

Polymerization

Synthetic polymers used in dentistry

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Dental materials

- Inorganic - gypsum products, investment materials, cements, ceramics
- Metals - denture frameworks, supraconstructions, implants, amalgams, orthodontic brackets, wires

Organic (polymer-based) materials

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Typical applications of polymers in dentistry

- Dentures (bases, artificial teeth, relining materials)
- Filling materials (composites, cements, adhesives)
- Impression materials
- Obturation materials (endodontology)
- Equipment (spatulas, measures, etc)

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What is the lecture about?

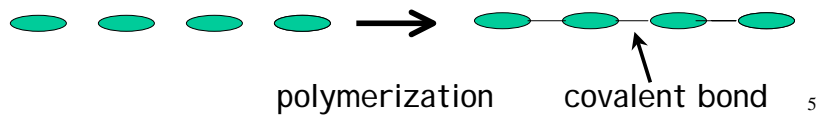
- Terms and definitions
- Structure of polymer chains
- Polymers in dentistry
- Polymerization
- Methyl methacrylate polymers
- Typical dimethacrylate resins

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Definition

Polymer – a chemical compound consisting of giant molecules „MACROMOLECULES“ formed by union of many „POLY“ small repeating units „mers“

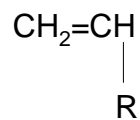
MONO“MER“ molecules POLY“MER“ chain, macromolecule



What controls polymer properties?

1. Chemical composition of polymers

type of monomer, its structure



Vinyl polymers

Examples:

R = H : polyethylene hydrophobic, semicrystalline polymers

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

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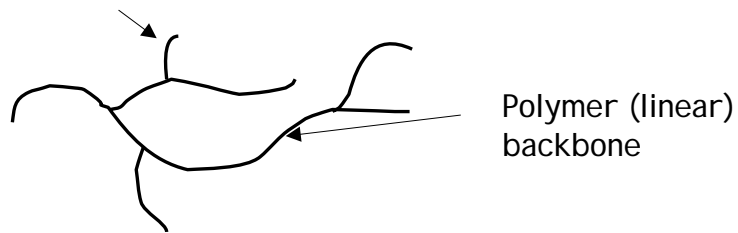
2. Topology of polymer chains

- Linear polymers

A-A-A-A-A-A-A-

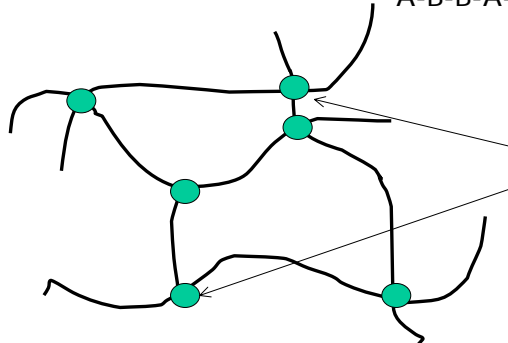
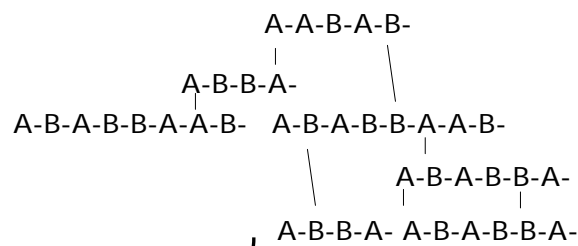
- Nonlinear (branched) polymers

Branches



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- Cross-linked polymer (polymer networks)



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

Temporary cross-links entanglements

3. Monomer distribution in copolymer chains

- Homopolymers (one type of monomer - A)

A-A-A-A-A-A-A- *linear/branched*

- Copolymers (2-3 comonomers)

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

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

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

-A-A-A-A-A- *graft/branched*

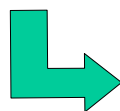
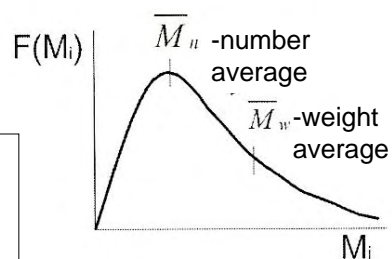
-B-B-B-B-B-
|

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4. Polymer molecular weight

Simple compounds -
composed of identical
molecules

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



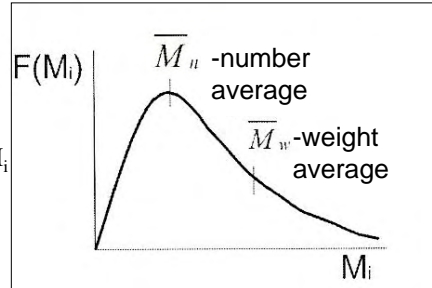
**Polymers are characterized by
molecular weight/polymerization
degree average**

Definitions of molecular weight averages

Number average, \bar{M}_n

$$\bar{M}_n = \frac{\sum M_i n_i}{\sum n_i} = \sum M_i x_i$$

x_i states for molefraction of molecules with M_i



Weight average, \bar{M}_w

$$\bar{M}_w = \frac{\sum M_i (n_i M_i)}{\sum n_i M_i} = \sum M_i \left(\frac{m_i}{m_{\text{total}}} \right) = \sum M_i w_i$$

w_i states for weight fraction of molecules with M_i

Polymerization degree

$$\bar{P}_w = \bar{M}_w / M_0$$

M_0 states for molecular weight of repeating unit

$$\text{Polydispersity } \bar{M}_w / \bar{M}_n$$

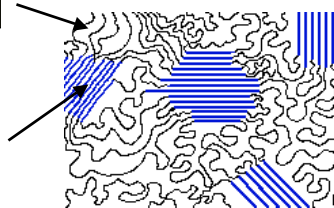
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5. Supramolecular structure (molecular organization)

