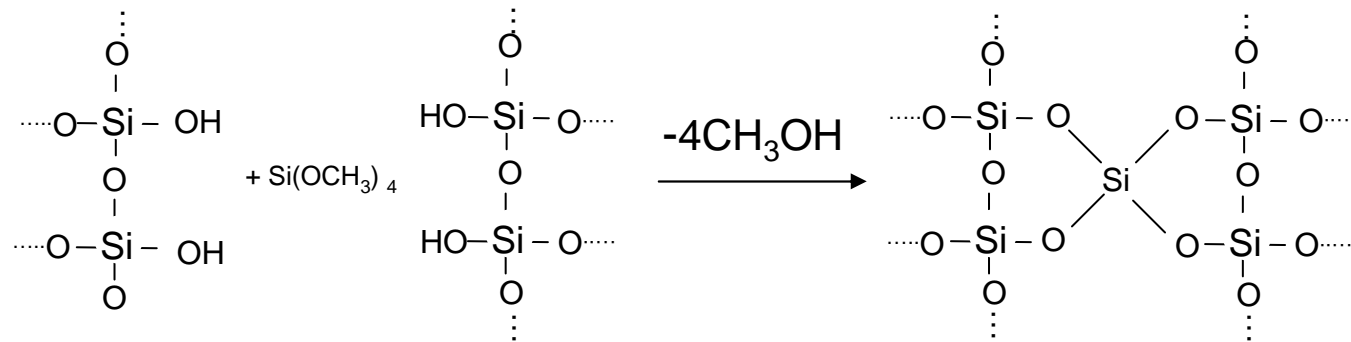
A retarder is a substance that reacts with a growing chain forming less reactive radical $B\cdot$ and thus making polymerization rate „slow“

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

Examples of step-growth polymerization

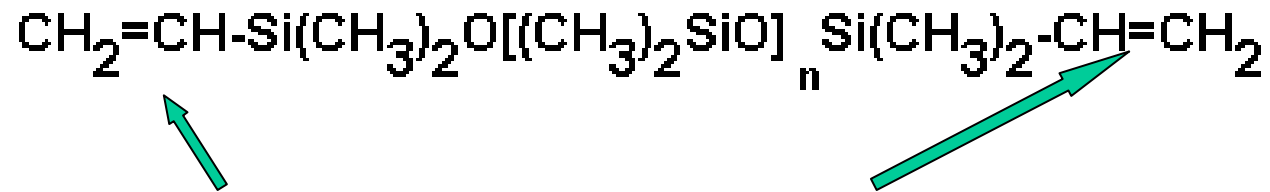
Polycondensation

Setting reaction of C-silicone impression materials



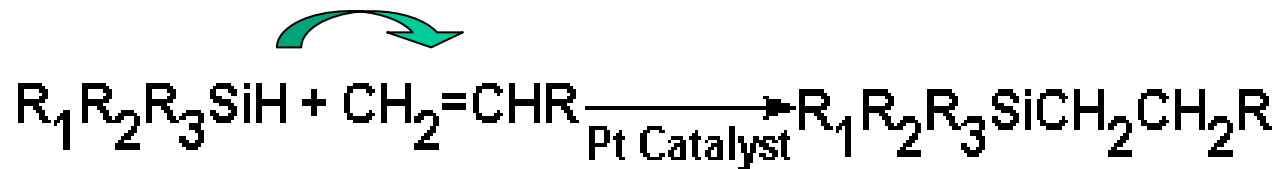
Polyaddition

Setting reaction of A-silicone impression materials



Vinyl terminated siloxane oligomer

Addition of -H on vinyl double bond

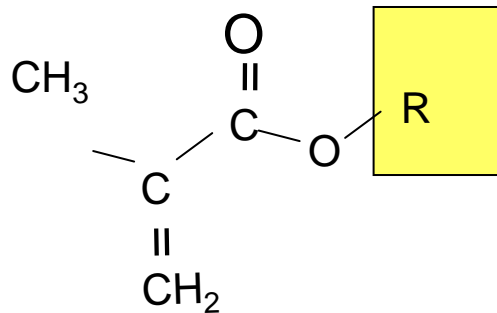


Methylhydro-dimethylsiloxane – a cross-linking agent

Methyl methacrylate (MMA) polymers

Most frequently used group of polymers in prosthetic dentistry

Based on MMA monomer



$\text{R} = \text{H}$ – methacrylic acid

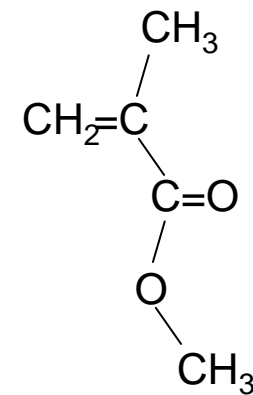
CH_3 - methyl methacrylate (MMA)

$\text{CH}_3\text{-CH}_2\text{-OH}$ - hydroxy ethyl methacrylate (HEMA)

Why? Because these materials can be easily adopted to individual purposes (fillings, prostheses), polymerization is fast and they are well accepted by the human body

Properties of MMA

- Colorless liquid
- Immisible with water but with organic solvents
- Melting point -48°C
- Boiling point 100.3°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
- Low absorption of visible and UV light (to 250 nm)
- Compression strength 90 - 100 MPa
- Very rigid - elastic modulus above 2.4 GPa
- Water sorption up to app. 1.0 wt %
- Temperature resistance $T_g = 120 - 125^\circ\text{C}$
- Soluble in organic solvents (MMA, acetone, toluene etc)

