Workshop: Lifecycle of Plastics

Basic Elements of Polymer Chemistry

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C-PlaNeT
CIRCULAR PLASTICS NETWORK
FOR TRAINING

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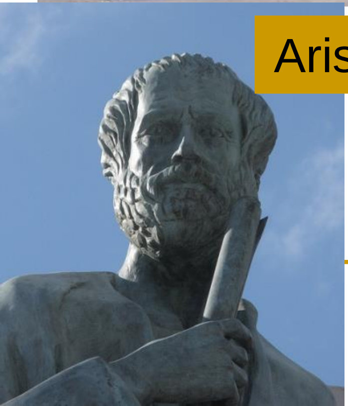

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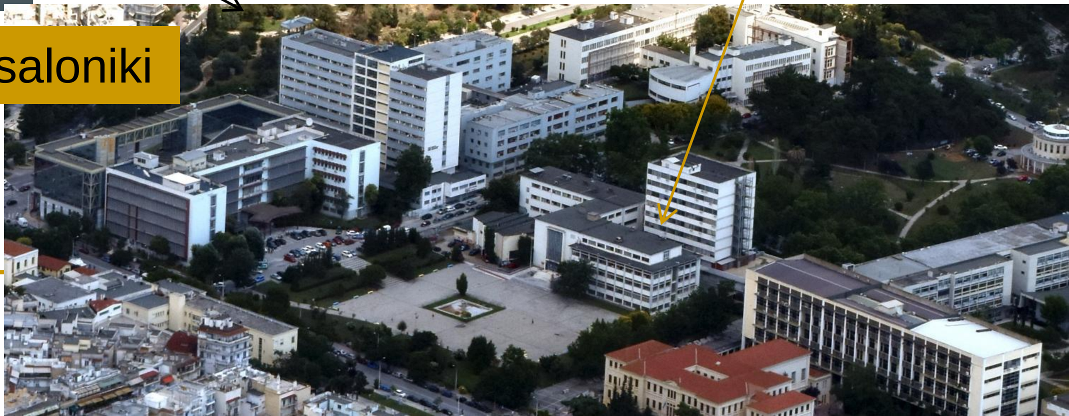


Introduction to polymer chemistry

- History
- Definitions (monomer, polymer, oligomer, structural unit)

Basic polymerization reactions

- Chain polymerization
  - Reaction mechanism, chemistry, kinetics
- Step Polymerization
  - Reaction mechanism, chemistry, kinetics

Polymerization techniques

- Issues in polymerization reactions
- Bulk, solution, suspension, emulsion

Copolymerization

- Copolymer composition
- Chain microstructure

Basic polymer properties

- Average molecular weights and molecular weight distribution
- Glass transition temperature
- Other thermophysical properties (melting, crystallization)
- Mechanical properties (stress-strain curves)

INTRODUCTION TO POLYMER CHEMISTRY

History of Polymers

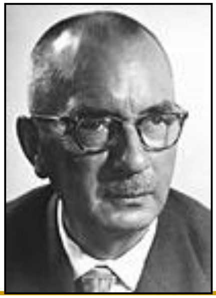
- 1839 - Natural Rubber - method of processing invented by **Charles Goodyear**
- **A century ago the term macromolecule belonged to the realm of science fiction!**
- In a landmark paper published in 1920, **Staudinger** concluded the structure of rubber and other polymeric substances**: “polymers were long chains of short repeating molecular units linked by covalent bonds.”**
- H. Staudinger termed makromoleküls paved the way for the birth of the field of polymer chemistry
- **Wallace Carothers, invented Nylon (1930 at DuPont).**

Nobel laureates in polymer scien

Scientist	Year	Field	Reason
Hermann Staudinger	1953	Chemistry	for contributions to the understanding of macromolecular chemistry
Karl Ziegler and Giulio Natta	1963	Chemistry	for contributions in polymer synthesis. (Ziegler-Natta catalysis)
Paul J. Flory	1974	Chemistry	for contributions to theoretical polymer chemistry
Pierre G. de Gennes	1991	Physics	for developing a generalized theory of phase transitions with particular applications to describing ordering and phase transitions in polymers
A.J. Heeger, A.G. MacDiarmid and H. Shirakawa	2000	Chemistry	for work on conductive polymers, contributing to the advent of molecular electronics

H. Staudinger
(1881-1965)

K. Ziegler
(1897-1973)



G. Natta
(1903-1979)

P.J.Flory
(1936-)

P.-G de Gennes
(1932-)

A.J.Heeger
(1910-1985)

A.G. MacDiarmid
(1927-)

H.Shirakawa
(1936-)

1953 **1963** **1974** **1991** **2000**

Definitions

- **Monomer** : mono- (μονο - single unit) -mer (μέρος – part)
- **oligomer** : oligo- (ολίγο – few) -mer
- **polymer** : poly-(πολύ – many) -mer
- **Macromolecule** : macro- (μακρυ – long) -molecule
- The terms polymer and macromolecule do not mean the same thing. A polymer is a substance composed of macromolecules.
- The IUPAC Gold Book definition of a macromolecule is: “A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.”

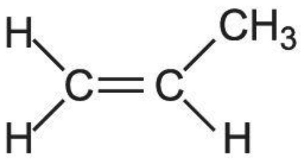
Definitions: Monomer(s) repeating structural unit

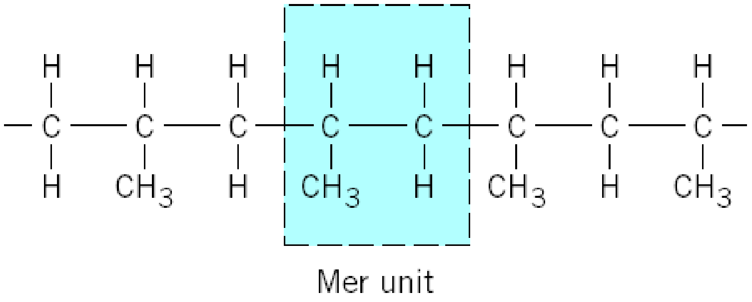
- The repeating structural unit is almost the same with the monomer in addition polymers but not in polymers produced from polycondensation

Polypropylene

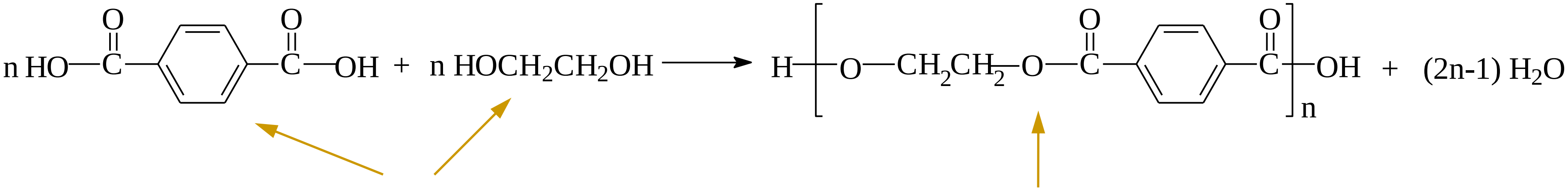
Monomer

Repeating structural unit - polymer





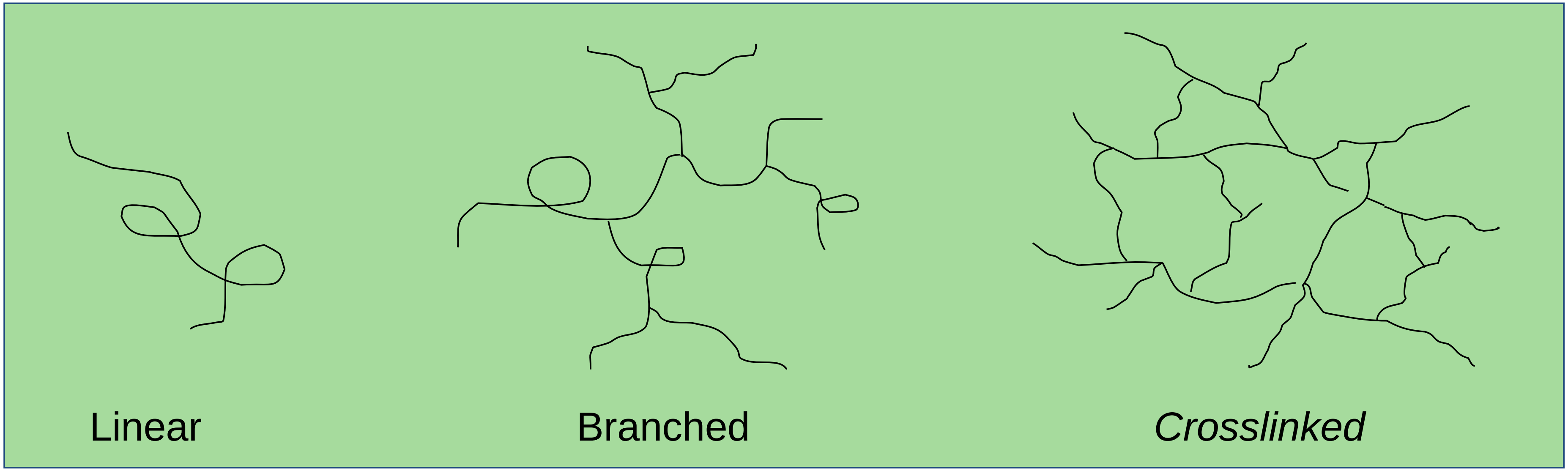
Synthesis of PET

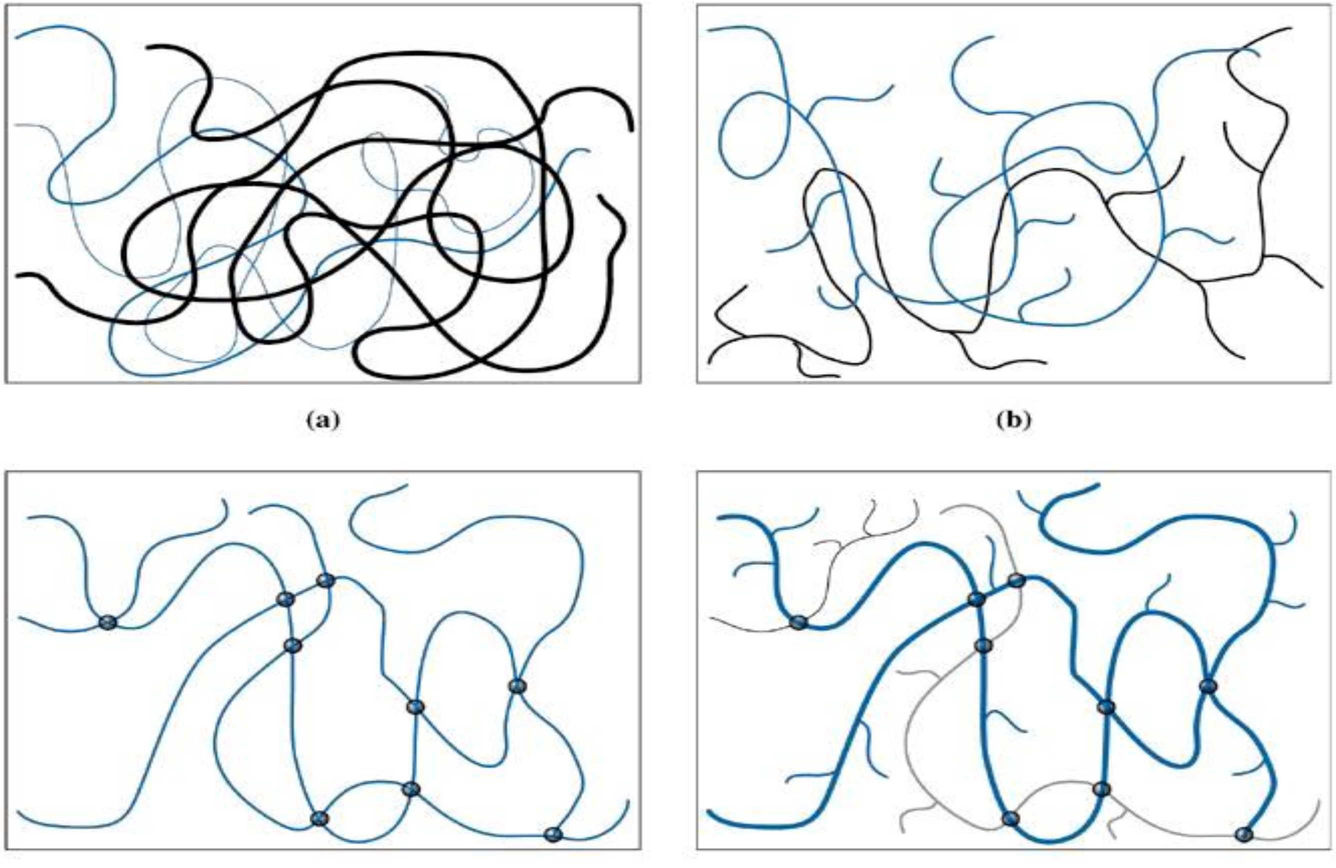


Monomers

repeating structural unit

Polymers depending on their chemical structure or production method may be linear (e.g. polystyrene, poly(methyl methacrylate), branched (e.g. poly(vinyl acetate, LDPE)) or crosslinked (e.g. Dimethacrylates, resins, etc.)