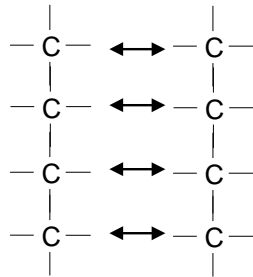
- Amorphous polymers - coiled irregular (random) shape of polymer chains
- Semicrystalline polymers - domains with regular (crystalline) structures acting as special type of cross-links

Amorphous domains

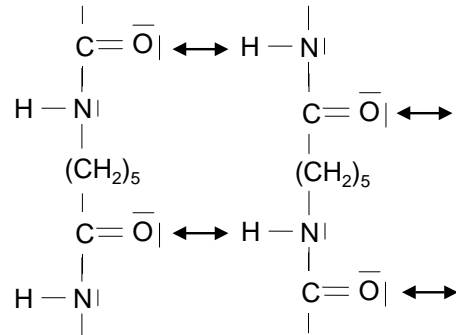
Crystallites



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Van-der-Waals interactions



H-bridges

Typical for polyamides, polyethylene, polypropylene etc.

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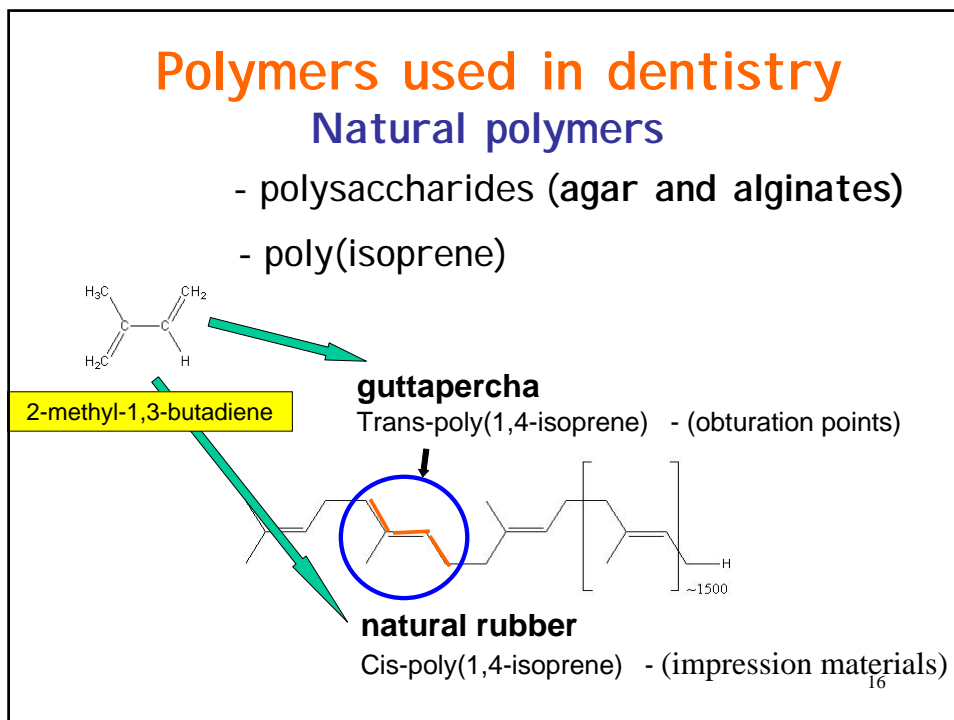
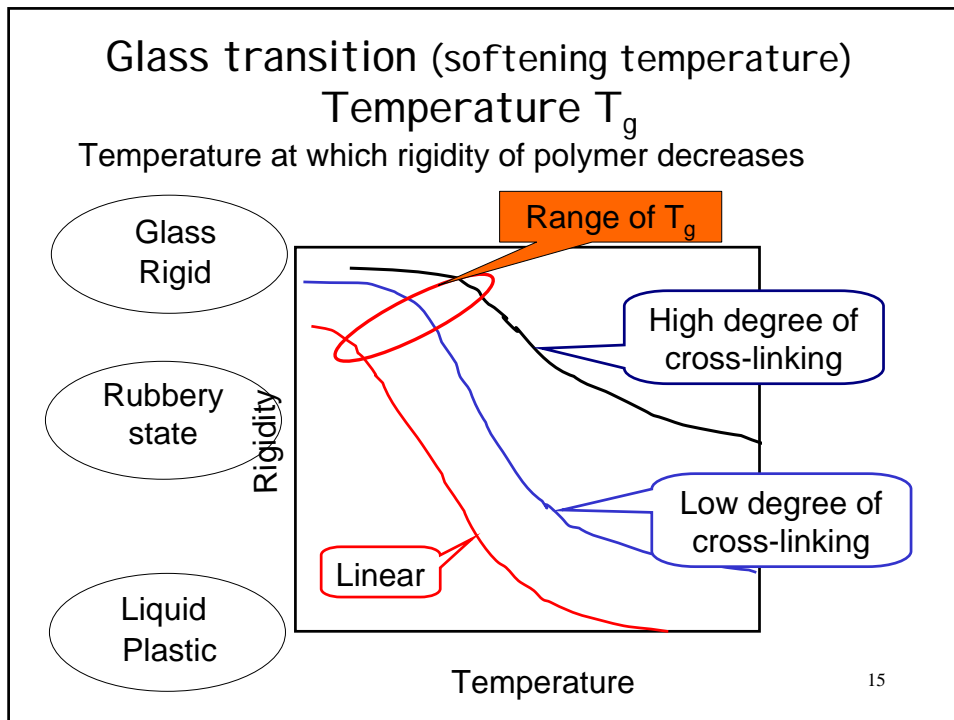
Influence of cross-links on physical properties of polymers

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

(usually soluble in organic solvents)

Cross-linked polymers - they cannot be reshaped on heating, do not melt, but decompose on heating, insoluble in organic liquids (**thermosetting polymers**).

