In dentistry we are concerned with controlling chemical reactions of materials during setting. Therefore, it is important to study the kinetics and mechanisms of polymerization.

POLYMERIZATION KINETICS
Reaction rates – temperature and concentration dependence

1. **Temperature Dependence:** The rate of reaction exponentially depends on the reaction temperature.

$$k_P = Ae^{-E^*/RT}$$

$\Delta T = 10°C$, leads to $k_x = 2x$
Most reactions are exothermic.
Reaction heat accelerates reaction.

2. **Concentration Dependence:** The rate of reaction is expressed in terms of the concentration (C) of the original reactants.

$$-dC/dt = k_P C^n$$ …..k_p = reaction rate; C= concentration of M

Very quickly, let's review a couple of key chemistry concepts. Reaction rates (i.e., polymerization kinetics) are a function of (1) the temperature and (2) the concentration of reactants. Let's look at each one here.

The Arrhenius expression describes the reaction rate in terms of temperature and activation energy. Temperature has an exponential effect. **[CLICK]** For every 10 degrees C of increase in temperature, there is a doubling of the reaction rate.

You can write the equilibrium expression for the reaction rate for polymerization (kp) in terms of the concentration of monomer (-dC/dt). For chain reaction polymerization reactions, this rate is very fast.
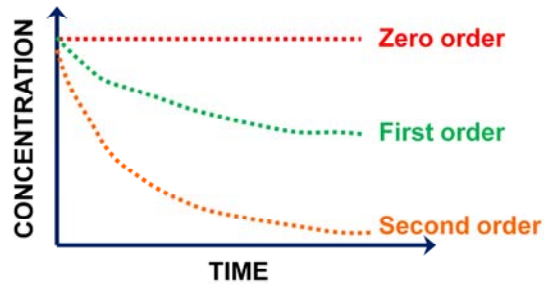
The reaction rate is rarely a simple relationship to the monomer concentration. **[CLICK]** It is represented as some power of the concentration, reflecting the challenges for getting the reaction to occur. We often talk in terms of **[CLICK]** zero order, **[CLICK]** first order, **[CLICK]** second order, or other orders of dependence. What this means in terms of actual consumption of monomer versus time is shown in the graph. We want the reaction to consume all the monomer, but as it proceeds there is less and less monomer. The challenge it to get it to diffuse to locations where it can react into the growing polymer. Many reactions do not go to completion.
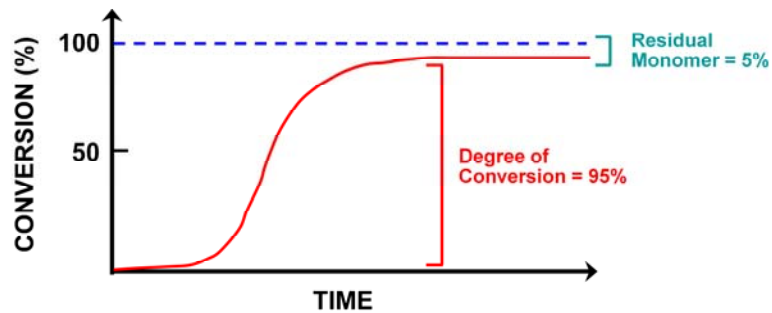
For reactions that occur in dentistry, we are very interested in knowing the extent of reaction **[CLICK]** which we call the **[CLICK]** REACTION CONVERSION, DEGREE OF CONVERSION (DC), or PERCENT CONVERSION. The value is expressed as a percentage. Left over material is called the RESIDUAL MONOMER **[CLICK]** and it is important to minimize it. There are several negative effects from residual monomer. It could diffuse out of the polymer and produce negative biological reactions. The residual monomer tends to impair mechanical properties. We will talk about this later.