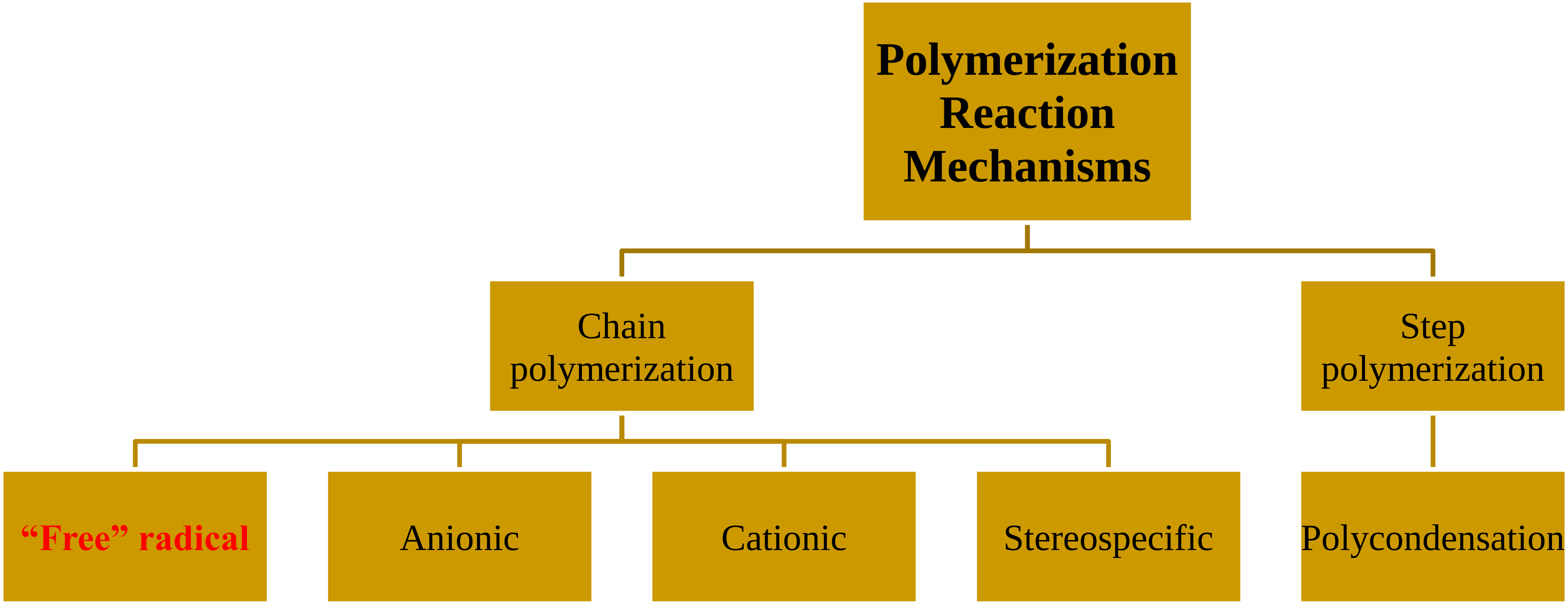




Schematic showing linear and branched polymers. Note that branching can occur in any type of polymer (e.g., thermoplastics, thermosets, and elastomers). (a) Linear unbranched polymer: notice chains are not straight lines and not connected. Different polymer chains are shown using different shades and design to show clearly that each chain is not connected to another. (b) Linear branched polymer: chains are not connected, however they have branches. (c) Thermoset polymer without branching: chains are connected to one another by covalent bonds but they do not have branches. Joining points are highlighted with solid circles, (d) Thermoset polymer that has branches and chains that are interconnected via covalent bonds. Different chains and branches are shown in different shades for better contrast. Places where chains are actually chemically bonded are shown with filled circles.

BASIC POLYMERIZATION REACTIONS

Polymerization mechanisms



Polymerization Reaction Mechanisms

- Chain polymerization
  - **“Free” radical**
  - Anionic
  - Cationic
  - Stereospecific
- Step polymerization
  - Polycondensation

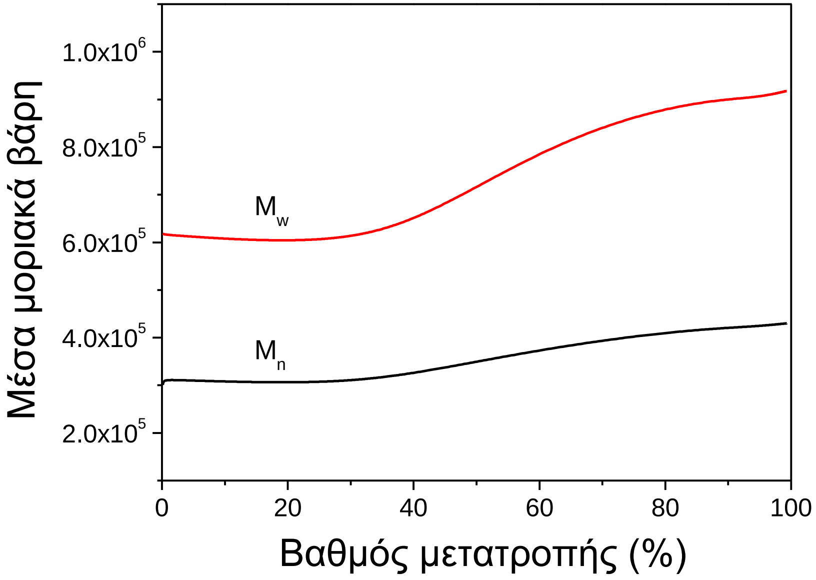
Chain vs Step polymerization

Chain polymerization	**Step polymerization**
Monomer(s) Should have at least 1 double bond	Monomer(s) Should have at least 2 characteristic terminal groups (–COOH, -OH, -NH_2, etc.)
Increasing the size of a macromolecule is very fast.	Increasing the size of a macromolecule is slow and gradual
Monomer(s) exist almost until the end of the reaction.	Disappearance of monomer(s) from the initial stages of the reaction
Exothermal reactions, non-reversible	Reversible reactions without producing significant heat
	Usually small-size byproducts are produced (H_2O, CH_3OH, HCl)

Chain vs Step polymerization

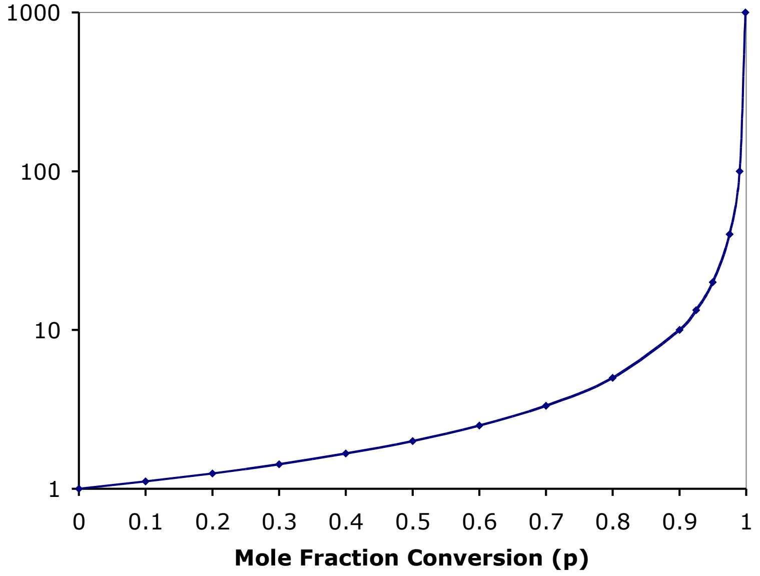
Chain polymerization

- Average molecular weights are high from the beginning of the reaction



Step polymerization

Average molecular weight increase significantly only at high conversions



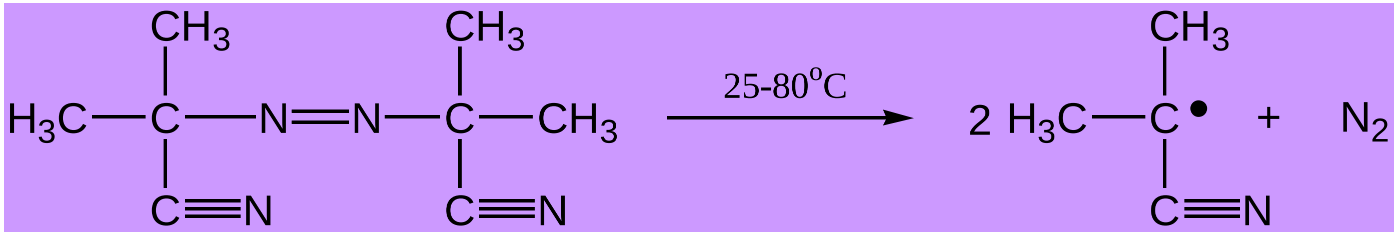
RADICAL CHAIN POLYMERIZATION

Main elementary reactions

- Initiation (Decomposition (thermal, redox or photo-) of the initiator and formation of primary radicals which find eventually a monomer molecule to start polymerizaton)
- Propagation (Macro-radicals react with monomer molecules to form polymer long chains)
- Termination (Macroradicals react either by combination or disproportionation to terminate and form dead polymer molecules)
- Side reactions
  - Chain transfer to monomer, solvent, other agent (reduction of molecular weight)
  - Chain transfer to polymer (formation of long chain branches)
  - Inhibition

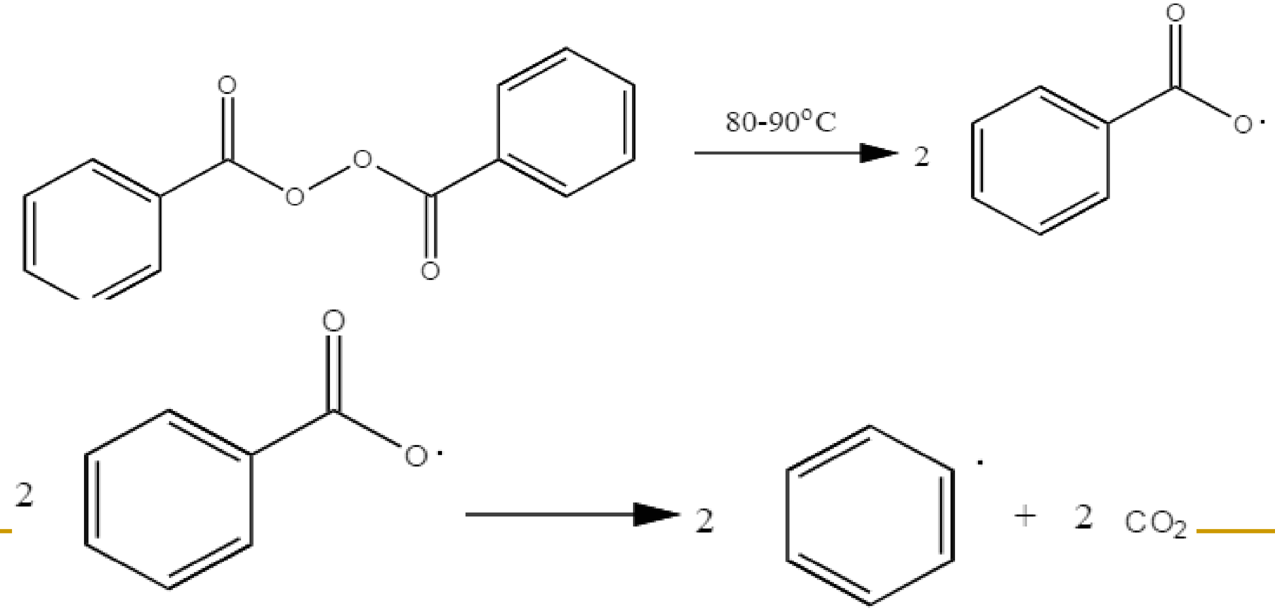
Typical initiators (thermal decomposition)

- Azo-bis isobutyronitrile, AIBN



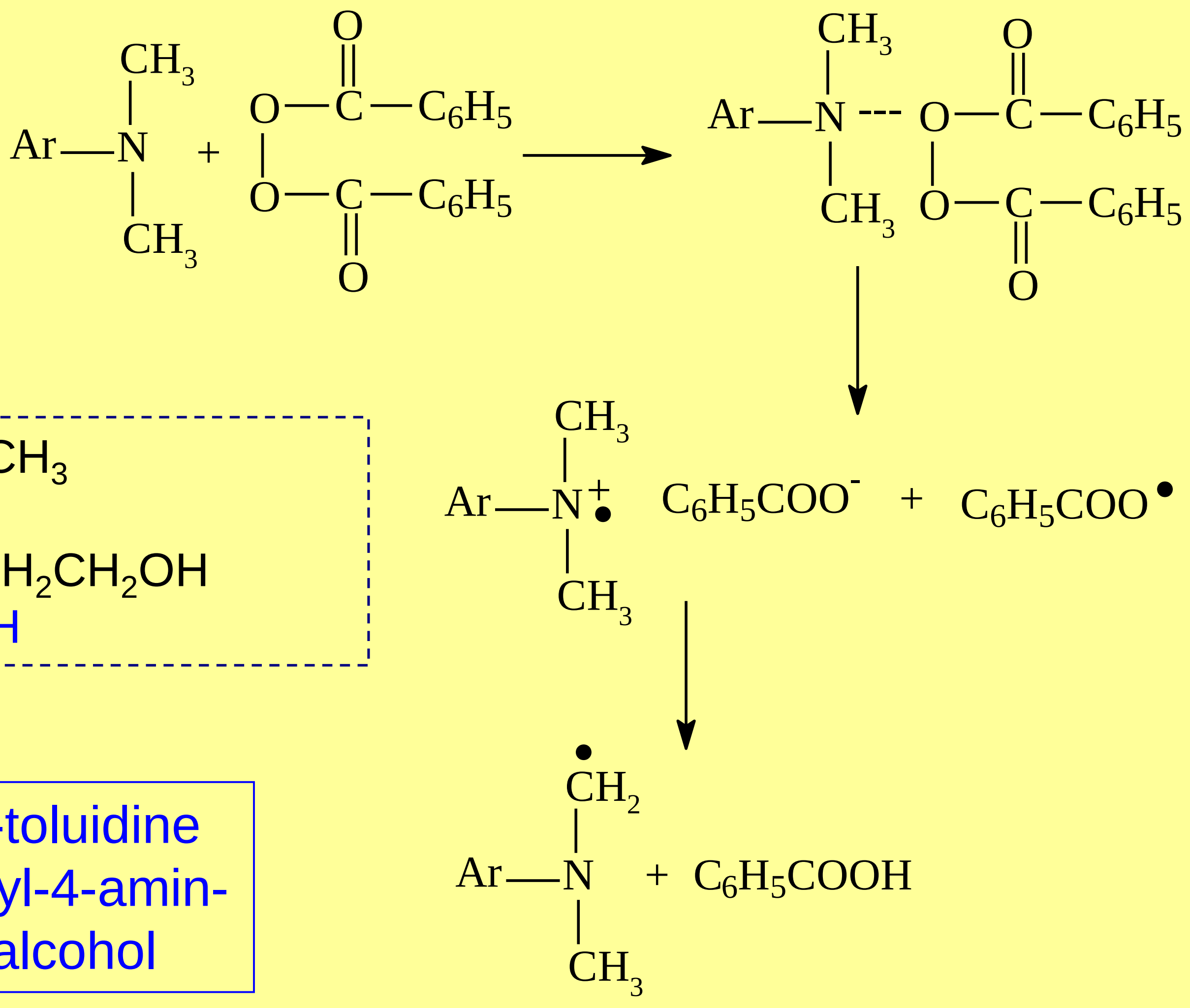
$$H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}-N=N-\overset{CH_3}{\underset{C\equiv N}{C}}-CH_3 \xrightarrow{25\text{-}80^{o}C} 2\ H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}{}^{\bullet} + N_2$$

- Dibenzoyl peroxide (BPO)