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Polymers used in dentistry

Synthetic polymers

Prepared via polymerization reactions:

- **Addition** (chain-growth) polymerization of monomers with a double bond
- **Step-growth polymerization** of bifunctional monomers, frequently with release of low molecular compounds (analogous reaction to low molecular weight compounds)

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Addition polymerization

Characteristics

- Starts from an active center (only these molecules are capable to react)
- π -bond of monomer is converted to σ -bond in the polymer
- Monomers add sequentially to the end of a growing chain
- Is very fast and exothermic
- Produces high molecular weight polymers

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Types of addition polymerizations:

- **Free-radical polymerization** - active center is a radical (contains unpaired electron) and the propagating site of reactivity is a carbon radical.
- **Cationic polymerization** - the active center is an acid, and the propagating site of reactivity is positively charged
- **Anionic polymerization** - the active center is a nucleophile, and the propagating site of reactivity is negatively charged

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Few common polymers prepared via addition polymerization

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

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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
- Combines two different reactants in an alternating structure

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- Polymers are formed more slowly than by addition polymerization
- Polymers are generally of lower molecular weight

Types of step-growth polymerization

- Polycondensation
- Polyaddition

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Few common polymers

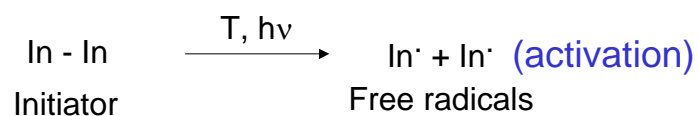
Formula	Type	Components	T _m °C
	polyester Mylar	Phthalic acids	Instruments, matrices
	polycarbonate	(Bisphenol A) phosgene	Artificial teeth, Veneering shells, Prefabricated crowns, orthodontic brackets
$-\text{CO}(\text{CH}_2)_4\text{CO}-\text{NH}(\text{CH}_2)_6\text{NH}-$	polyamide Nylon 66	$\text{HO}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H}$ $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	Surgical suture materials
$-\text{CO}(\text{CH}_2)_5\text{NH}-$	polyamide Nylon 6 Perlon		Surgical suture materials
	polyamide Kevlar	para $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ para $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	Fibre reinforced splints
	Toluene diisocyanate	$\text{HOCH}_2\text{CH}_2\text{OH}$ 	Die materials

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A. Stages of free radical polymerization

1. Initiation/induction – process starts

- Primary radical formation



- Addition of primary radical on the double bond of monomer

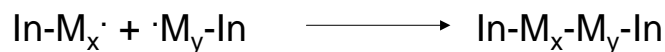


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2. Propagation - the addition of monomer to an active center (free radical) to generate a new active center



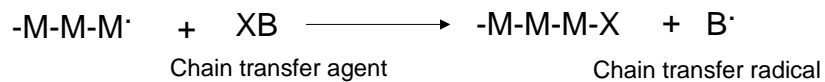
3. Termination - the growing chain is stopped
 - Radical coupling/recombination (most common)



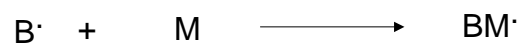
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4. Chain transfer - An atom is transferred to the growing chain, terminating the chain growth and starting a new chain.

1. Chain termination




2. New chain growth starts



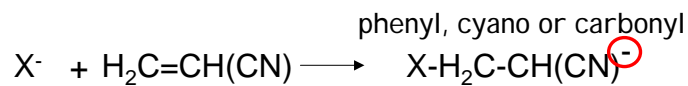
XB	Consequences
Monomer	Mol. weight decrease
Polymer	Branching
Chain transfer agent	Mol. weight regulation
Retarder/Inhibitor	Polymerization is stopped

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

An inhibitor is a „retarder“ that reacts **rapidly** with active radicals to form **stable** compounds (BX^{\cdot}) unable of addition to monomer  completely stops or “inhibits” polymerization.

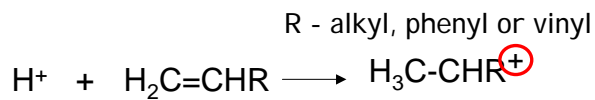
B. Anionic polymerization



Initiated with e.g. n-butyllithium, alkaline metals
Used in superglues for methyl 2-cyanoacrylate polymerization

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C. Cationic polymerization

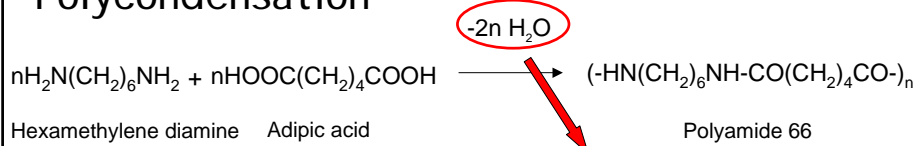


H^+ - strong acids

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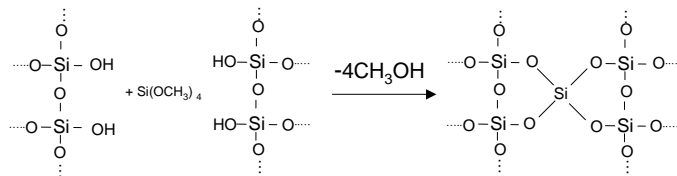
Step-growth polymerization