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

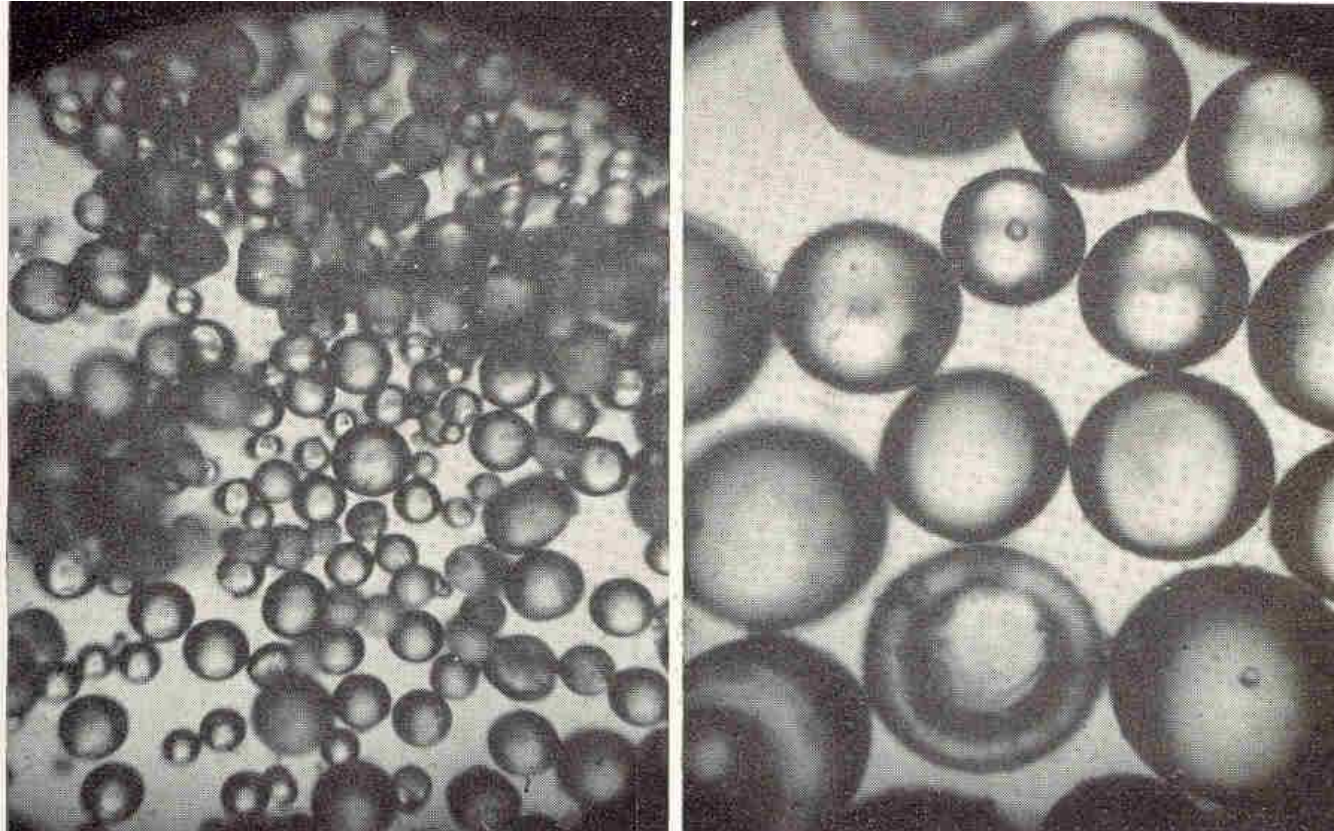
Application of PMMA in dentistry

How to overcome polymerization shrinkage ????

- First applications for dentures via compression moulding of molten PMMA powder (too expensive and complicated)
- 1936 - Kulzer: powder/liquid system
 - Powder - PMMA prepolymer with residuals of DBP
 - Liquid - MMA monomer and additives
 - When mixed together a workable - plastic mass (dough) is formed and polymerized in individually fabricated mould
 - Decreased polymerisation shrinkage (app. 6 vol %) at powder/liquid ratio 3-2,6/1

PMMA prepolymer beads

Prepared by suspension polymerization

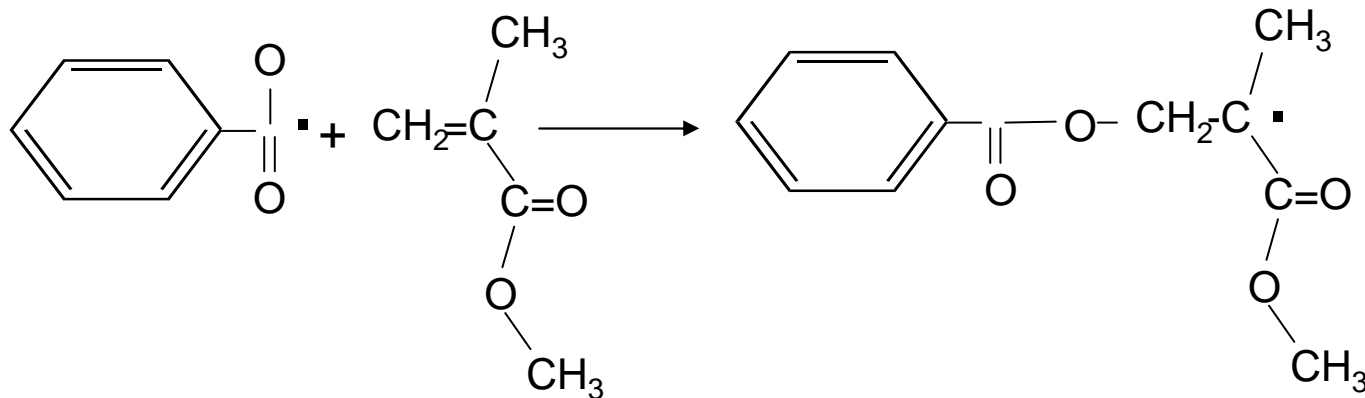
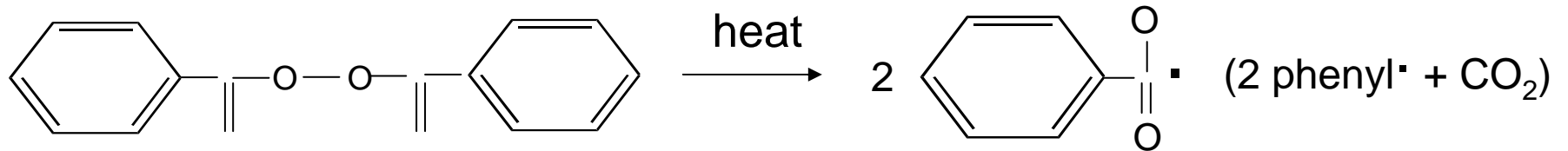