Reaction Rates

$-dC/dt = k_P C^n$ .....k_p = reaction rate; C= concentration of M

M (monomer) $\xrightarrow{k_p}$ P (polymer)
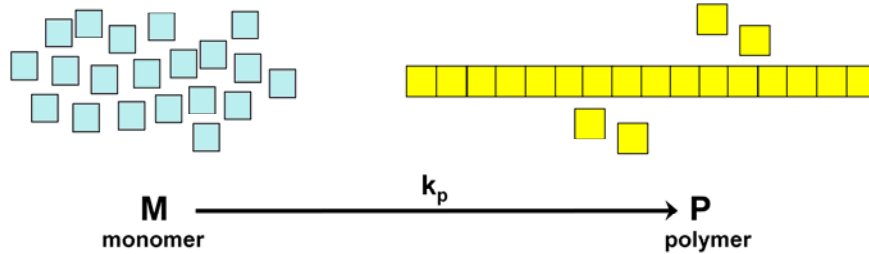
$k_P = k_a + k_i + k_p + k_t$

P = POLYMERIZATION
a = activation
i = initiation
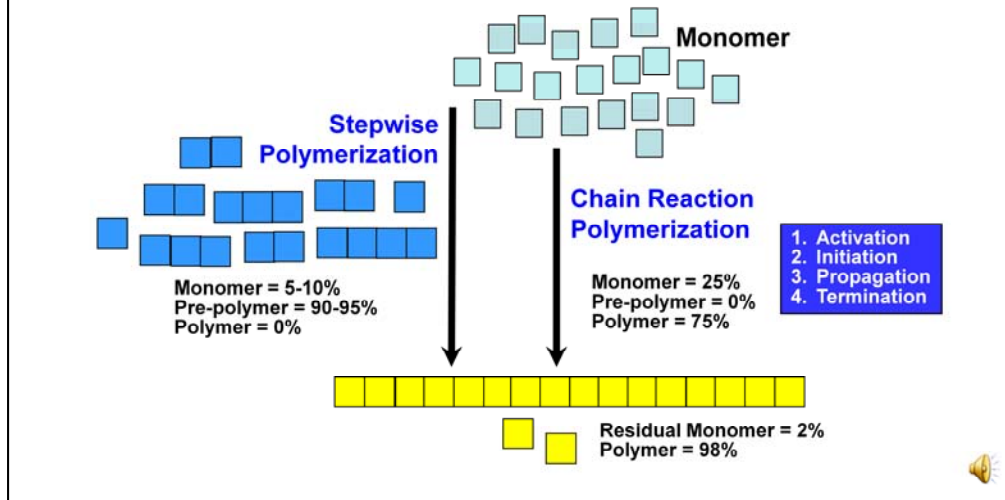p = propagation
t = termination

The reaction rate is actually an oversimplification for a polymerization reaction -- because it is affected by several events. **[CLICK]** For chain reaction polymerization, which we will study next, these stages include – activation, initiation, propagation, and termination. Each one can be thought of having its own reaction rate.

POLYMERIZATION MECHANISMS
Stepwise versus chain reaction polymerization paths.

1. **Stepwise Polymerization:** SLOW / intermediate species
2. **Chain Reaction Polymerization:** FAST / no intermediate species
3. **Template Polymerization:** SLOW / no intermediate species

Monomer

Stepwise Polymerization

Chain Reaction Polymerization

1. Activation
2. Initiation
3. Propagation
4. Termination

Monomer = 5-10%
Pre-polymer = 90-95%
Polymer = 0%

Monomer = 25%
Pre-polymer = 0%
Polymer = 75%

Residual Monomer = 2%
Polymer = 98%

Remember that we have classified polymerizations as (1) stepwise, (2) chain reaction, and (3) template types.