Polycondensation



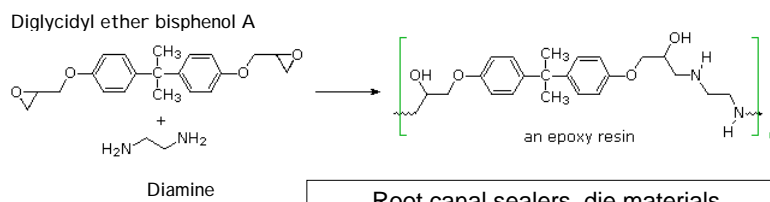
Water release from the reaction mixture:
1. controls mol. weight, 2. contributes to contraction of the system

1. Setting reaction of C-silicone impression materials



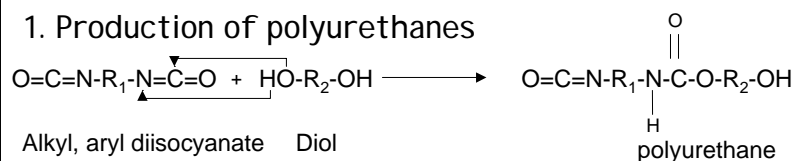
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2. Setting reaction of epoxies



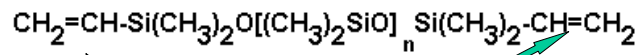
Polyaddition

1. Production of polyurethanes



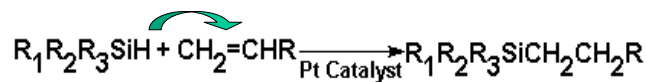
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2. Setting reaction of A-silicone impression materials



Vinyl terminated polysiloxane prepolymer

Addition of -H on vinyl double bond



Methylhydro-dimethylsiloxane – a cross-linking agent

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Methyl methacrylate (MMA) polymers

Most frequently used group of polymers in dentistry

Why? Because these materials can be easily adopted to individual purposes (fillings, prostheses) and can be in contact with human body

- Suitable manipulation/processing properties (easy to mix, shapable, simple to process and cure)
- Good mechanical properties (rigidity, strength, wear resistance)
- Biocompatible (tasteless, odourless, non-toxic or non-irritating, resistance to microbial colonization)

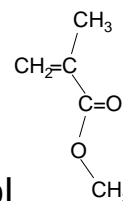
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- Aesthetic properties translucency and transparency (colour and optical properties of tooth tissues)
- Chemical resistance in oral environment, to disinfectants etc.
- Acceptable cost of both material and processing method

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Properties of MMA

- Melting point -48°C
- Boiling point 100.3°C
- Density 0.945 g/mL
- Heat of polymerization 54.3 kJ/mol
(!! exothermic reaction !!)
- Colourless liquid
- Immiscible with water but miscible with organic solvents
- Irritant
- **!! Flammable !!**



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Properties of poly(methyl methacrylate)

- Transparency and high clarity
- Low absorption of visible and UV light (to 250 nm)
- Density 1.19 g/cm³ (causes polymerization contraction/shrinkage app. 22 vol %)
- 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.)

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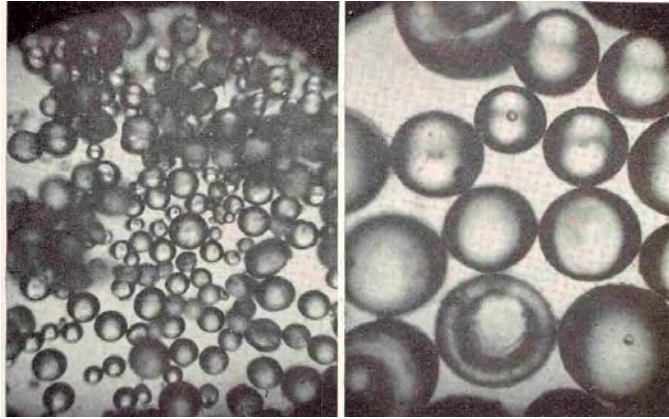
Methyl methacrylate polymers in dentistry

- First applications for dentures (thermoplastic compression molding) 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 workable plastic mass (dough) is formed and polymerized in plaster individually fabricated mold
 - Decreased polymerisation shrinkage (app. 6 vol %)

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PMMA prepolymer beads

Prepared by suspension polymerization



Average particle size 0.005-0.100 mm

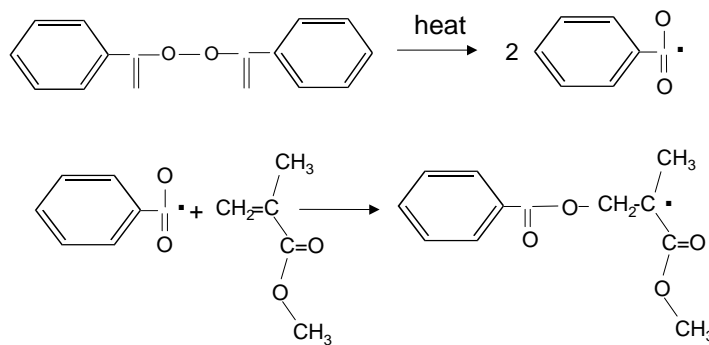
Acrylics and Other Synthetic Resins Used in Dentistry

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Polymerization scheme of MMA monomers

• Initiation

- Decomposition of dibenzoyl peroxide (DBP) during heating

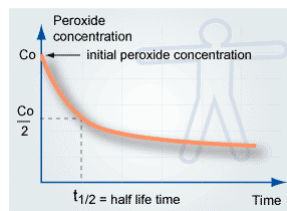


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Thermal decomposition of peroxides

C = concentration of peroxide
k = kinetic constant
t = time

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



T=const.