Average particle size 0.005-0.100 mm

Polymerization scheme of MMA monomers

- Initiation

- Thermal decomposition of dibenzoyl peroxide (DBP)



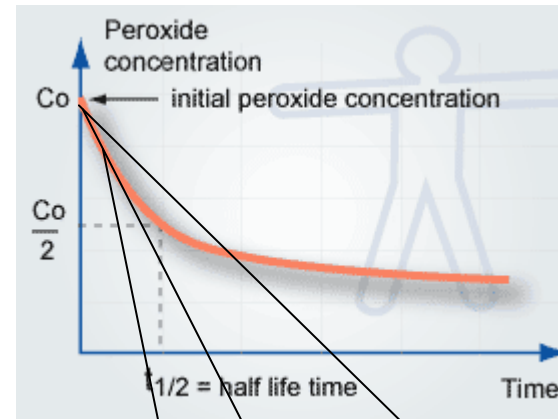
Thermal decomposition of peroxides

C = concentration of peroxide

k = kinetic constant

t = time

$$C = C_0 \cdot e^{-kt}$$



Effect of temperature

The temperature dependence of kinetic constant is given by an Arrhenius law:

$$k(T) = A \cdot e^{-E_a/RT}$$

with : $k(T)$ = kinetic constant at temperature T (K)

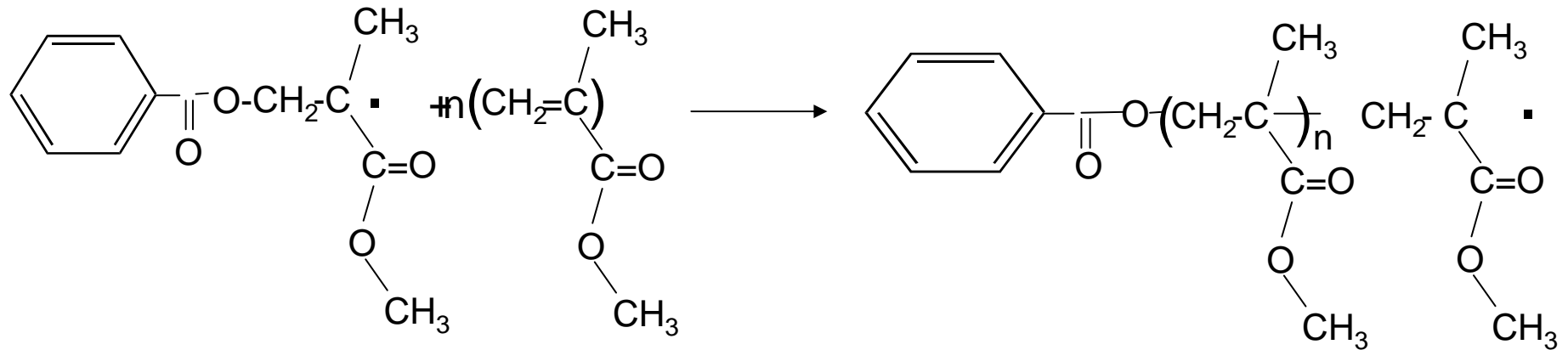
E_a = Activation energy

R = Gas constant

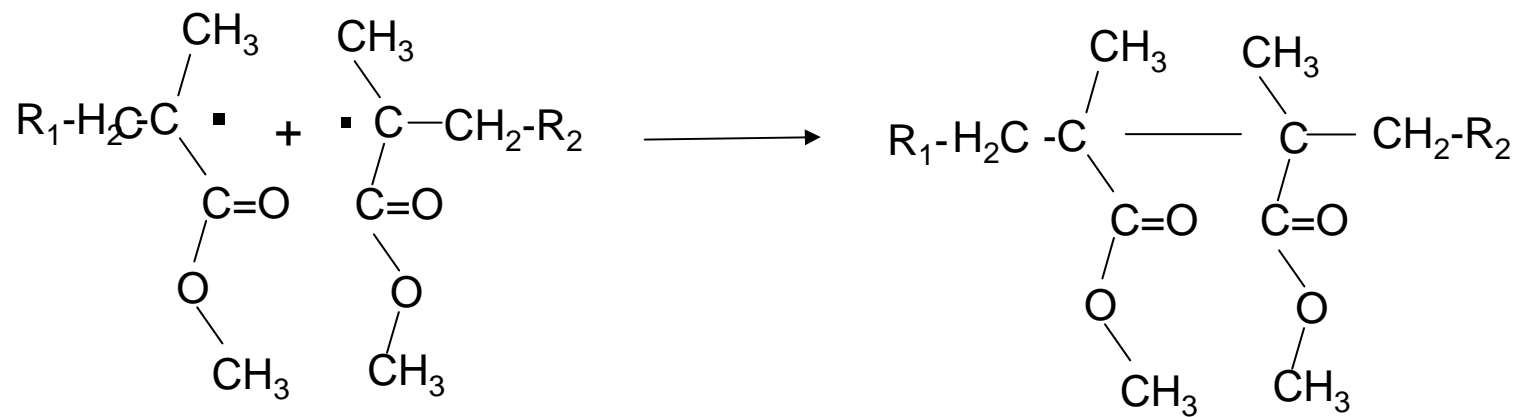
T = Temperature in K

The higher temperature - the higher concentration of radicals and higher polymerization rate