[CLICK] We will only study the first two types – **[CLICK]** stepwise and chain reaction polymerization. Typically, a specific polymer is produced conveniently by one or the other path. **[CLICK]** Both will produce high polymer with a little bit of unreacted monomer typically in the mixture. However, **[CLICK]** stepwise polymerization goes through a stage of many smaller segments in the process of being connected. At any point, the mixture will have mostly pre-polymer and perhaps no polymer until near the end of the reaction. **[CLICK]** With chain reaction polymerization, monomer quickly zips up into a polymer. There is practically never any intermediate species that occur.
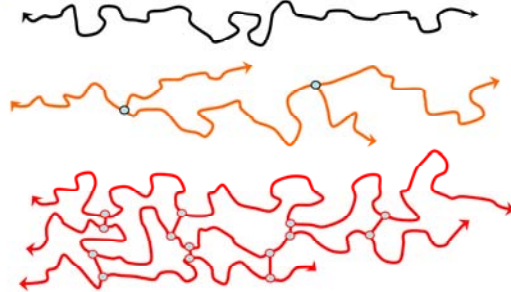
In a second, we will study how this happens and the factors affecting chain reaction polymerization. **[CLICK]** The stages are (1) activation, (2) initiation, (3) propagation, and (4) termination. Sometimes you will see these four stages as collapsed into 3 stages of initiation, propagation, and termination.

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As we have discussed in classifying polymers, the conformations can be (1) linear, (2) branched, or (3) crosslinked. It is also possible that linear and branched polymers can become crosslinked with further reactions between side-groups on the polymer. We will discuss that in detail later. The conformation of the initial polymer is governed by the functionalilty of the monomer and the type of polymerization.

Monomers are defined as mono-, di-, tri-, etc. functional ones. The functionality of the monomer and the type of polymer formed can be confusing. Be careful here. For chain reaction polymerization, **[CLICK]** mono-functional monomers produce linear polymers. However, for step-wise polymerizations, **[CLICK]** di-functional monomers can produce linear polymers. We have already talked about glycolic acid monomer which has acid and alcohol groups on its ends that react between adjacent molecule to produce ester links and create a linear polymer. For similar reasons, di-functional molecules can produce branched or crosslinked polymers. **[CLICK]** Tri- or poly-functional molecules produce crosslinked structures.

We are generally concerned with acrylic monomers such as MMA that polymerizes into PMMA. The monomer is mono-functional and forms a linear polymer. We are also very interested in BIS-GMA which is di-functional -- and polymerizes into a crosslinked structure.
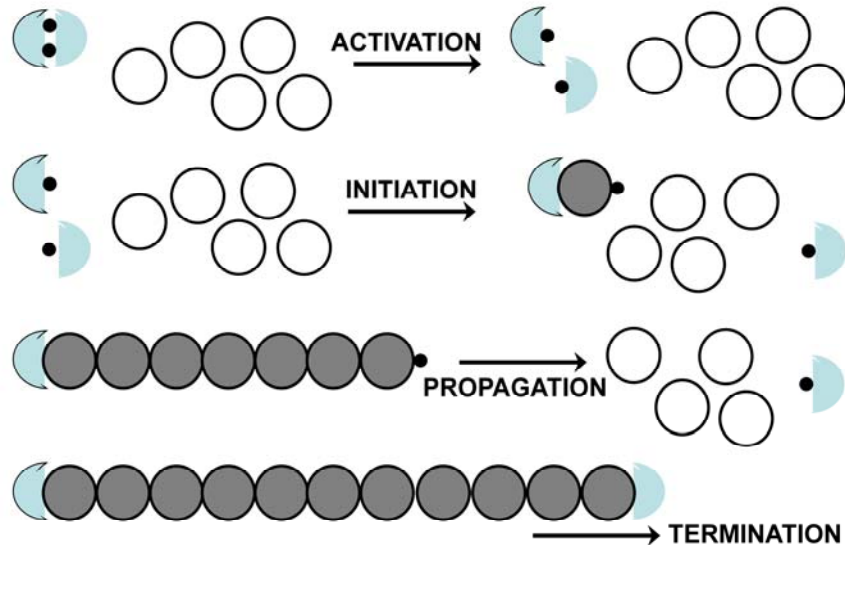
Now it is important to examine the polymerization mechanism for chain reaction polymerization that involves 4 stages – **[CLICK]** (1) activation, **[CLICK]** (2) initiation, **[CLICK]** (3) propagation, and **[CLICK]** (4) termination. KNOW THIS DIAGRAM. This is typical for all acrylic resin chemistry based on double-bond reactions. In just a moment we will provide more of the details.