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)

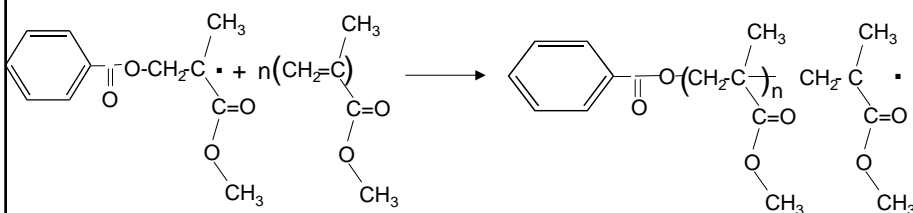
E_a = Activation energy

R = Gas constant

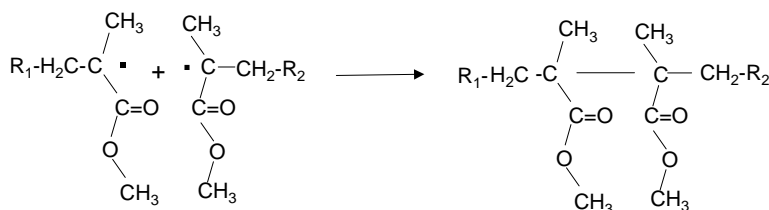
T = Temperature in K

The higher T - the higher k and higher conc. of radicals

•Propagation

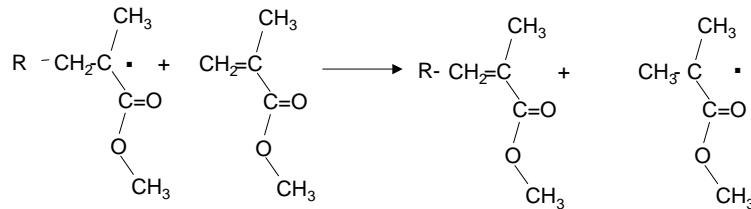


•Chain termination

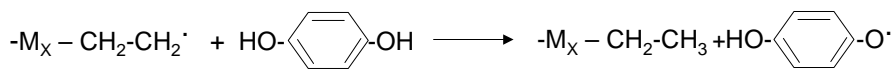


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•Chain transfer to MMA monomer

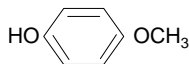


•Chain transfer to phenolic inhibitors



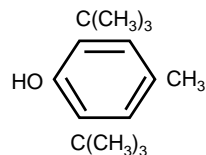
Hydroquinone (HQ)

Stable hydroquinone radical will not propagate/stop other chain radical



Methoxy phenol (hydroquinone monomethyl ether) MEHQ

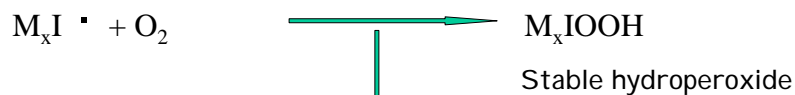
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2,6-di-tert-butyl-4-methylphenol
(Butylated hydroxytoluene - BHT)

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

Oxygen inhibition



Oxygen-inhibited layer on the composite/adhesive surfaces

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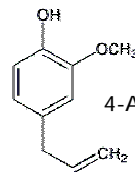
Why polymer inhibitors are added?

Usually 0.01 – 0.005 wt %

1. To extend monomer shelf life by restricting spontaneous polymerization
2. Decrease sensitivity to ambient light
3. To prolong working time

Note:

Eugenol = phenol
(inhibits polymerisation)



4-Allyl-2-methoxyphenol

Negative interaction with Zinc oxide-eugenol materials

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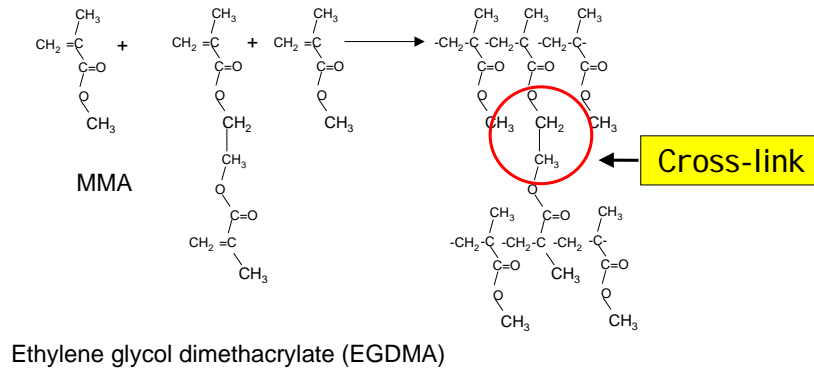
Modifications of PMMA for dental applications

Cross-linking

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

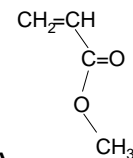
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Example: MMA cross-linked with ethylene glycol dimethacrylate (EGDMA)



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- **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



Methyl acrylate

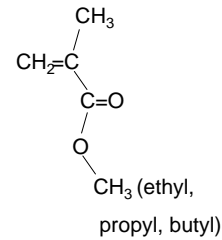
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Glass transition temperature (softening) of various methacrylic polymers

rigid



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



Soft, faster
dissolution

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plasticizing – high-boiling compounds swelling the polymer (phthalates – dibutyl/dioctyl phthalates)

- to reduce stiffness, hardness and softening point

- to prepare flexible polymers (acrylic relining materials – combinations of MMA copolymers with plasticizers)

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Classification of polymers/resins according to initiation reactions (activation)