Initiator decomposition at room temperature

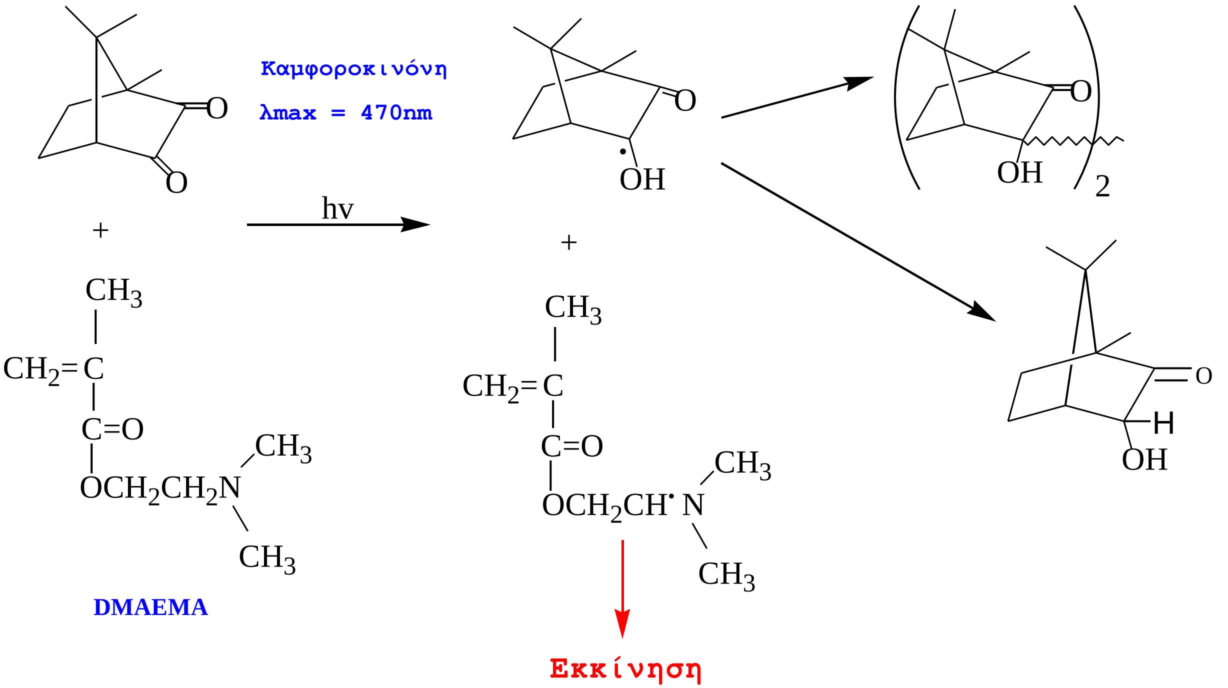
Dibenzoyl peroxide
+ Amine



Ar : $C_6H_5\text{-}CH_3$
for DMT
Ar : $C_6H_5CH_2CH_2OH$
for DMPOH

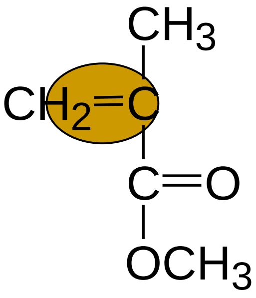
DMT: N,N dimethyl-π-toluidine
DMPOH: N, N-dimethyl-4-amin-phenylethyl-alcohol

Photo-polymerization (Camphoroquinone + Amine at $\lambda_{max} = 470$ nm



Common monomers used in radical polymerization reactions

Methacrylates

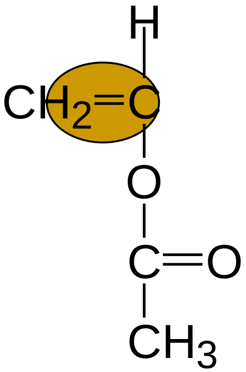


$CH_2{=}C(CH_3)C({=}O)OCH_3$

MMA

Methyl methacrylate

Vinyl esters

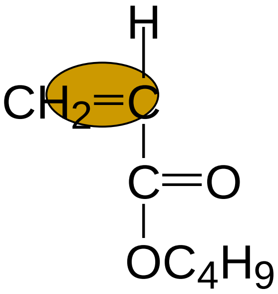


$CH_2{=}C(H)OC({=}O)CH_3$

VAC

Vinyl acetate

Acrylates

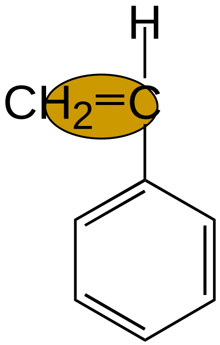


$CH_2{=}C(H)C({=}O)OC_4H_9$

BuA

Butyl acrylate

Styrene

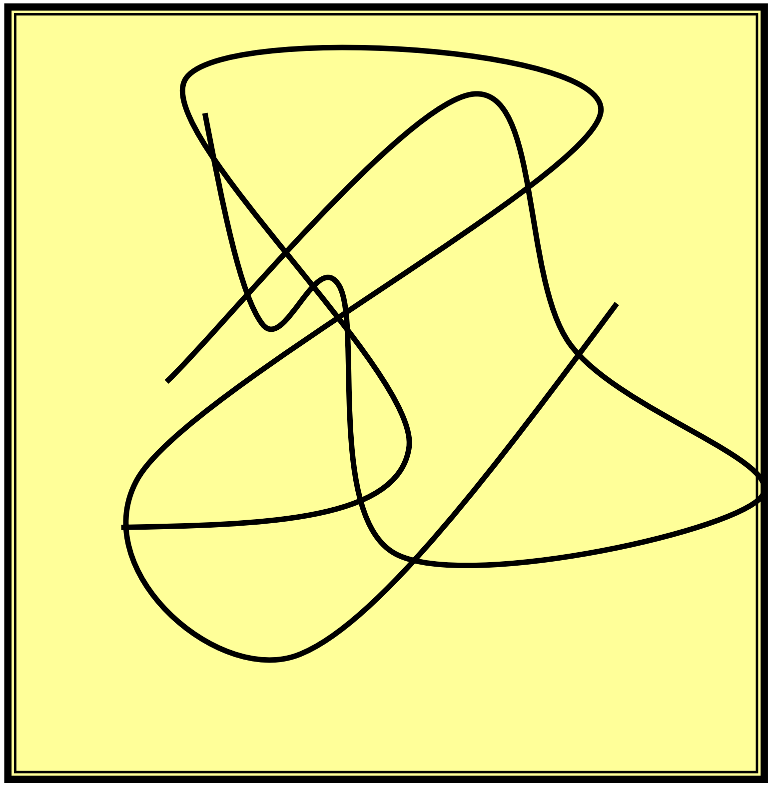


S

Styrene

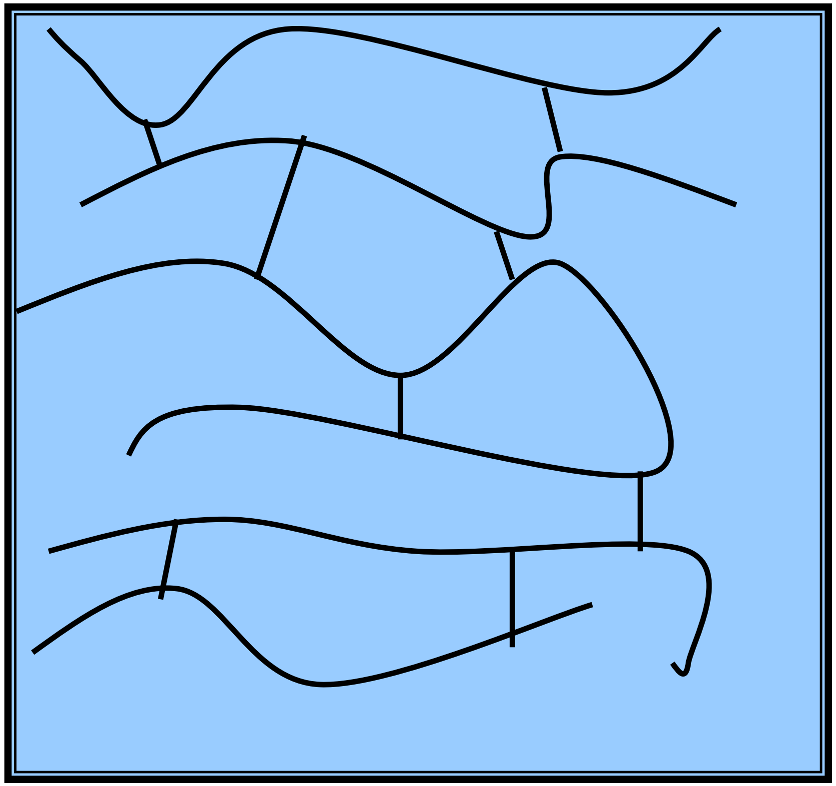
Monomers with one double bond result in linear polymers, monomers with two or more double bonds result in crosslinked structures

Linear polymer



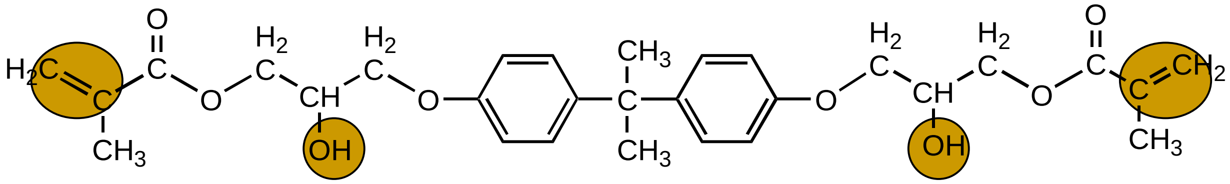
Macromolecular chains entangled but not joint with covalent bonds

Crosslinked polymer



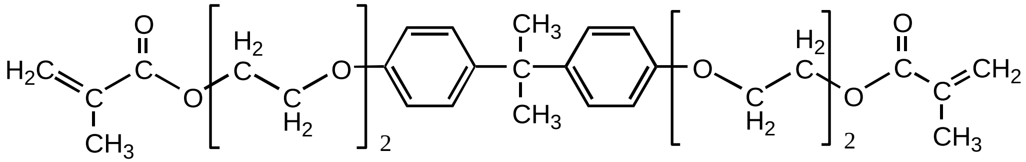
Macromolecular chains joint together with covalent bonds

Di-methacrylate monomers (dental materials)



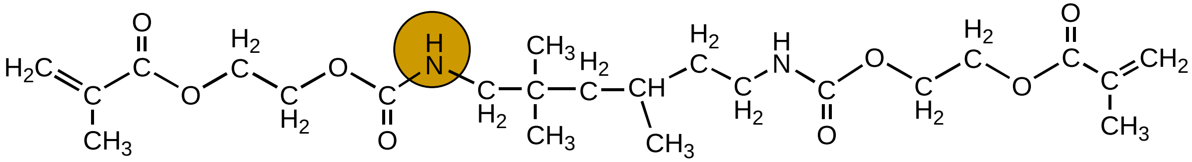
Bis-GMA

2,2-bis[p-(2'-hydroxy-3'methacryloxypropoxy)phenylene]propane



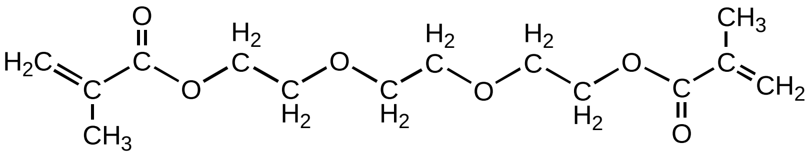
Bis-EMA (4)

Bisphenol A ethoxylated dimethacrylate



UDMA

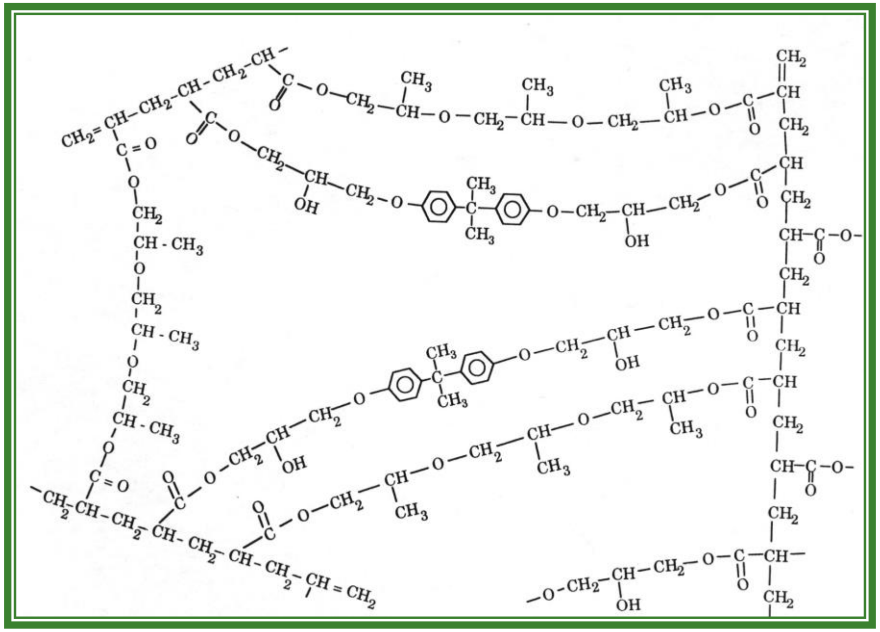
Urethane dimethacrylate



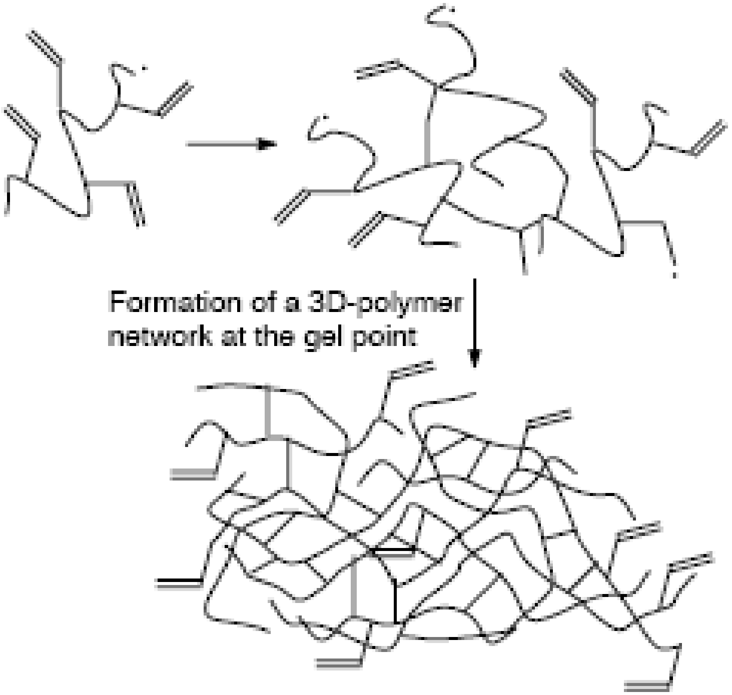
TEGDMA

Triethylene glycol dimethacrylate

Formation of crosslinkages during free radical polymerization of the dimethacrylates