>Activation provides a free radical for starting the reaction.

>Initiation is the free radical attacking the monomer unit to start a chain reaction.

>Propagation is the fast addition of more and more monomer while passing along the radical.

>Termination is the completion of the chain, and generally that is accomplished with annihilation of the free radical.

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Activation and initiation are a much easier path to start monomer reaction for chain reaction polymerization than via a bi-molecular reaction. A bi-molecular reaction is not energetically favorable. It would require that 2 monomer units collide, break open both double bonds, bond to each other, and form radicals on either end of the dimer that is formed. The energy barrier for this process is very high.

Activation is the Alternative

This is very "likely."

Free Radical • ⟶

H   CH₃
  \   /
   C=C
  /   \
H   COOCH₃

Requires opening of only ONE double bond to produce bonding -- with the formation of ONE free radical.

              H   CH₃
                \   /
Free Radical ----- C--C• ➡
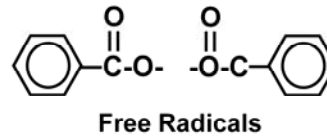   /   \
              H   COOCH₃
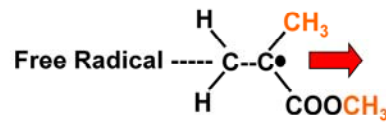
The advantage for activation is that it breaks down the starting steps. Free radicals are easier to form first. Then, the radical readily attacks the monomer double bond. Eliminating that double bond releases energy and, although a radical remains on the monomer, and it is used to continue to attack more double bonds.
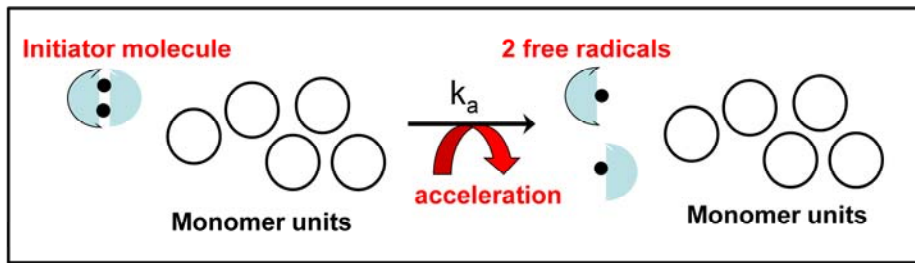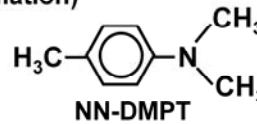
Technically the reaction can be initiated by free radicals, anions, or cations, but we are primarily interested in free radicals. Any process that speeds up the activation stage is called "acceleration."

The most commonly used initiator molecule for generating free radicals is BENZOYL PEROXIDE. **[CLICK]** It is unstable by itself and **[CLICK]** wants to break into two free radicals. **[CLICK]** This process goes faster with accelerators. Accelerators can be chemical ones, heat, or light.

[CLICK] The most commonly encountered chemical accelerators are tertiary amines. N,N-dimethyl para-toluidine (NN-DMPT) has been frequently used in dentistry but tends to encourage yellowing over time of the polymer – so it has been replaced with other tertiary amines in modern systems.