- Heat activated (heat cured/heat curing resins) (two component systems)
- Chemically activated (self cured/curing, cold curing, autopolymerizing, fast curing) resins (two component systems)
- Light activated (LC/UV cured) resins (one component system)

Note

Dual-cure (a combination of chemically and light activated materials, LC modified GIC, luting materials)

Tri-cure (a combination of acid-base setting reaction, LC and chemical activation [peroxide/amine] activating system)

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

Composition:

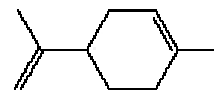
powder: PMMA prepolymer with dibenzoyl peroxide (up to 0.5 - 0.6 wt %)

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

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

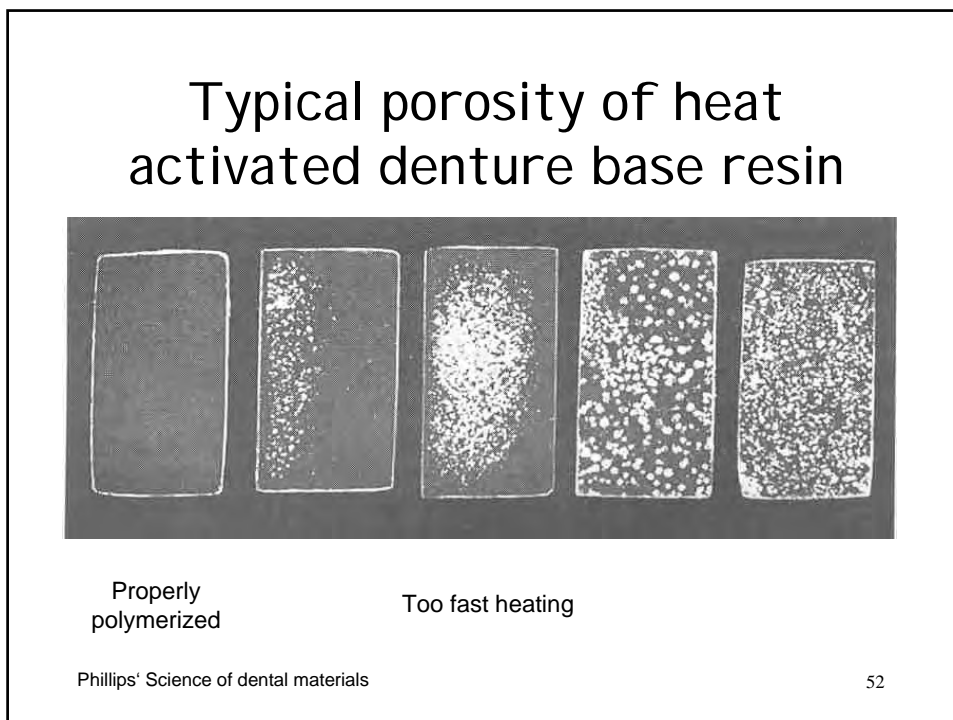
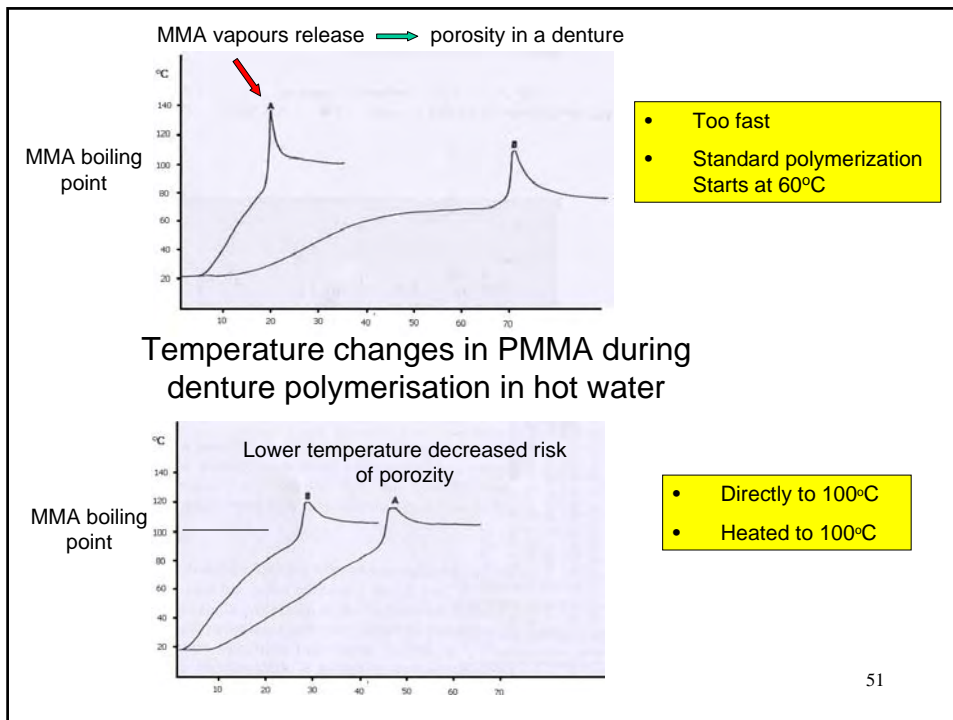
Regulators – decrease the rate of polymerization heat release

Enable fast curing process



1-methyl-4-(1-methylethenyl)cyclohexene)

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Chemically activated resins (denture reparations, relining, orthodontic appliances, pouring resins)

Composition:

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

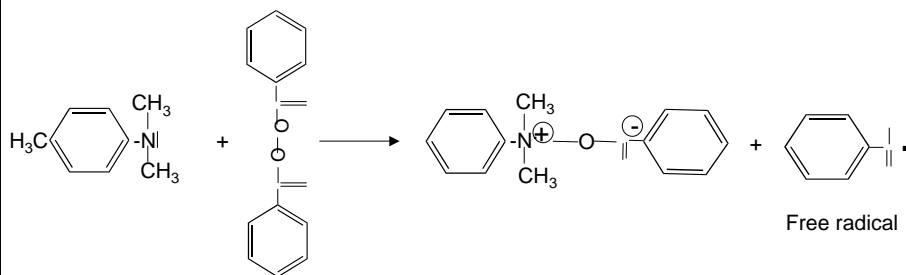
liquid: MMA, cross-linking agents, inhibitors, accelerators (1-4 wt %), UV absorbers

Accelerators

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

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Scheme of DBP decomposition accelerated by tert. 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 colour stability due to oxidation of aromatic amine accelerators

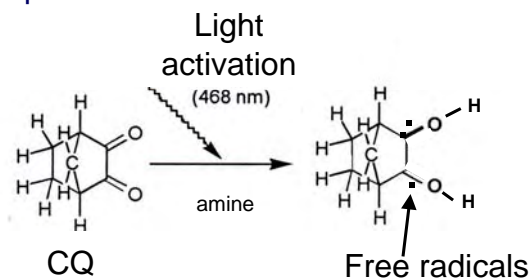
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Light activated resins

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

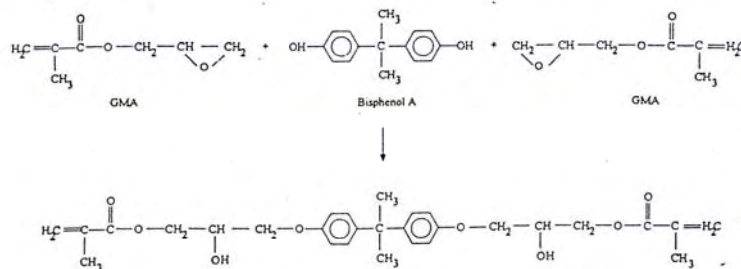
Composition (usually one component):

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

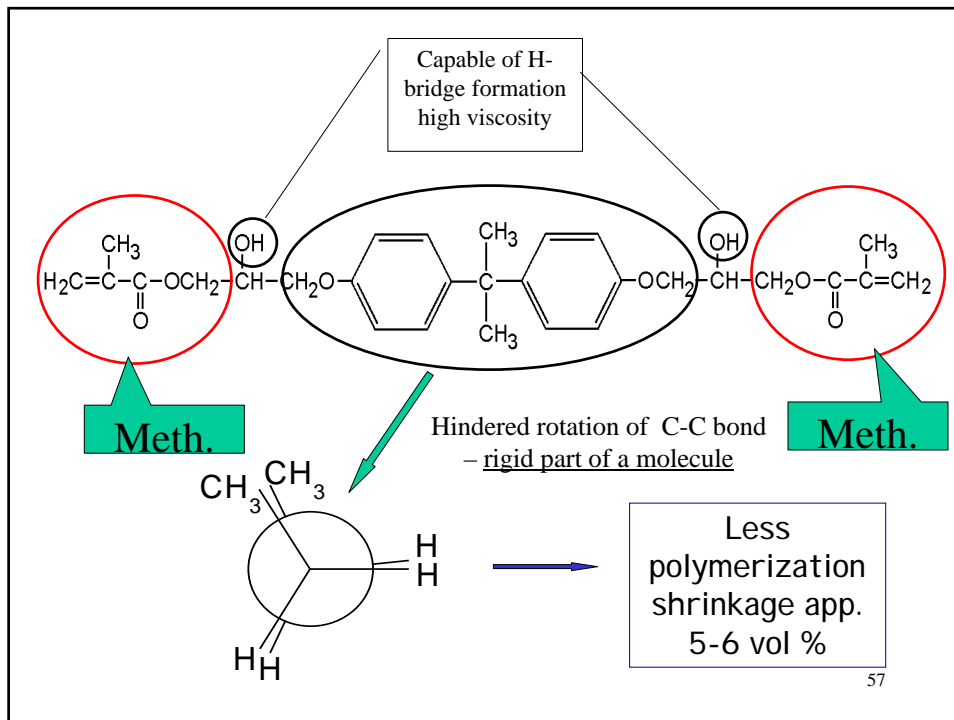


Typical dimethacrylate resins

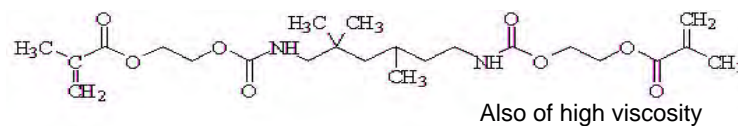
- BIS-GMA 2,2-bis[4-(2hydroxy-3-metakryloyloxypropoxy)phenyl]propane
(Bowen monomer, 1955)



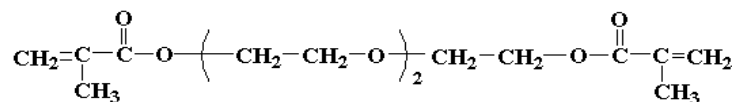
higher molecular weight - less polymerization
shrinkage



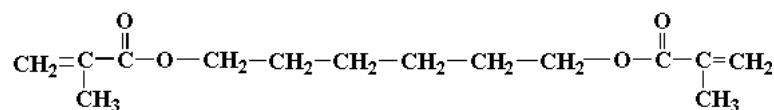
2. Urethane dimethacrylate (UDMA) (2,2,4-trimethylhexamethyle-bis-(2-carbamoyl-oxyethyl)dimethacrylate)