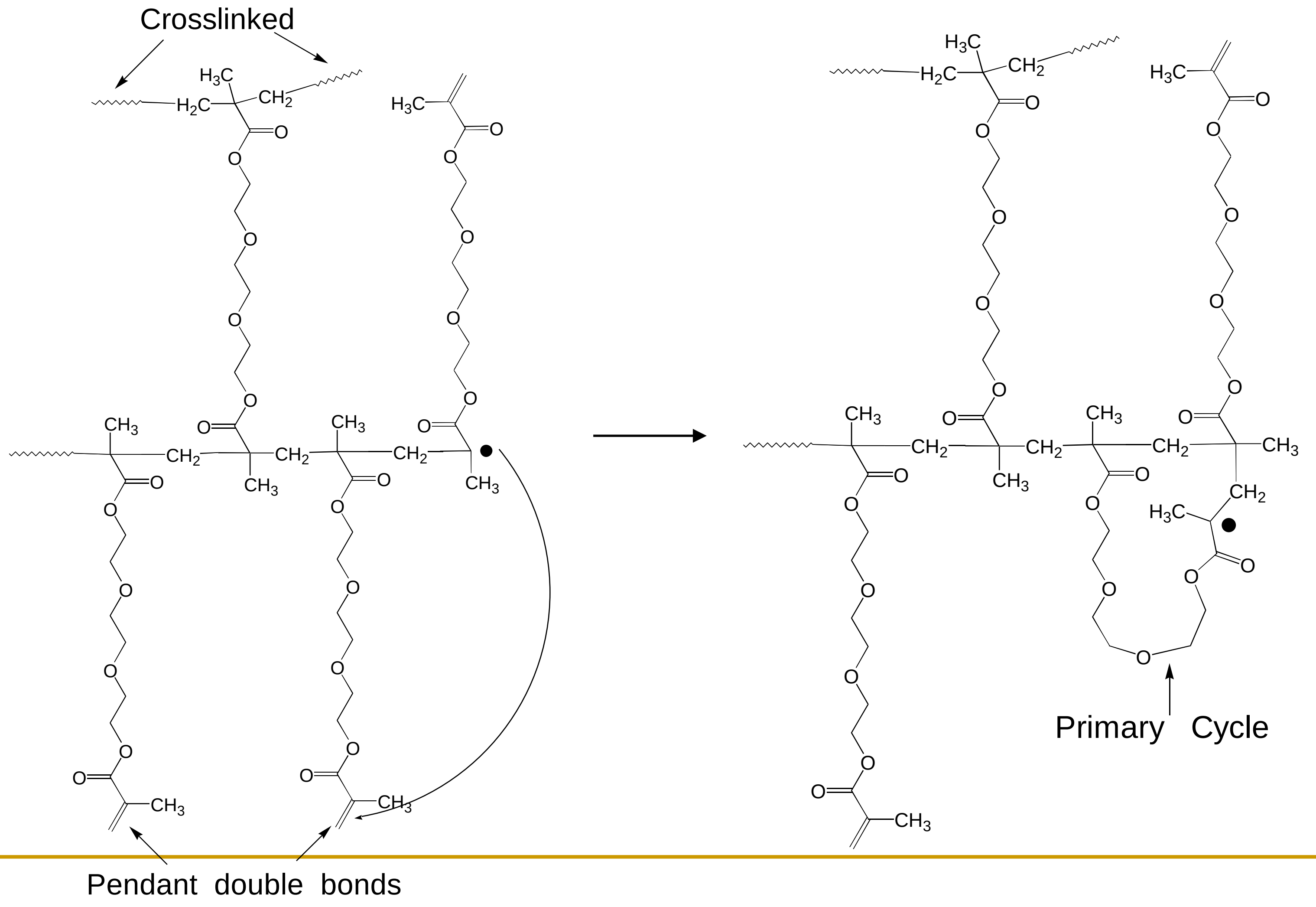
Crosslinked network structure of a copolymer formed from Bis-GMA and TEGDMA



Undesirable side reactions during crosslinking:

Cyclization reactions during polymerization of TEGDMA

Intramolecular reaction of pendant double bonds with the propagating radical

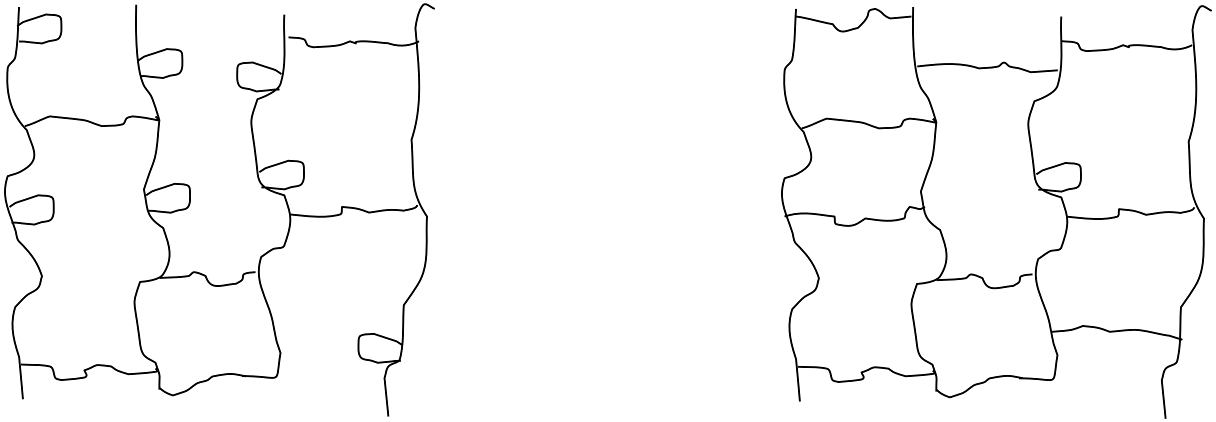


Crosslinked

Primary Cycle

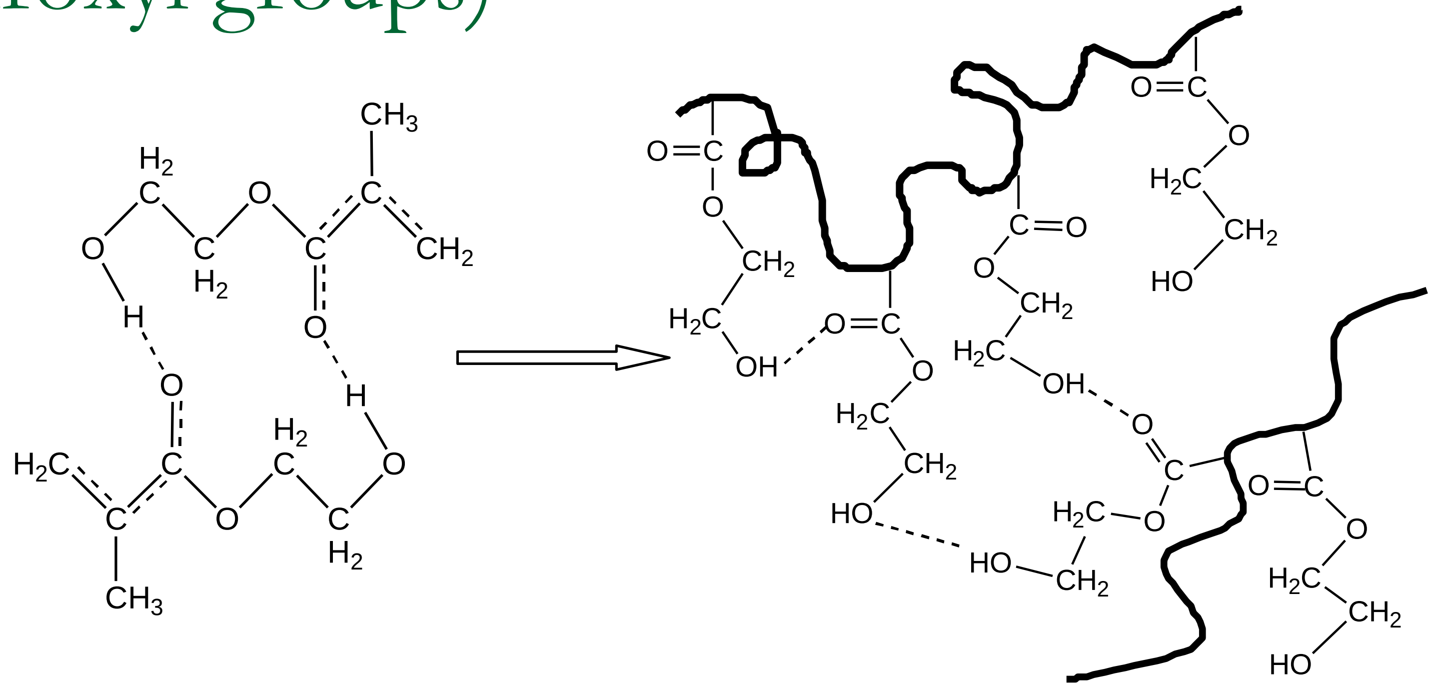
Pendant double bonds

Polymeric network with a high and a low degree of cyclization



Primary cyclization reactions are generally undesirable, since they do not contribute to overall crosslinking density, but does promote network heterogeneity, incomplete conversion and reduced mechanical strength

During polymerization, side bonds (e.g. Hydrogen bonds) can also be formed if the monomer has characteristic side units (e.g. hydroxyl groups)

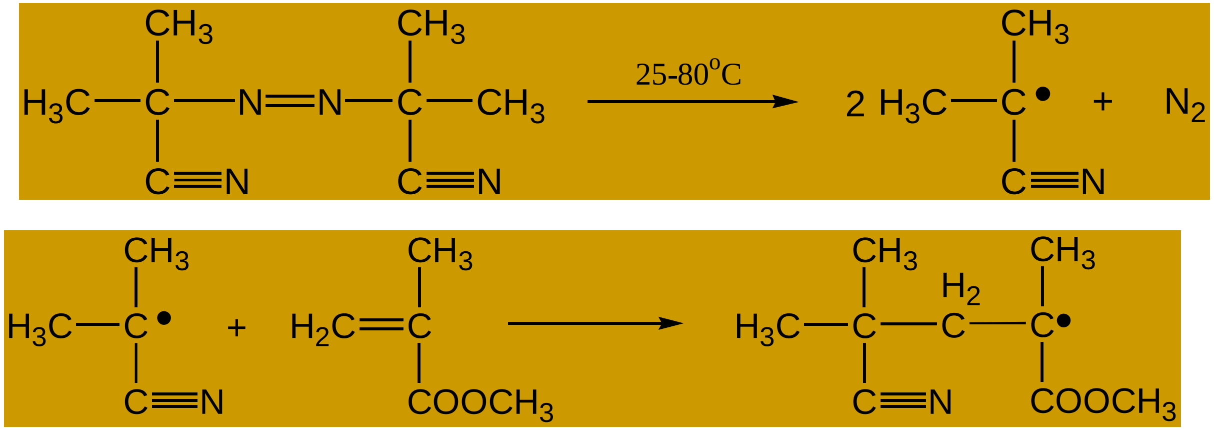


HEMA Polymerization PHEMA

Radical Polymerization Mechanism

Initiation:

Formation of primary radicals from the thermal decomposition of the Initiator

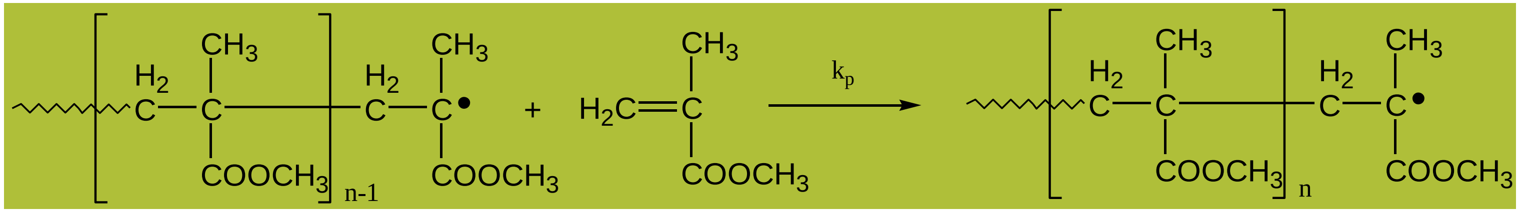


$$H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}-N=N-\overset{CH_3}{\underset{C\equiv N}{C}}-CH_3 \xrightarrow{25\text{-}80^{o}C} 2\ H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}\bullet + N_2$$

$$H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}\bullet + H_2C=\overset{CH_3}{\underset{COOCH_3}{C}} \longrightarrow H_3C-\overset{CH_3}{\underset{C\equiv N}{C}}-\overset{H_2}{C}-\overset{CH_3}{\underset{COOCH_3}{C}}\bullet$$

Propagation:

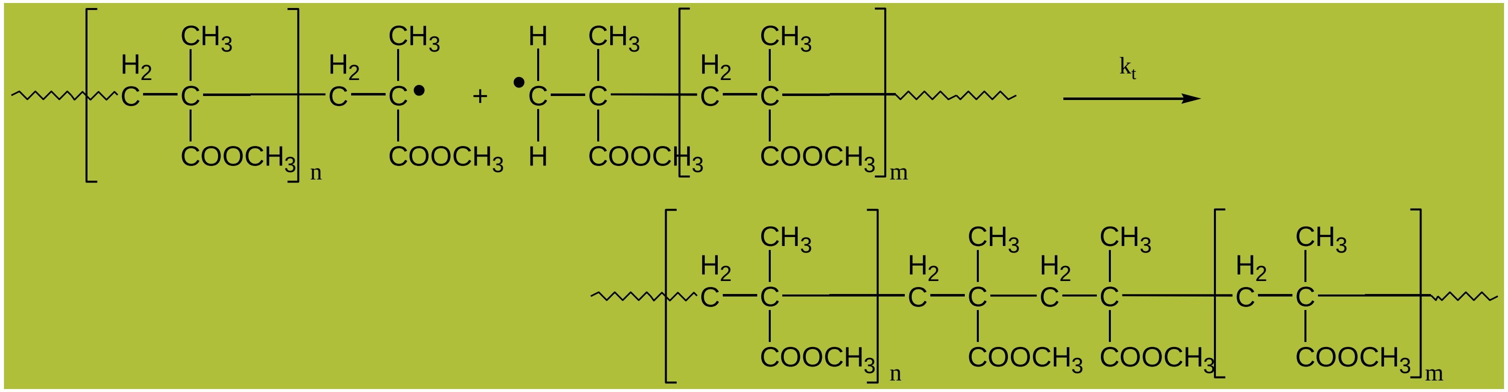
Formation of macro-radicals from the addition of several monomer molecules



$$\sim\sim\left[\overset{H_2}{C}-\overset{CH_3}{\underset{COOCH_3}{C}}\right]_{n-1}\overset{H_2}{C}-\overset{CH_3}{\underset{COOCH_3}{C}}\bullet + H_2C=\overset{CH_3}{\underset{COOCH_3}{C}} \xrightarrow{k_p} \sim\sim\left[\overset{H_2}{C}-\overset{CH_3}{\underset{COOCH_3}{C}}\right]_{n}\overset{H_2}{C}-\overset{CH_3}{\underset{COOCH_3}{C}}\bullet$$