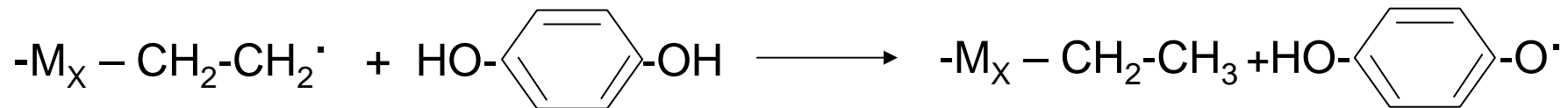
• Propagation



• Chain termination

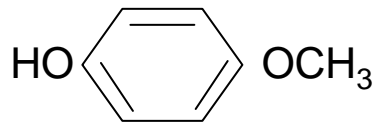


• Chain transfer to Phenolic inhibitors

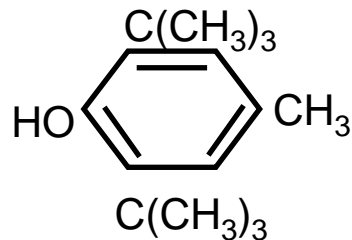


hydroquinone (HQ)

Stable hydroquinone radicals will not propagate - stop polymerization reaction



methoxy phenol (hydroquinone mono methyl ether) MEHQ

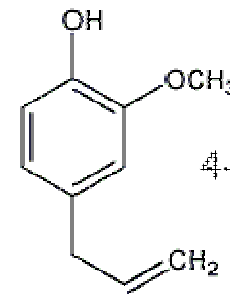


2,6-di-tert-butyl-4-methylphenol
(butylated hydroxytoluene - BHT)

Sterically hindered phenols – less efficient but reduced color change after polymerization - **Synergetic mixtures**
HQ + MEHQ

Note

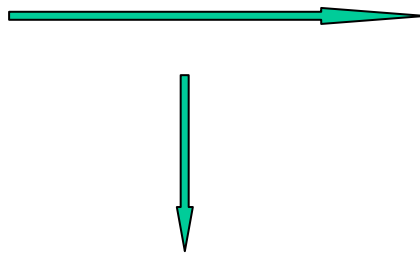
1. **Eugenol** = phenol
(inhibits polymerisation)



4-Allyl-2-methoxyphenol

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

2. Oxygen inhibition



Stable hydroperoxid

Oxygen-inhibited layer on the
composite/adhesive surfaces

Why polymer inhibitors are added?

Usually 0.01 – 0.005 wt %

1. To extend monomer shelf-life by restricting spontaneous polymerization
2. To decrease sensitivity of monomers to ambient light
3. To prolonge the working time

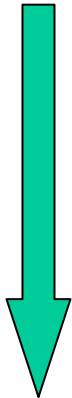
PMMA is often modified for dental application by:

- **Cross-linking** (effect of a molecular weight increase)
 - improves hardness and stiffness
 - improves wear and solvent resistance but increase brittleness
 - increases thermal resistance (polymers are easily finished - grinded and polished without melting)
 - increases crazing resistance (small cracks originating at the teeth-denture margin)

- **Copolymerization** (with acrylic and methacrylic monomers, *PVC*, *PVAc*, *butadiene*) disturbs regular intermolecular order of a homopolymer
 - decreases softening temperature
 - improves fatigue and impact resistance
 - increase dissolution rate in MMA
- **Blending** of various MMA polymers
 - increase rate of dissolution in MMA
 - decreases softening temperature

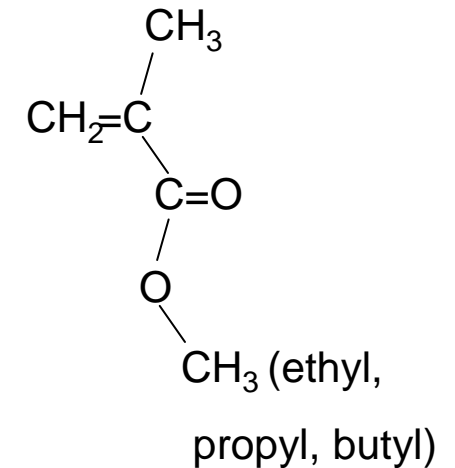
Glass transition temperature (softening) of various methacrylic polymers

rigid



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

Soft, faster
dissolution



- **Plasticizing -**

- to reduce stiffness, hardness and softening temperature
- to prepare flexible polymers (acrylic relining materials - combinations of MMA homo or copolymers with plasticizers)

Plasticizers

high-boiling compounds swell polymers (phthalates - dibutyl/dioctyl phtalates) - leachable potentially harmful

Classification of methacrylate polymers according to initiation reactions (activation)

- Heat activated (heat cured/heat curing) resins (prosthetic polymers)
- Chemically activated (self cured/curing, cold curing, autopolymerizing, fast curing) resins (prosthetic polymers, restorative composites, resin cements, and adhesives)
- Light activated (LC/UV cured) resins (restorative composites, resin cements and adhesives)

Heat activated resins

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

Composition:

powder: PMMA prepolymer with dibenzoyl peroxide (up to 0.5 - 0.6 wt %)

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

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

Chemically activated resins

(denture reparations, relining materials,
orthodontic appliances, pouring resins)

Composition:

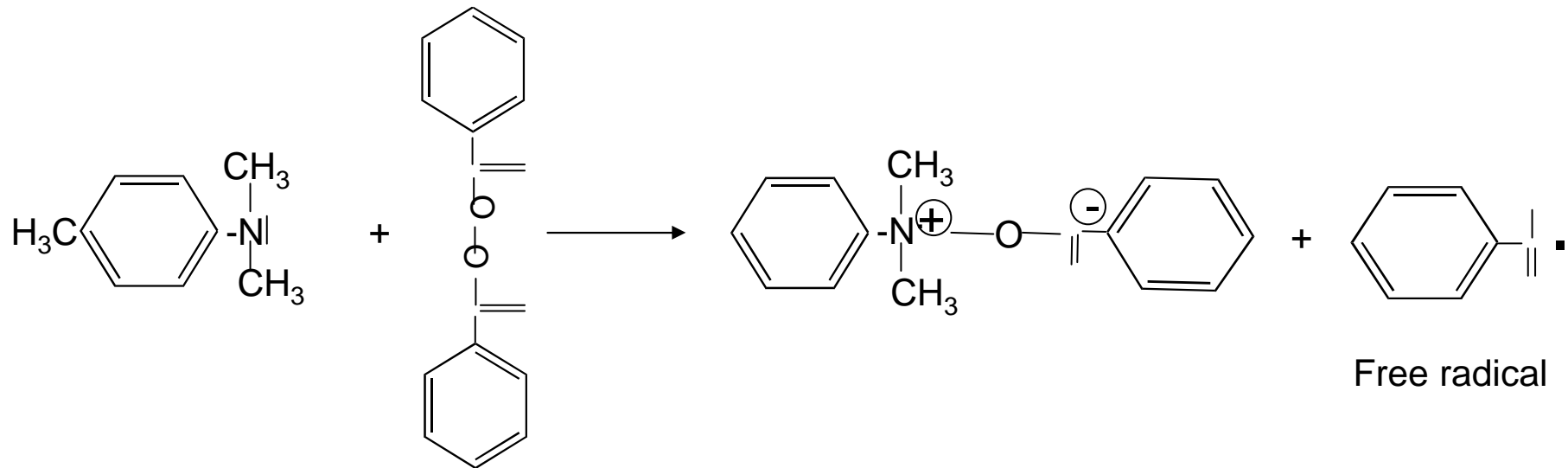
powder: PMMA prepolymer or copolymer (fine particle size), dibenzoyl peroxide

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

Acclerators

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

Scheme of DBP decomposition accelerated by terc. amine



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

Compared to heat activated resins:

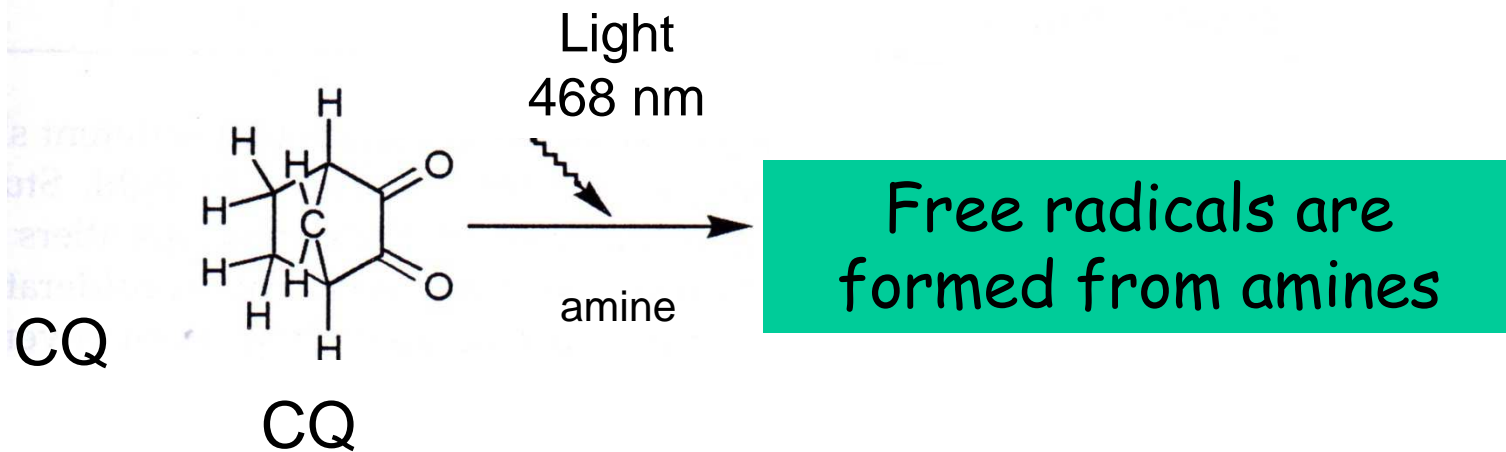
- Lower molecular weight
- Higher amount of free monomer 3-5 wt %, heat activated app. up to 1 %
- Less color stability due to oxidation of aromatic amine accelerators

Light activated resins

(light cured denture base materials, composite materials, adhesives, light cured glass-ionomer cements)

Composition (usually one component):