Retarders and Inhibitors

Effects:
  a. **Retarders** = consume free radicals and "slow" activation.
  b. **Inhibitors** = consume free radicals and "prevent" activation.
Control of the INITIATION step (k_i)

2 free radicals

k_i

monomer units

retarders, inhibitors

HO—⬡—OH

Hydroquinone (HQ)
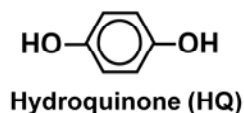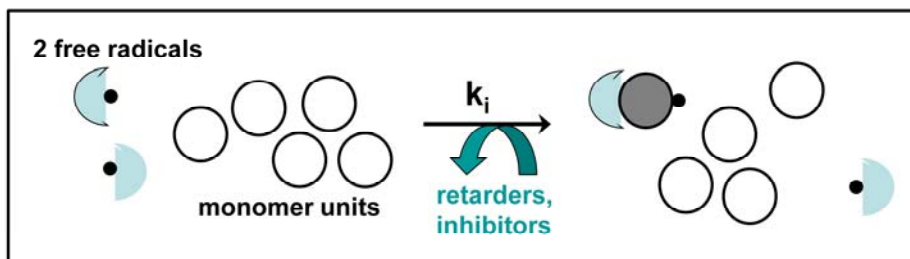
While accelerators may be speeding up activation, it is possible to slow down or prevent initiation by using retarders or inhibitors to take the free radicals out of commission. Retarders are less efficient than inhibitors. **[CLICK]** The most common inhibitor is HYDROQUINONE (abbreviated HQ).

You might wonder if retarders or inhibitors are present, how would you ever get a reaction to start? If you speed up acceleration to the rate that retarders or inhibitors can not keep up, then the reaction starts. Small amounts of retarders or inhibitors are routinely added to all monomers to stabilize them during storage. Storage container surfaces, air, or other contaminants are also sources of free radicals and would otherwise start the polymerization.
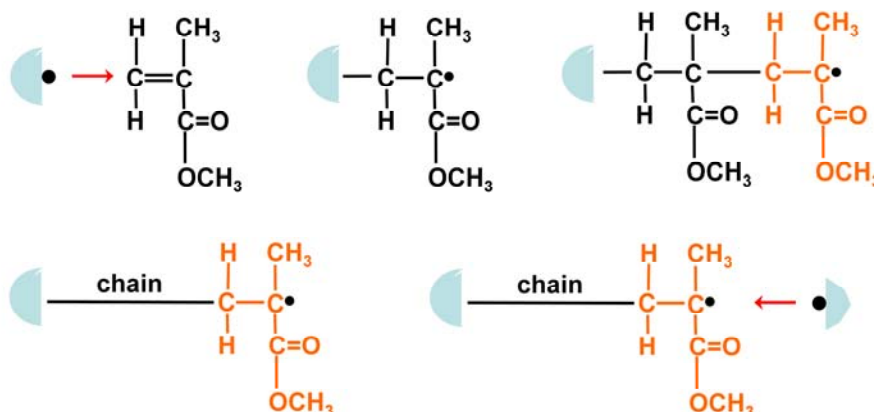
Now lets look at the details of MMA polymerization. Activation (not shown) generates free radicals which **[CLICK]** attack the double bond in the MMA monomer unit to form a new free radical that **[CLICK]** attacks the next monomer unit and keeps **[CLICK]** growing the polymer chain and passing along the free radical.

This PROPAGATION process occurs at incredible speeds **[CLICK]** and is usually estimated to involve 1-to-2 million units being added per second. **[CLICK]** Heat is released as the double bond is opened which contributes to accelerating the process to go even faster. **[CLICK]** In large quantities of monomer, the reaction heat can be explosive.

[CLICK] At some point, monomer is no longer easily available, and the chain stops growing. **[CLICK]** The free radical end can (a) recombine with a free radical, (b) disproportionate the radical into the chain, (c) transfer it, or (d) just continue to exist inactively (decay).

In a subsequent module we will talk about ways to characterize the size of the polymer formed. As a preview, one of these it to report the number of monomer units hooked together to form the chain. That is called the DEGREE OF POLYMERIZATION or DP. If 1 million monomer units are involved, the chain has a DP=1 million.