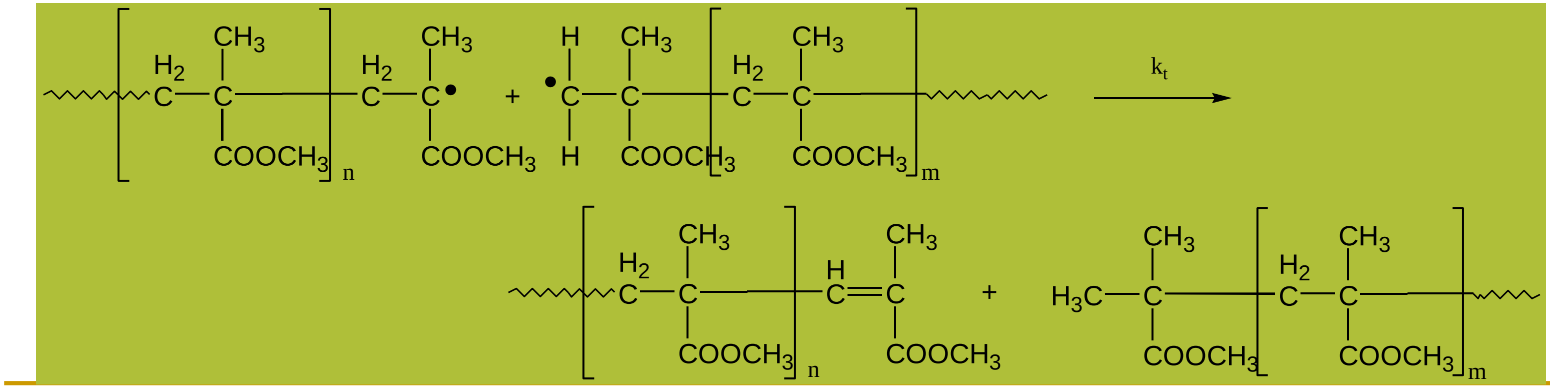
Termination by combination:

Formation of a macromolecule from the reaction of two macro-radicals



Termination by disproportionation:

Formation of two macromolecules (one with a terminal double bond) from the reaction of two macro-radicals



Simple mechanism of free radical polymerization

Initiation:

$$I \xrightarrow{k_d} 2I^{\bullet}$$

$$I^{\bullet} + M \xrightarrow{k_I} R_1^{\bullet}$$

Propagation:

$$R_n^{\bullet} + M \xrightarrow{k_p} R_{n+1}^{\bullet}$$

Chain transfer to monomer:

$$R_n^{\bullet} + M \xrightarrow{k_{tr,m}} R_1^{\bullet} + D_n$$

Termination by combination / disproportionation:

$$R_n^{\bullet} + R_m^{\bullet} \begin{cases} \xrightarrow{k_{tc}} D_{n+m} \\ \xrightarrow{k_{td}} D_n + D_m \end{cases}$$

More complicated mechanism of radical polymerization

- *Initiation:* $\boxed{I \xrightarrow{k_d} 2\,I^\bullet}$; $\boxed{I^\bullet + M_j \xrightarrow{k_{ij}} R^\bullet_{2-j,j-1,j}}$
- *Propagation:* $\boxed{R^\bullet_{n,m,i} + M_j \xrightarrow{k_{pij}} R^\bullet_{n+2-j,m+j-1,j}}$
- *Termination by combination:* $\boxed{R^\bullet_{n,m,i} + R^\bullet_{r,q,j} \xrightarrow{k_{tcij}} P_{n+r,m+q}}$
- *Termination by disproportionation:* $\boxed{R^\bullet_{n,m,i} + R^\bullet_{r,q,j} \xrightarrow{k_{tdij}} P_{n,m} + P_{r,q}}$
- *Chain transfer to monomer:* $\boxed{R^\bullet_{n,m,i} + M_j \xrightarrow{k_{fij}} R^\bullet_{2-j,j-1,j} + P_{n,m}}$
- *Chain transfer to polymer:* $\boxed{R^\bullet_{n,m,i} + P_{r,q} \xrightarrow{k_{fpij}} R^\bullet_{r,q,j} + P_{n,m}}$

Mechanistic modelling of radical polymerization - Material balances

- *Initiator:*

$$\boxed{\frac{1}{V}\frac{d(VI)}{dt}=-k_d I}$$

- *Monomers:*

$$\boxed{\frac{1}{V}\frac{d(VM_j)}{dt}=r_{M_j}=-\left[\sum_{i=1}^{2}\left(k_{p_{ij}}+k_{f_{ij}}\right)\lambda_0^i+k_{i_j}I^{\bullet}\right]M_j} \quad ;\ j = 1, 2$$

- *Reaction volume:*

$$\boxed{\frac{1}{V}\frac{d(V)}{dt}=-\sum_{i=1}^{2}r_{M_i}MW_i(1/\rho_i-1/\rho_p)}$$

- Reaction conversion:

$$x = [V_0(M_{10}+M_{20})-V(M_1+M_2)] / [V_0(M_{10}+M_{20})]$$

Population balances of ‘live’ radicals and polymer chains

- *Radicals of length (n+m):*

$$\frac{1}{V}\frac{d(VR^{\bullet}_{n,m,i})}{dt}=\sum_{j=1}^{2}k_{p_{ji}}M_{i}R^{\bullet}_{n+i-2,m+1-i,j}-\left(A_i+\sum_{j=1}^{2}k_{p_{ij}}M_{j}\right)R^{\bullet}_{n,m,i}-\sum_{j=1}^{2}k_{dp_{ij}}R^{\bullet}_{n,m,i}\sum_{r=0}^{\infty}\sum_{q=0}^{\infty}P_{r,q}$$
$$+\sum_{j=1}^{2}k_{fp_{ji}}R_0^{j}(n^{2-i}m^{i-1}P_{n,m})+\sum_{j=1}^{2}k_{dp_{ji}}\sum_{r=0}^{n}\sum_{q=0}^{m}P_{r,q}R^{\bullet}_{n-r,m-q,j}$$

- *Polymer of length (n+m):*

$$\frac{1}{V}\frac{d(VP_{n,m})}{dt}=\frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}k_{tc_{ij}}\sum_{r=1}^{n-1}\sum_{q=1}^{m-1}R^{\bullet}_{r,q,i}R^{\bullet}_{n-r,m-q,j}+\sum_{i=1}^{2}\left(A_i-\sum_{j=1}^{2}k_{tc_{ij}}R_0^{j}\right)R^{\bullet}_{n,m,i}-\sum_{i=1}^{2}\sum_{j=1}^{2}k_{dp_{ij}}R_0^{i}P_{n,m}$$
$$-\sum_{i=1}^{2}\sum_{j=1}^{2}k_{fp_{ji}}R_0^{j}(n^{2-i}m^{i-1})P_{n,m}$$

- where:

$$A_i=\sum_{j=1}^{2}\left(k_{f_{ij}}M_{j}+k_{t_{ij}}R_0^{j}\right)+\sum_{j=1}^{2}k_{fp_{ij}}\sum_{r=0}^{\infty}\sum_{q=0}^{\infty}(r^{2-j}q^{j-1}P_{r,q})$$

Estimation of the average molecular weights

- In order not to solve the set of infinite differential equations, usually the method of moments is invoked to solve a set of only 6 differential equations
- Definition of moments

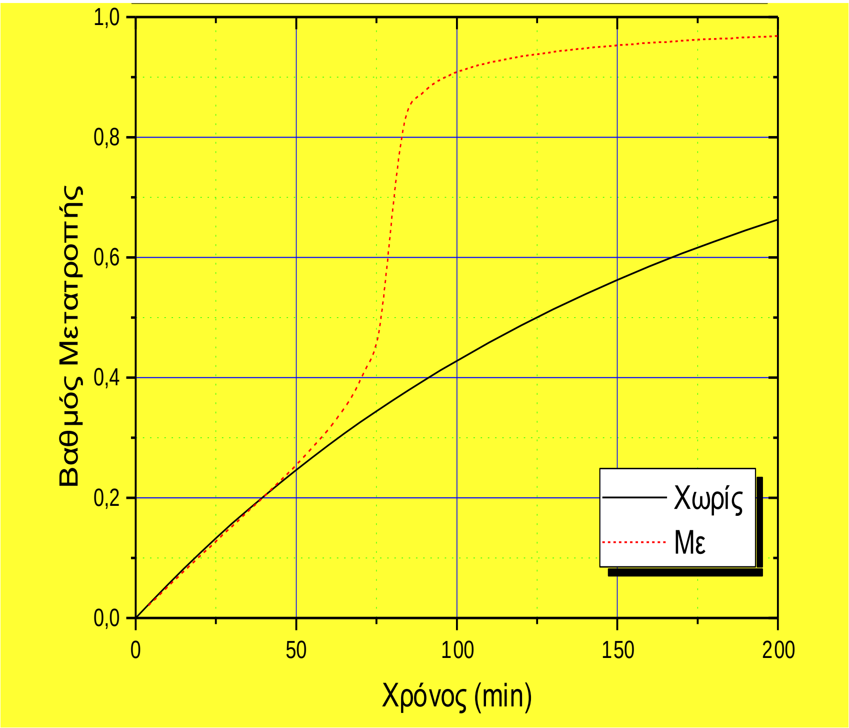
$$\lambda_k = \sum_{n=0}^{\infty} n^k P_n \;\; ; \mu_k = \sum_{n=0}^{\infty} n^k D_n \;\; ; \mathrm{k{=}0,\ 1,\ 2}$$

- Molecular weight distribution
- Number and weight average molecular weights (M_n, M_w):

$$\boxed{M_n = \frac{(\mu_1 + \lambda_1^1 + \lambda_1^2)}{(\mu_0 + \lambda_0^1 + \lambda_0^2)} \cong \frac{\mu_1}{\mu_0}} \qquad \boxed{M_w = \frac{(\mu_2 + \lambda_2^1 + \lambda_2^2)}{(\mu_1 + \lambda_1^1 + \lambda_1^2)} \cong \frac{\mu_2}{\mu_1}}$$

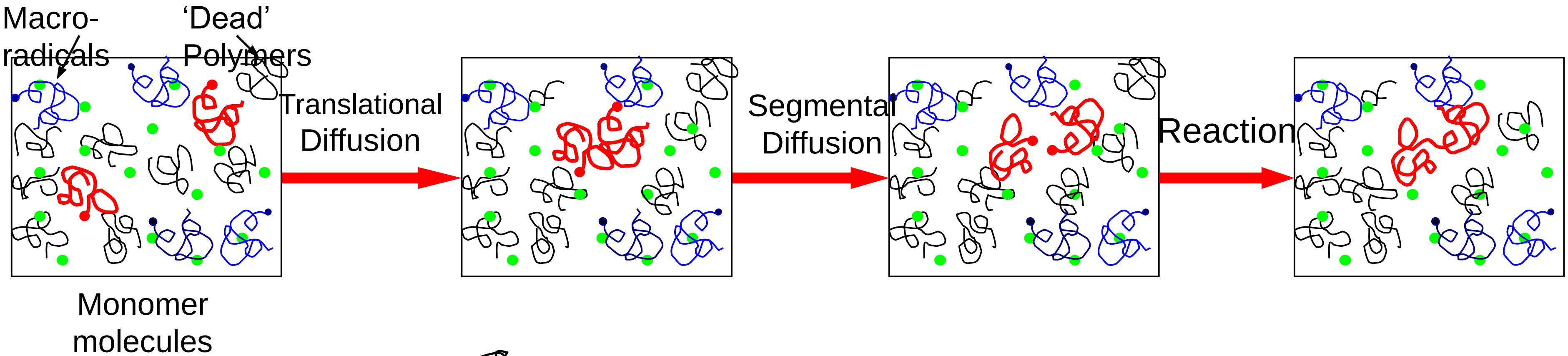
Effect of diffusion-controlled phenomena on the polymerization kinetics

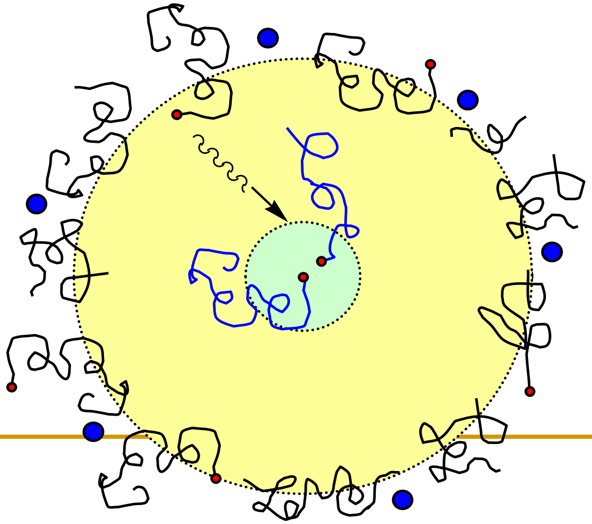
- Autoacceleration during polymerization results in higher conversions at the same time and much higher average molecular weight together with broader molecular weight distribution.
- Typical example Polymerization of methyl methacrylate in bulk



Effect of diffusion controlled phenomena on the termination reaction (gel effect)

Macroradical diffusion in the autoacceleration region



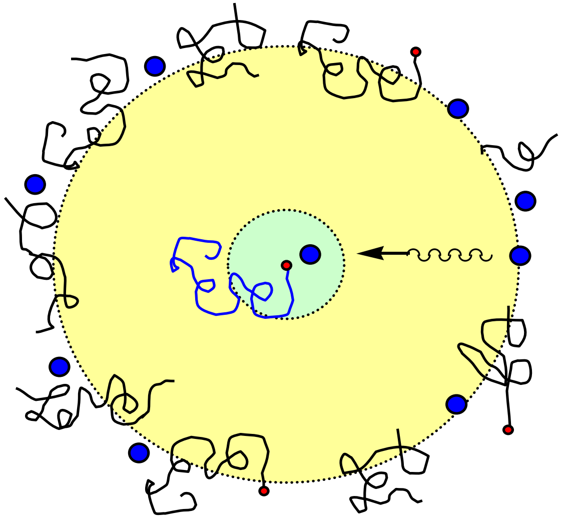


$$\frac{1}{k_{t_{ij}}} = \frac{1}{k_{t_{ij}0}} + \frac{1}{4\pi N_A r_t D_p}$$

Effect of diffusion controlled phenomena on the propagation (glass effect) and initiation reactions (cage effect)