3. Triethylene glycol dimethacrylate TEGDMA (low viscosity diluent)

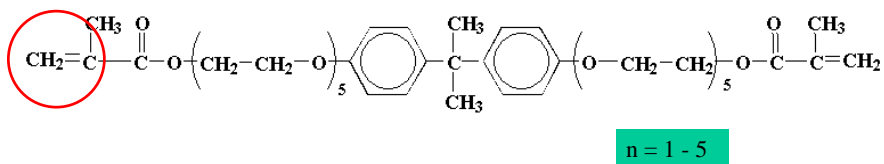


4. 1,6 hexane dioldimethacrylate



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5. Ethoxylated bis-GMA

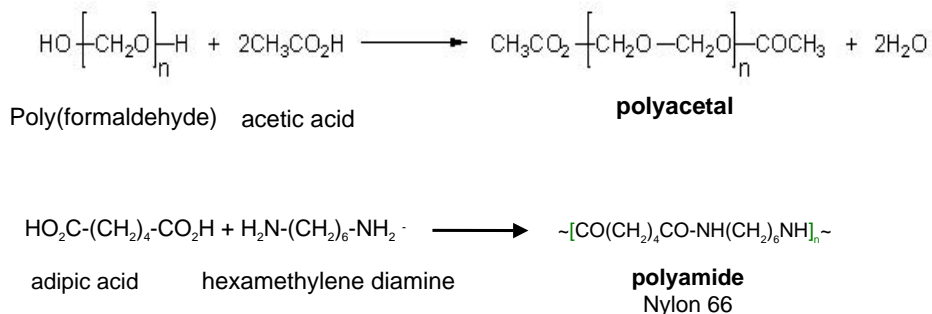


Low viscosity monomer

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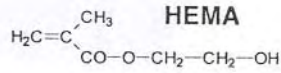
Other polymers - alternatives to acrylic denture base polymers

Thermoplastic semicrystalline polymers/injection molding at high temperatures

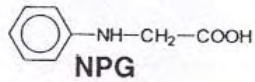


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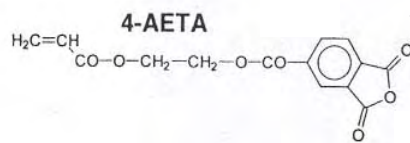
Few monomers used in dental adhesives



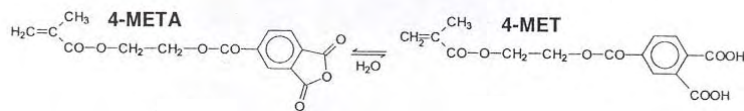
2-hydroxyethyl methacrylate



N-phenylglycine

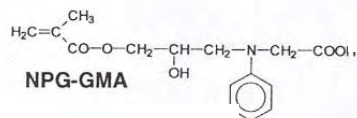


4-acryloxyethyl trimellitic acid anhydride

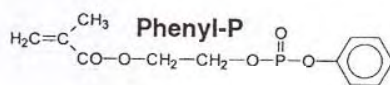


4-methacryloxyethyl trimellitic acid anhydride/acid

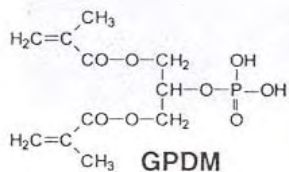
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N-phenylglycine glycidyl dimethacrylate

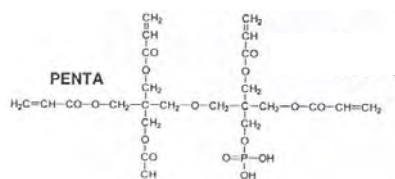


2-methacryloxyethyl phenyl hydrogen phosphate

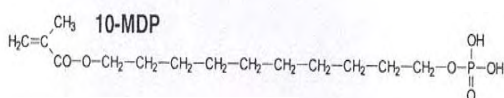


Glycerophosphoric acid dimethacrylate

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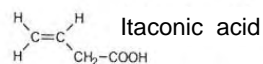
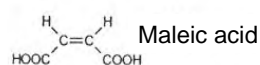
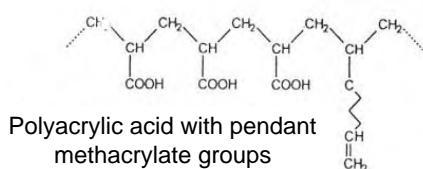


Dipentaerythritol penta acrylate monophosphate



10-methacryloyloxydecyl dihydrogenphosphate

Polymers and monomers for GIC



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Standards on synthetic polymers and resinous materials

- EN ISO 4049: Dentistry - Polymer-filling, restorative and luting materials
ČSN EN ISO 4049: Stomatologie - Výplňové, rekonstrukční a fixační polymerní materiály
- EN ISO 10477: Dentistry - Polymer-based crown and bridge materials
ČSN EN ISO 10477: Stomatologie - Korunkové a můstkové pryskyřičné materiály
- EN ISO 1567: Dentistry - Denture base polymers
ČSN EN ISO 1567: Stomatologie - Bazální protézové pryskyřice
- EN ISO 6874: Dental resin-based pit and fissure sealants
ČSN EN ISO 6874: Dentální pryskyřičné materiály pro pečetění jamek a fisur

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Summary

1. Polymers, characterization, properties (molecular structure)
2. Polymerization – addition (free radical, ionic); step-growth-polycondensation and polyaddition
3. Phases of free radical polymerization
4. Properties of MMA, polymerization of PMMA
5. Types of activation reactions, inhibitors
6. Characteristics of heat, chemical and light activation systems
7. Dimethacrylate resins used in composite materials
8. Other monomers and polymers

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