1. Dimethacrylate resin, light initiating system camphorquinone (CQ) - amine, inhibitors

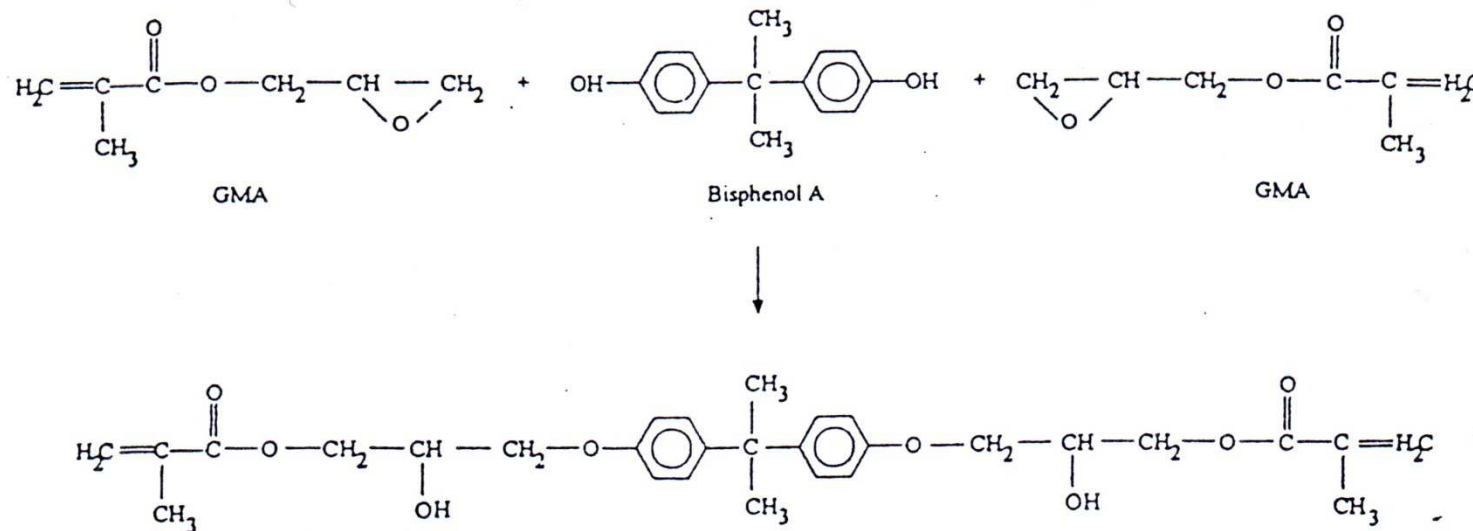


2. Filler particles

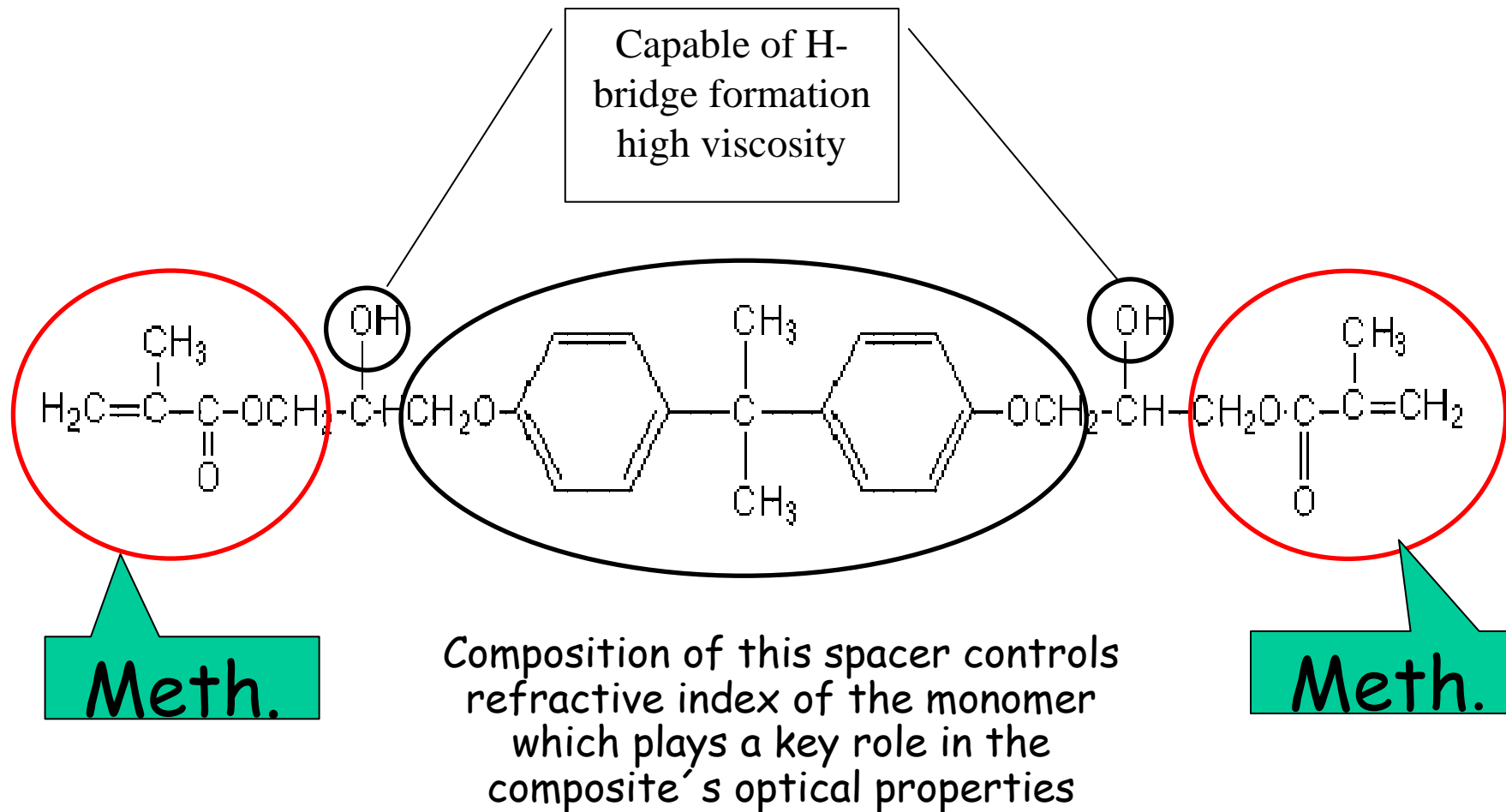
Typical dimethacrylate monomers (resins)