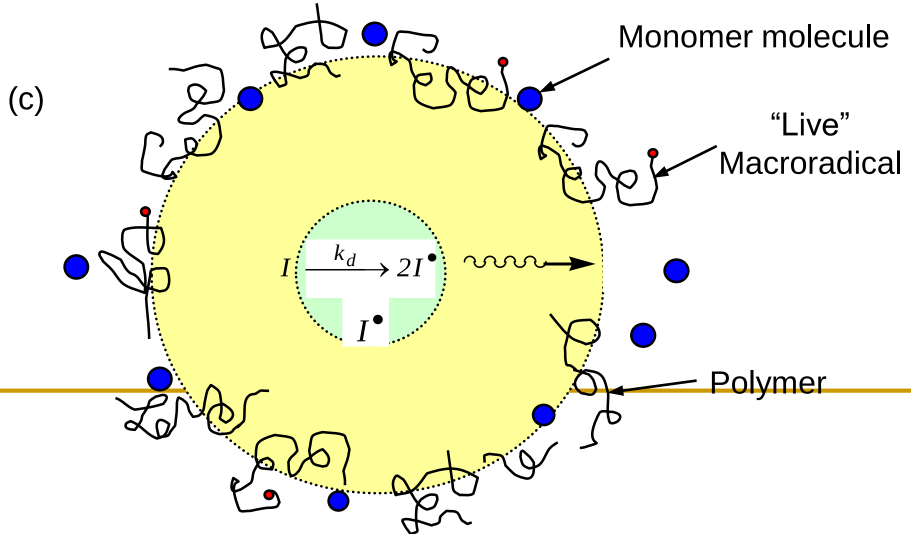
Propagation

$$\boxed{\frac{1}{k_{p_{ij}}} = \frac{1}{k_{p_{ij0}}} + \frac{1}{4\pi N_A r_p D_{m,j}}}$$

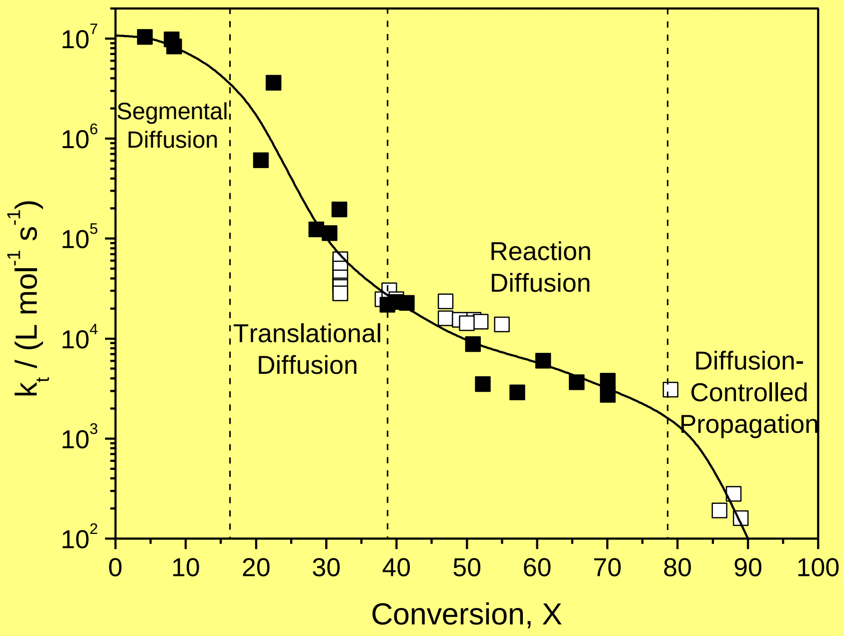


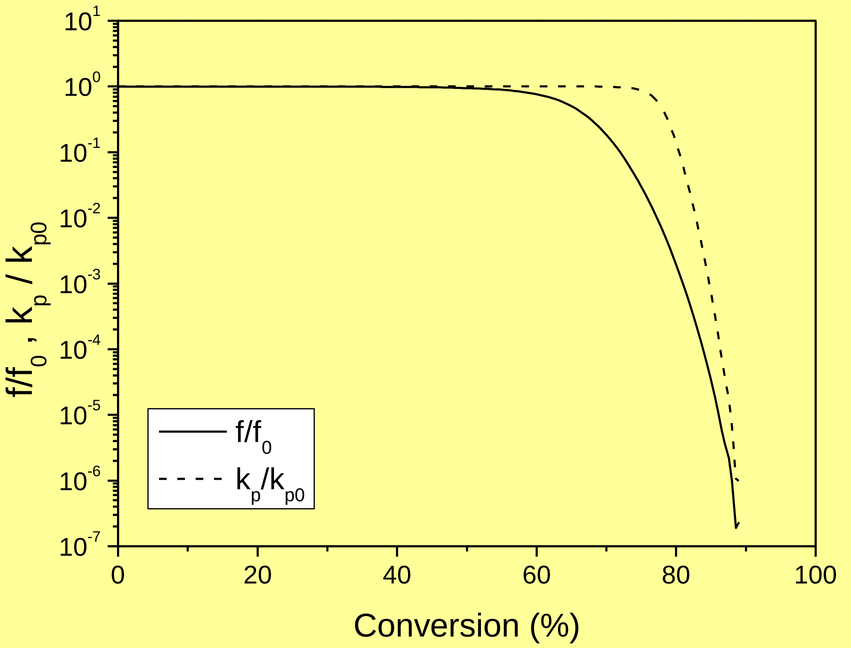
Initiation

$$\boxed{\frac{1}{f} = 1 + \frac{r_0 k_0}{D_I}}$$



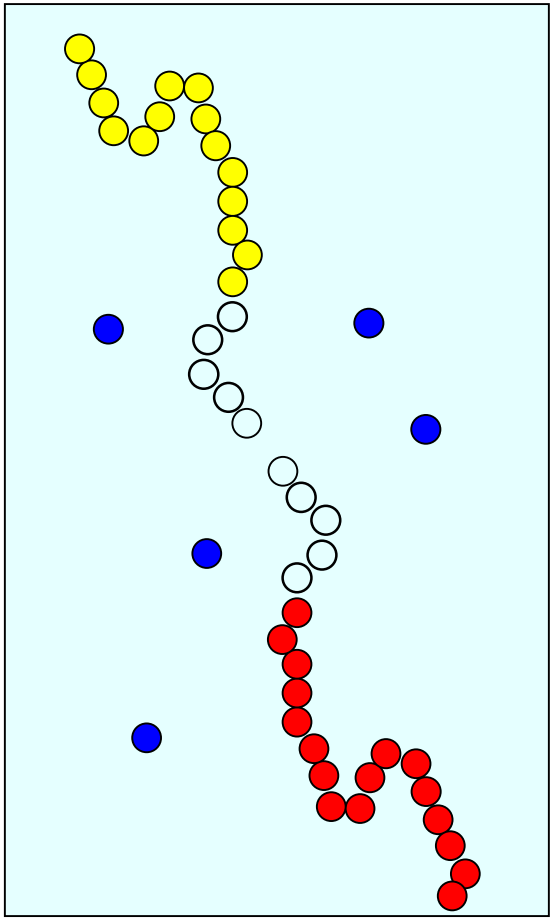
The termination rate coefficient decreases with monomer conversion due to the effect of diffusion-controlled phenomena (gel-effect), but also the propagation rate coefficient decreases at high monomer conversions (glass effect) together with the initiator efficiency (cage effect).





Reaction diffusion at high conversions

- Diffusion of macroradicals even at very slow center-of-mass diffusion of chains.
- Implicit movement in space due to the addition of monomer molecules in the radical through the propagation reaction.

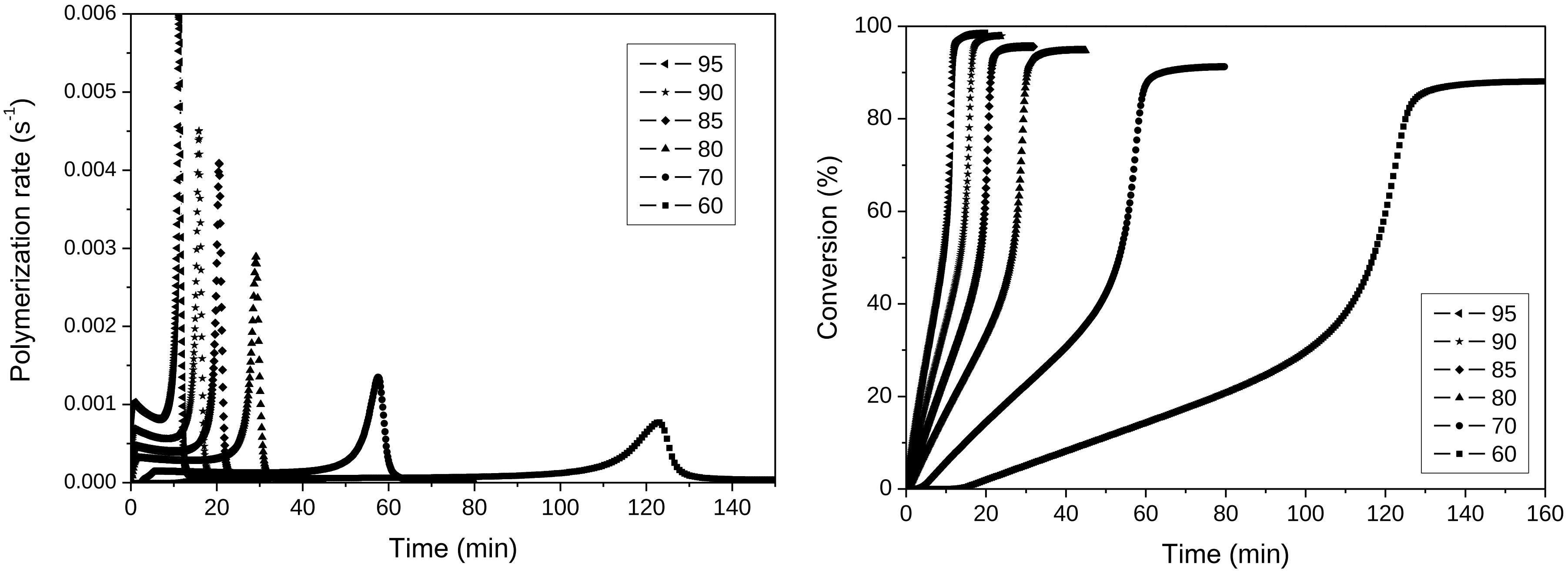


$$\boxed{D_{p,rd} = \bar{k}_p([M_1]+[M_2])\frac{a^2}{6}}$$

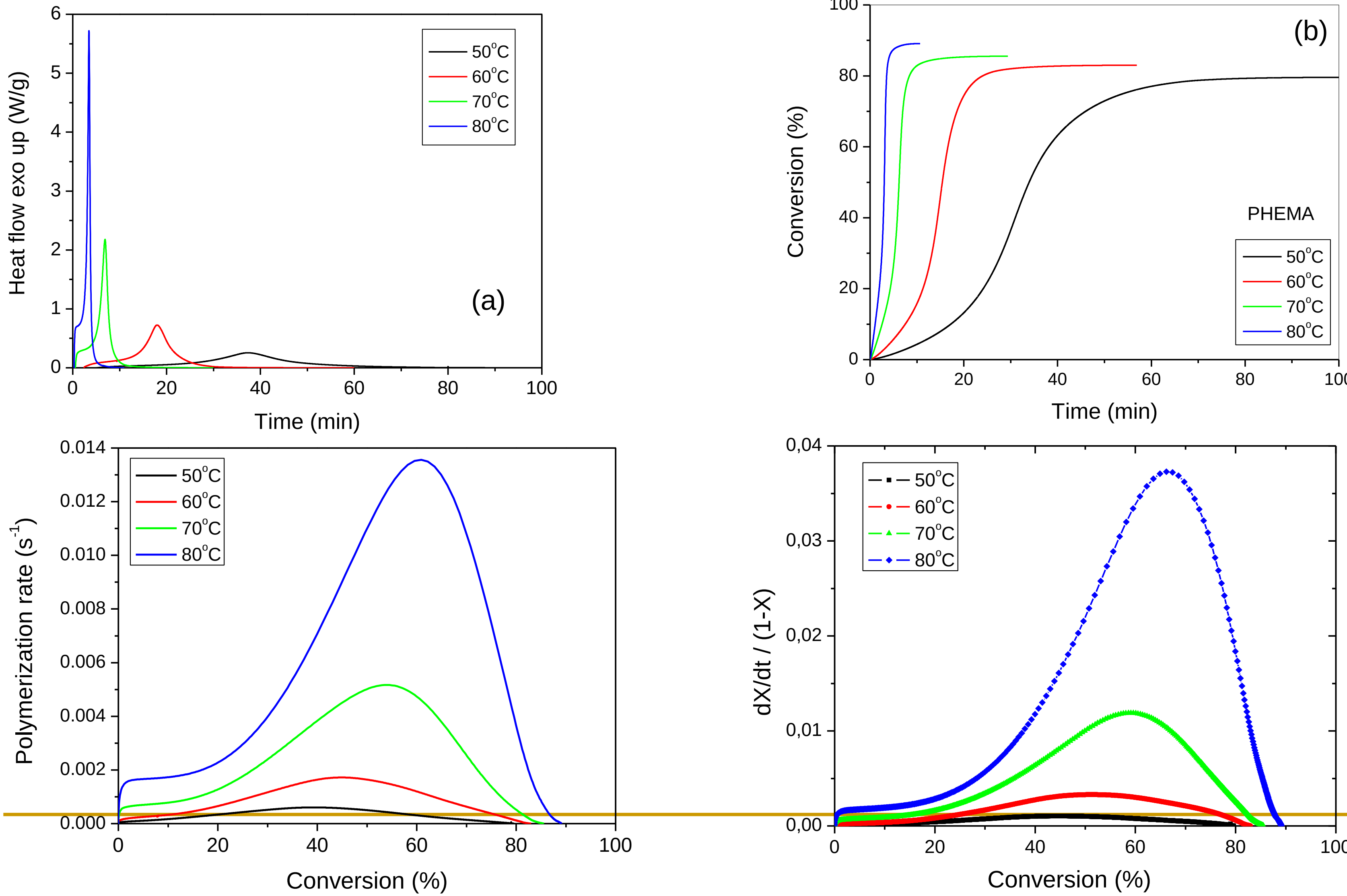
Isothermal polymerization kinetics experimental data from Differential Scanning Calorimetry measurements

Effect of temperature during bulk polymerization

Polymerization rate and conversion versus time during bulk polymerization of MMA at different temperatures.