Monomer Characteristics

Special information concerning 2 key monomers.

MMA
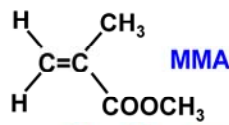
MW = 100 gms/mole
T_{bp} = 100 C
T_g = 100 C
Viscosity lower than water.
Sweet odor that irritating.

PMMA
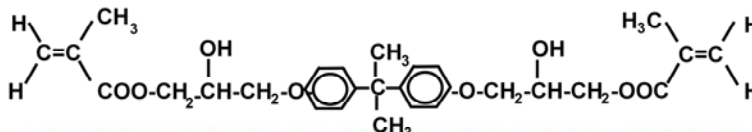
di-glycidyl methacrylate adduct of bisphenol-A = BIS-GMA

PBIS-GMA

MW = 454 gms/mole
Extremely viscous at 25C
Difficult to purify.

Two of the most common monomers used in dentistry in the last 50 years are MMA and BIS-GMA. Let's look at some characteristics of each one that impact how they are used.

[CLICK] Methyl methacrylate has a molecular weight of 100 gms per mole, boils at 100C, and has a glass transition of 100C. It is low viscosity and less viscous than water. Because of that it is hard to use just by itself in fabrication of things. Generally it is mixed with PMMA polymer to make a dough that is pliable before polymerization of the monomer. MMA has a sweet odor. About 1:45 people are allergic to it. It can cause skin irritation and breathing difficulties. There must be good air management where it is being used.

[CLICK] BIS-GMA is 4-5 times larger than MMA and has a MW of 454 gms per mole. It is a very viscous liquid and usually requires dilution for effective placement and flow during clinical use. It can not be crystallized and is difficult to purify by other means.

DENTAL EXAMPLES

Acrylic monomers are used widely in dentistry.

Acrylic Denture Bases:

    Heat Activation: Mixed to form dough and heated to set.
        PMMA Polymer Powder + BPO
        MMA Liquid Monomer

Space Maintainers:

    Chemical Activation: Mixed together to set chemically.
        PMMA Polymer Powder + BPO
        MMA Liquid Monomer + HQ + N,N-DMPT

Tooth-Colored Restorations:

    Visible Light Activation: Pre-mixed and visible light added.
        BIS-GMA Monomer + Ceramic Filler + CQ + HQ

Acrylic monomers are very common in dental applications. Here are just a few examples -- formation of acrylic denture bases, fabrication of temporary removable space maintainers, and matrix phase for light-cured tooth-colored restorations. We will examine all of these in detail in applied dental materials modules.

QUICK REVIEW

Review of polymerization factors, types, and details.

- **What is the effect on reaction rate of raising the temperature?**
  10C TEMPERATURE INCREASE, DOUBLES THE REACTION RATE.

- **What is the residual monomer content for 95% DC?**
  5%

- **What are the 4 stages of chain reaction polymerization?**
  ACTIVATION; INITIATION; PROPAGATION; TERMINATION.

- **Which things affect the activation and initiation rates?**
  (1) ACCELERATORS; and (2) RETARDERS or INHIBITORS.

- **What are some of the important characteristics of MMA?**
  MW=100 gms/mole; Tm =100C; Tg=100C; Viscosity less than water;
  Sweet odor; Irritating to some individuals; Mono-functional; Forms
  linear polymer; Reacts by chain reaction;

Here is a quick review of the concepts from this module.

[CLICK] (1) What is the effect on reaction rate of raising the temperature?
[CLICK]

[CLICK] (2) What is the residual monomer content for 95% DC?
[CLICK]

[CLICK] (3) What are the 4 stages of chain reaction polymerization?
[CLICK]

[CLICK] (4) Which things affect the activation and initiation rates?
[CLICK]

[CLICK] (5) What are some of the important characteristics of MMA?
[CLICK]

THANK YOU.