Main applications: composite resins, adhesives, cross-linkers

1. BIS-GMA 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (Bowen monomer, 1955)

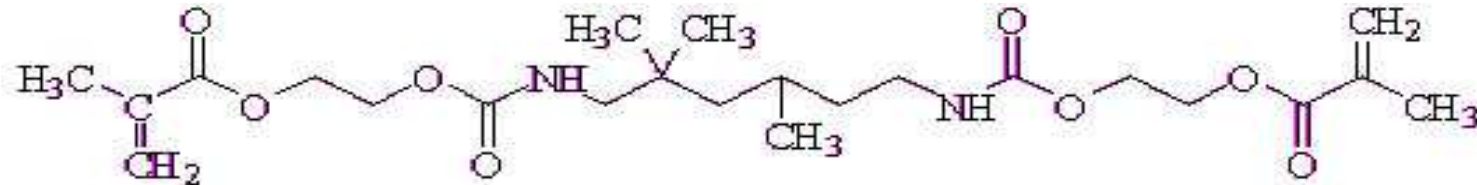


higher molecular weight - less polymerization shrinkage, high boiling point, no odor



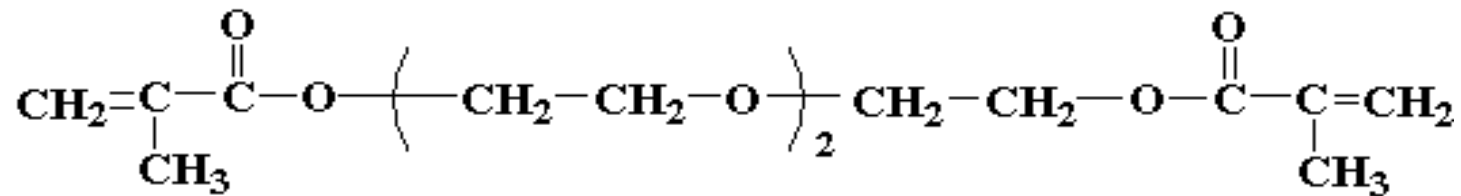
Increased molecular mass - less polymerization shrinkage app. 5-6 vol %

2. Urethane dimethacrylate (UDMA) (2,2,4-trimethylhexamethylene-bis-(2-carbamoyl-oxyethyl)dimethacrylate)



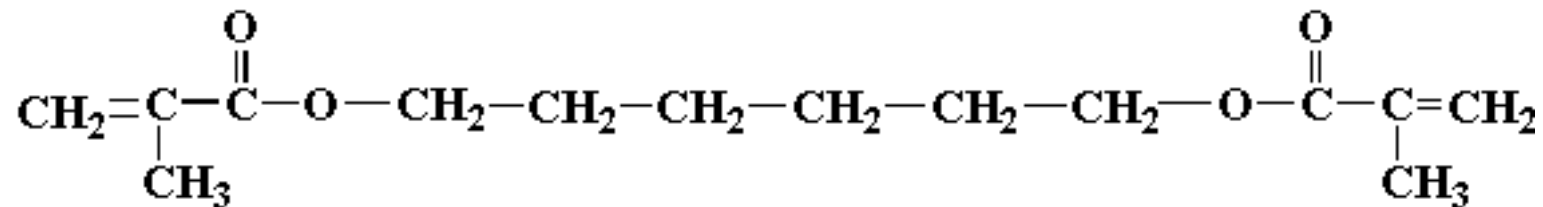
Also of high viscosity

3. Triethylene glycoldimethacrylate TEGDMA (low viscosity diluent)

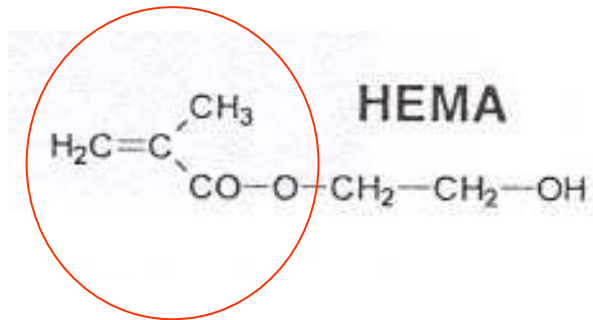


n=1 ethylene glycoldimethacrylate (EGDMA)