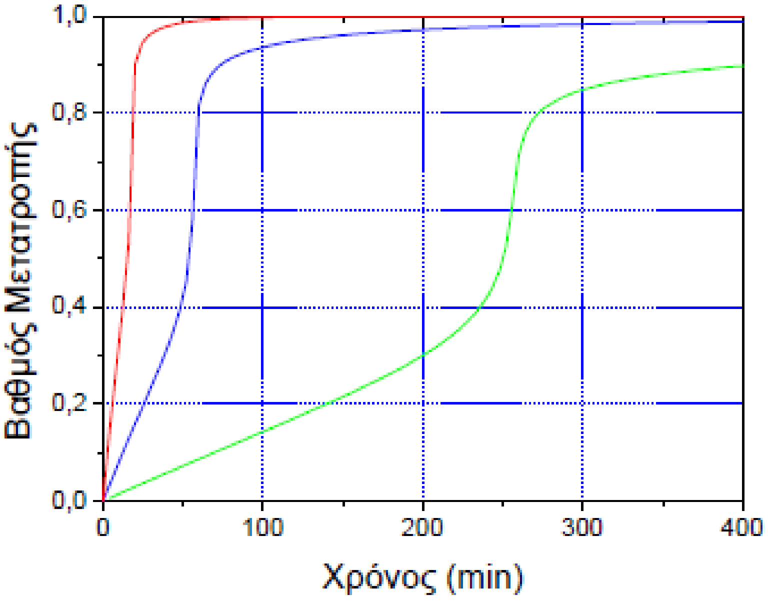


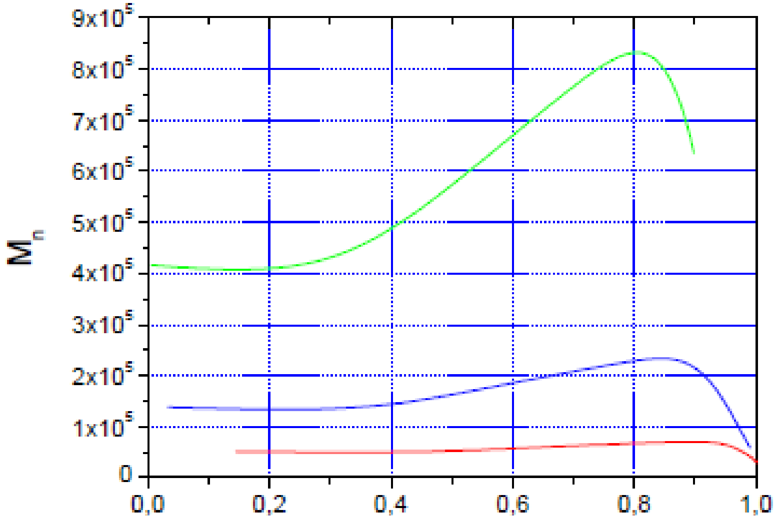
Isothermal polymerization of HEMA at different temperatures

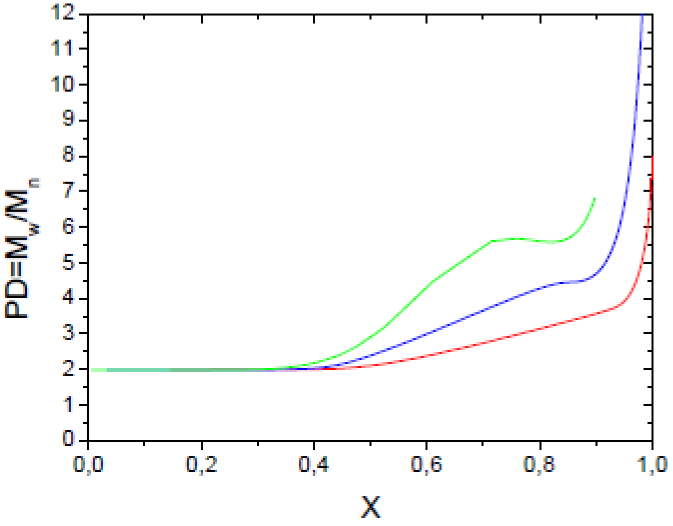


Effect of temperature on polymer average molecular weight

Polymerization of MMA at 50 °C (green line), 70 °C (blue line and 90 °C (red line)

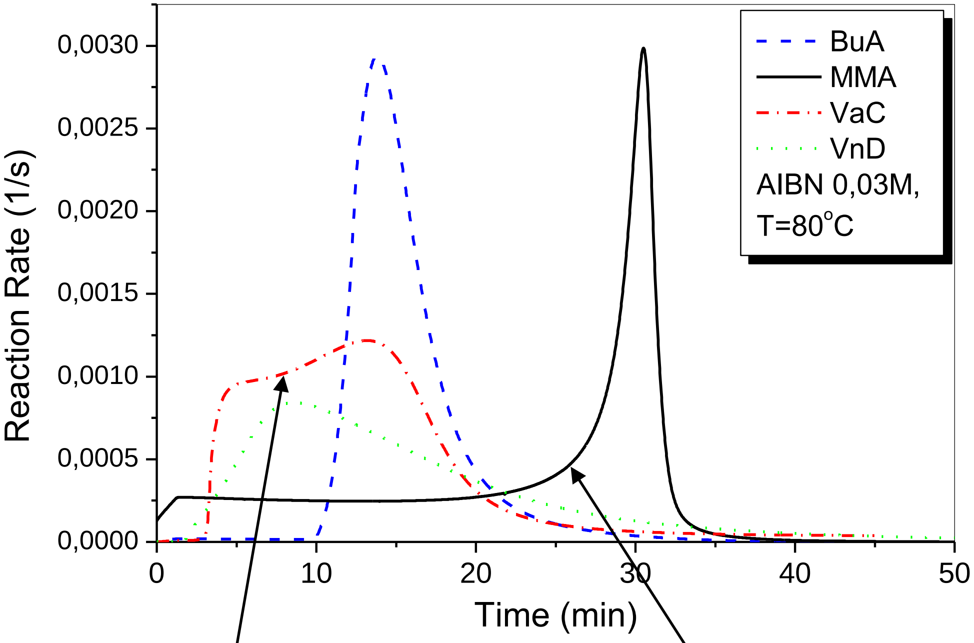






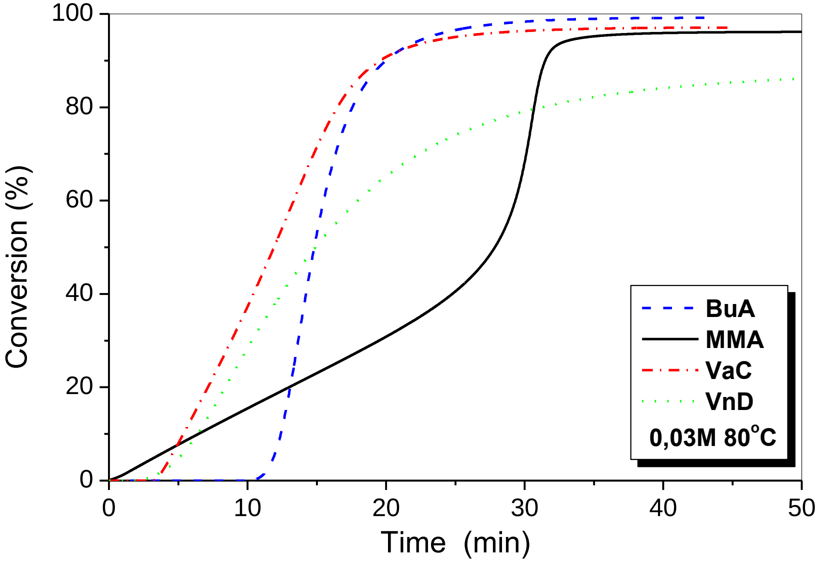
Bulk polymerization (monomer + initiator)
Effect of the monomer chemical structure

AIBN 0.03M, T=80°C



Branched polymers

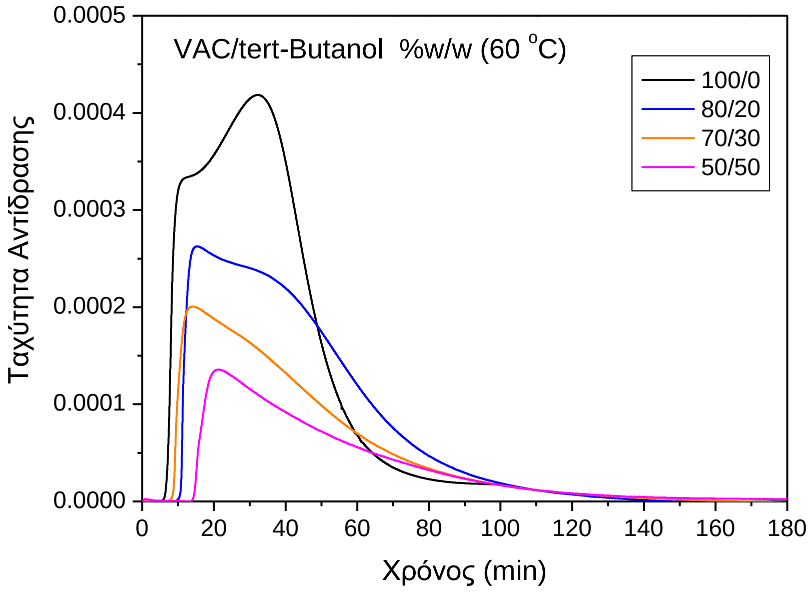
Linear polymers

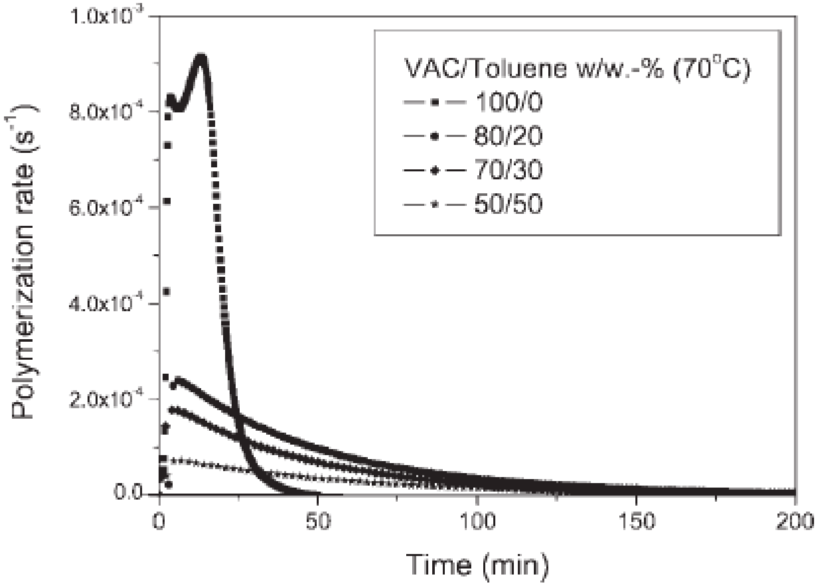


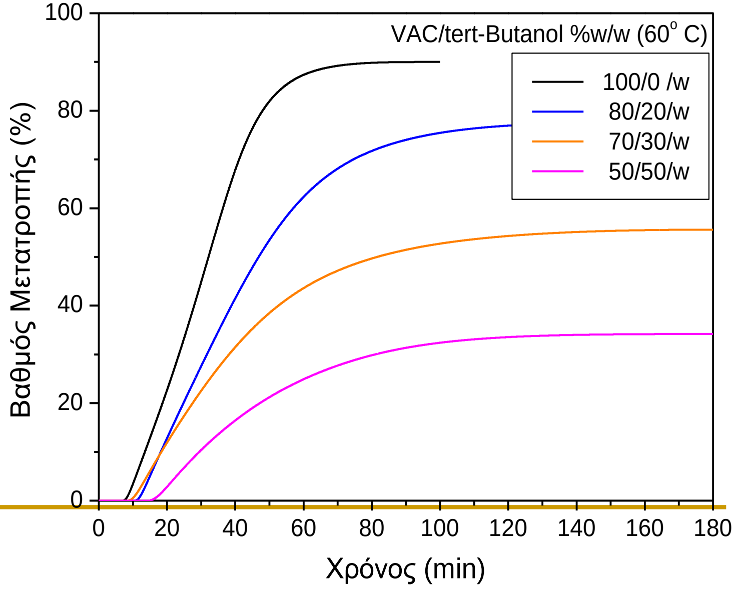
Solution polymerization

- Polymerization of Vinyl acetate in different relative amounts of the solvent t-Butanol.

- Possible existence of side chain transfer to solvent reactions.