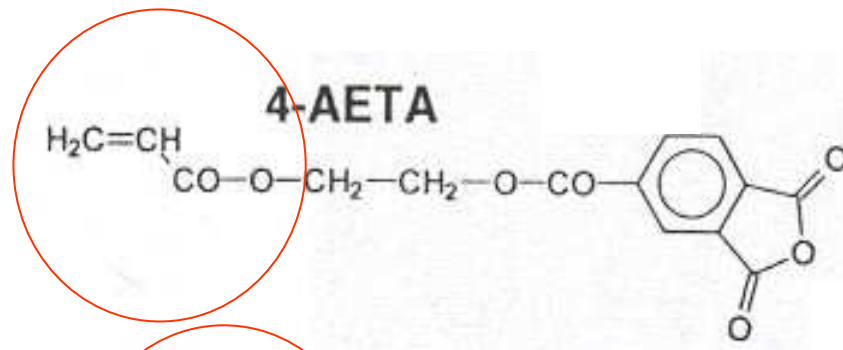
4. 1,6 hexane dioldimethacrylate



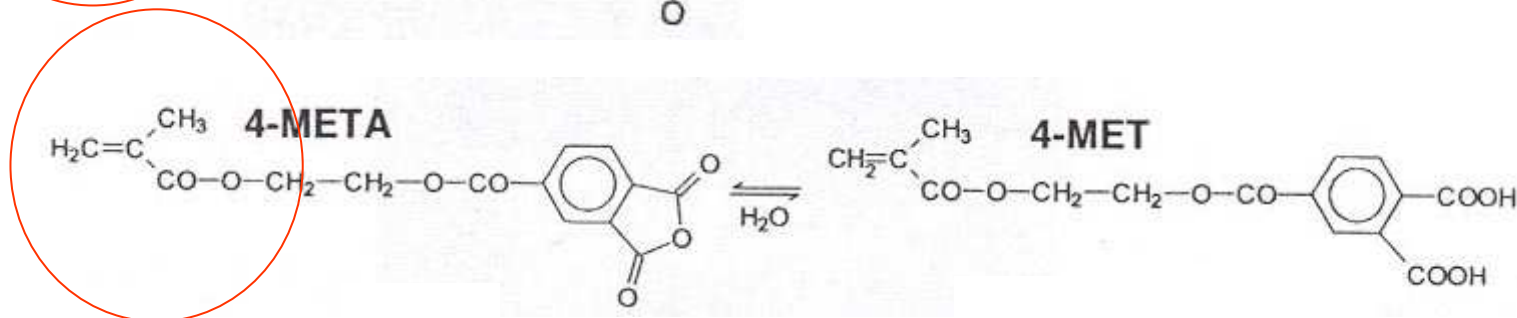
Examples of monomers used in dental adhesives



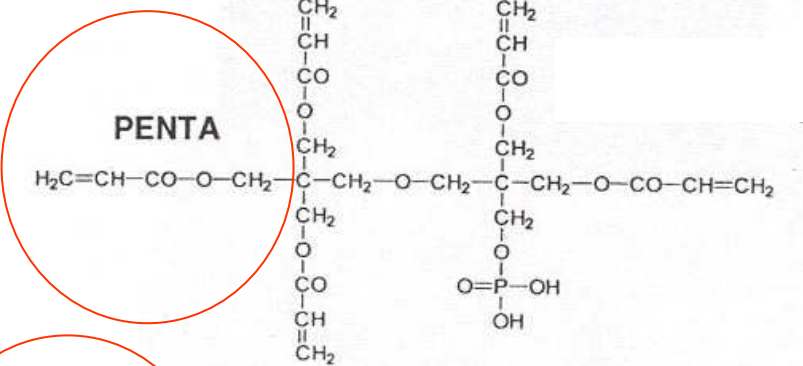
2-hydroxyethyl methacrylate



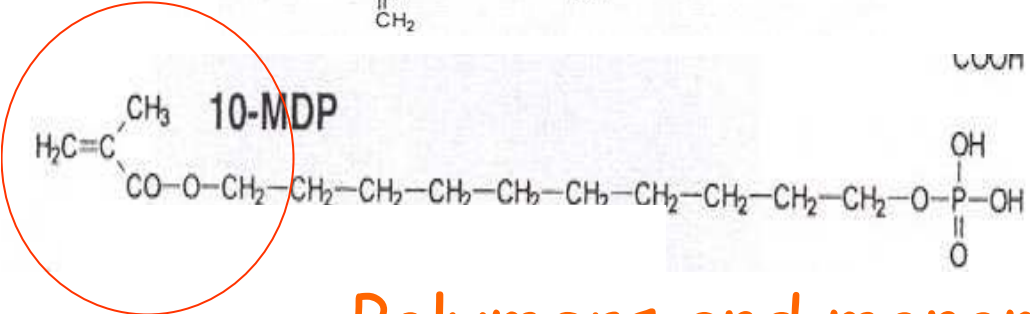
4-acryloxyethyl trimellitic acid anhydride



4-methacryloxyethyl trimellitic acid anhydride/acid

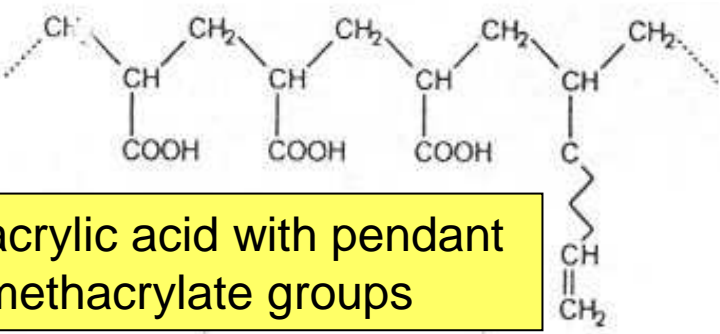


Dipentaerythritol penta acrylate monophosphate

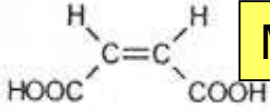


10-methacryloyloxydecyl dihydrogenphosphate

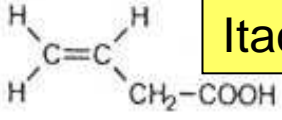
Polymers and monomers for GIC



Polyacrylic acid with pendant methacrylate groups



Maleic acid

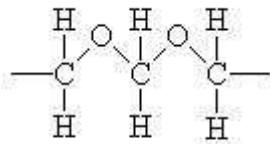


Itaconic acid

Other polymers

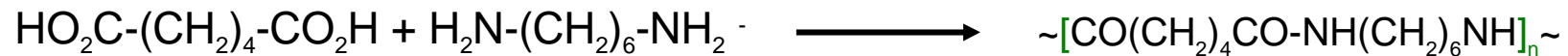
Alternatives to acrylic denture base polymers

Thermoplastic semicrystalline polymers/injection molding at high temperatures



Polyoxymethylene

Polyacetal, POM



adipic acid

hexamethylene diamine

polyamide
Nylon 66

Summary

1. Polymers, characterization, properties (molecular structure)
2. Chain-growth polymerization (free radical); step-growth (polycondensation 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

Actual editions of these text books