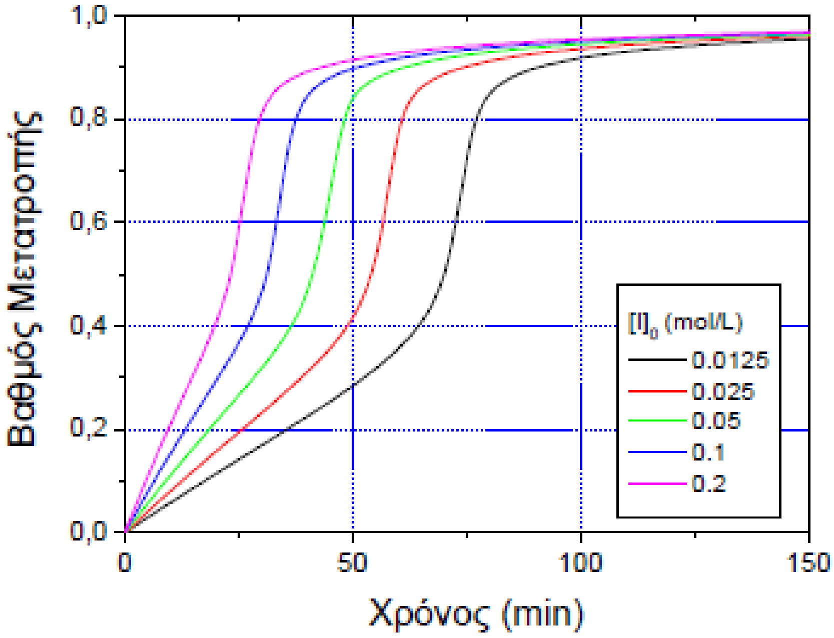


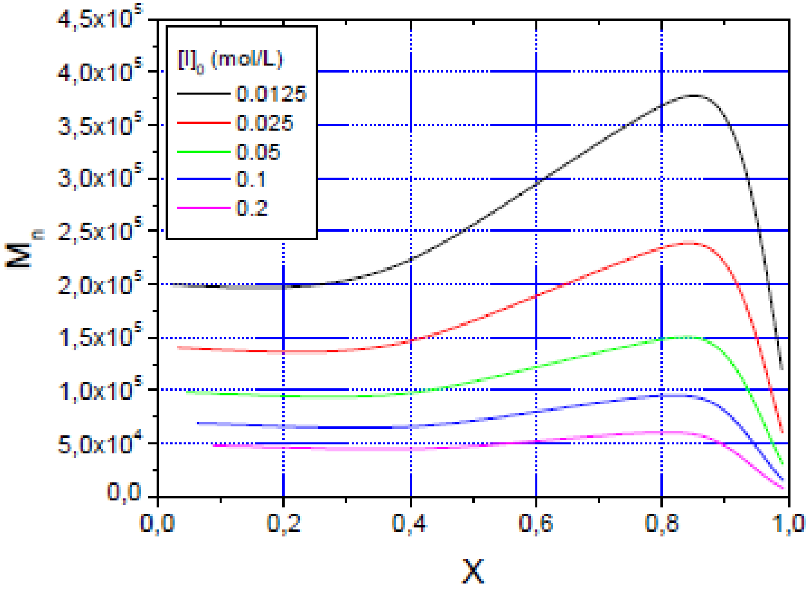




Effect of the initial initiator concentration

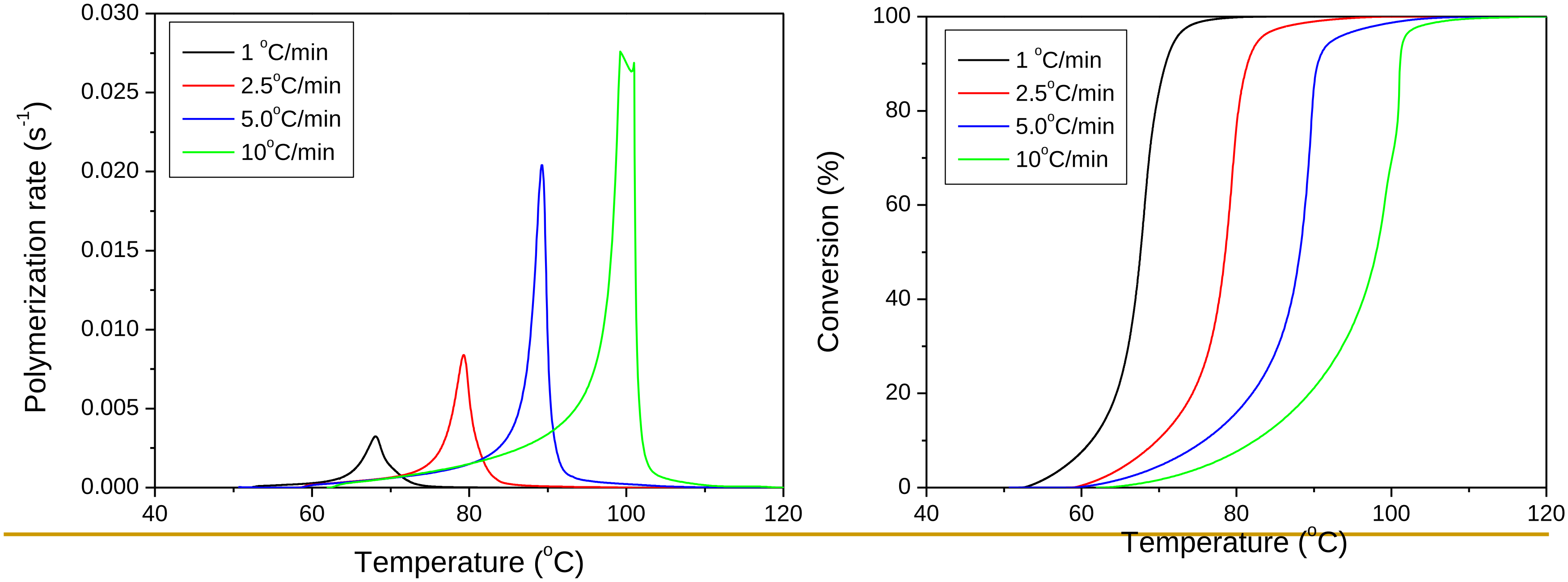
As $[I]_0$ increases, polymerization rate and monomer conversion increase whereas the average molecular weigh decrease





Non-isothermal experiments of PHEMA

- Effect of heating rate on the variation of polymerization rate (a) and conversion (b) with temperature during non-isothermal bulk polymerization of HEMA with 0.03 M BPO



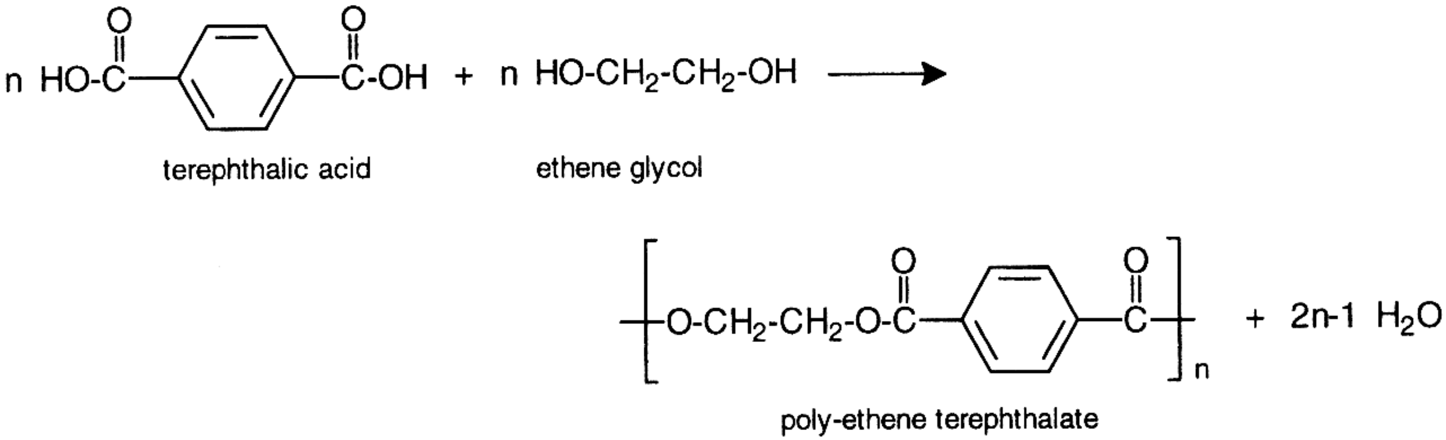
Experimental techniques for measuring the variation of polymerization rate and conversion in chain polymerization

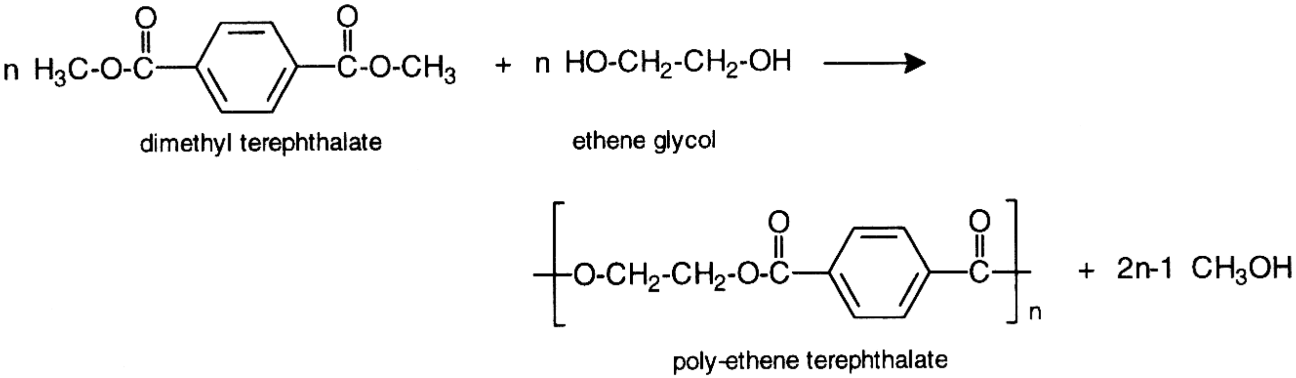
- Gravimetric (direct weighing)
- Dilatometry, measure the variation of reaction volume
- Measurement of physical properties (density, viscosity, refractive index)
- Light scattering
- Chromatographic methods (GC)
- Phasmatophotometry (UV, FTIR)
- Thermochemical methods (DSC)

STEP POLYMERIZATION

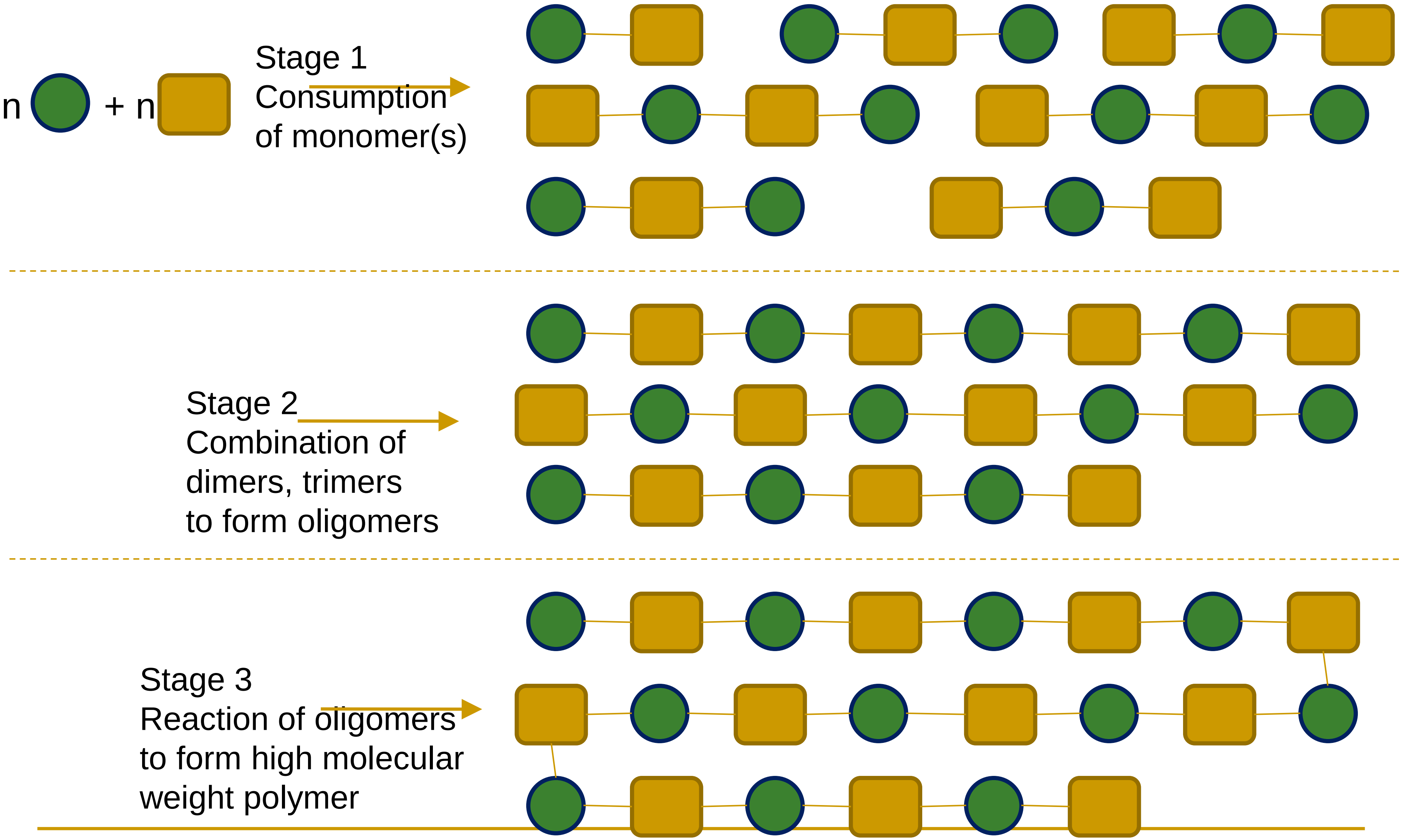
Main features of step polymerization

- The reacting monomer(s) should have at least two characteristic terminal groups
- A small molecule is produced as by-product





Stages in Step polymerization



n ● + n ■

Stage 1
Consumption
of monomer(s)

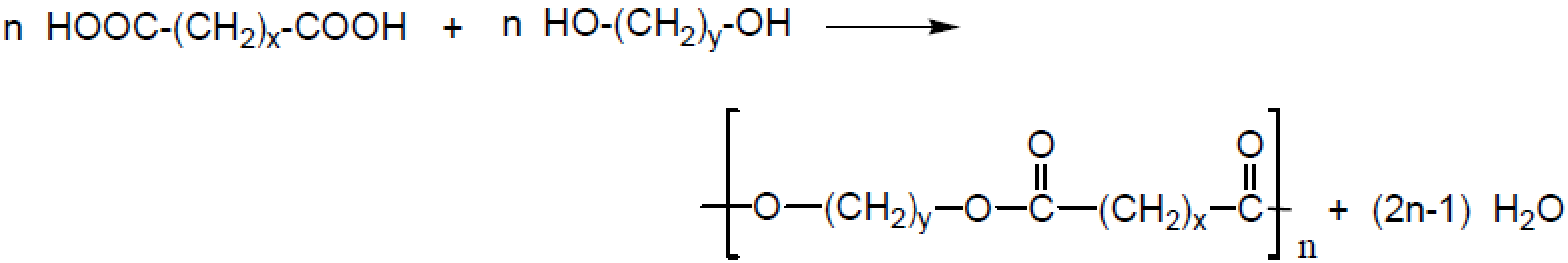
Stage 2
Combination of
dimers, trimers
to form oligomers

Stage 3
Reaction of oligomers
to form high molecular
weight polymer

Synthesis of polyesters

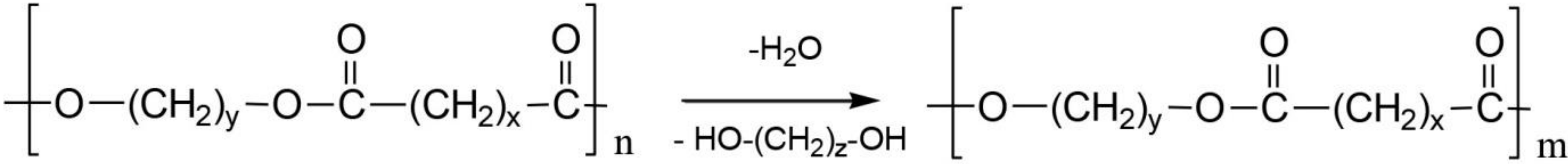
dicarboxylic acid + diol → polyester + water

1st Step Esterification



$$n\ \mathrm{HOOC\text{-}(CH_2)_x\text{-}COOH} + n\ \mathrm{HO\text{-}(CH_2)_y\text{-}OH} \longrightarrow \left[\mathrm{O}-(\mathrm{CH_2})_y-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_x-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \right]_n + (2n-1)\ \mathrm{H_2O}$$

2nd step Polycondensation

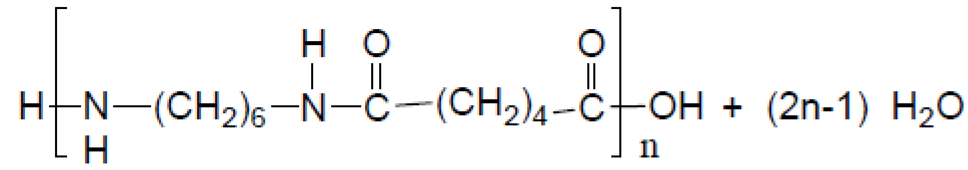


$$\left[\mathrm{O}-(\mathrm{CH_2})_y-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_x-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \right]_n \xrightarrow[-\ \mathrm{HO\text{-}(CH_2)_z\text{-}OH}]{-\mathrm{H_2O}} \left[\mathrm{O}-(\mathrm{CH_2})_y-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_x-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \right]_m$$

Oligomers

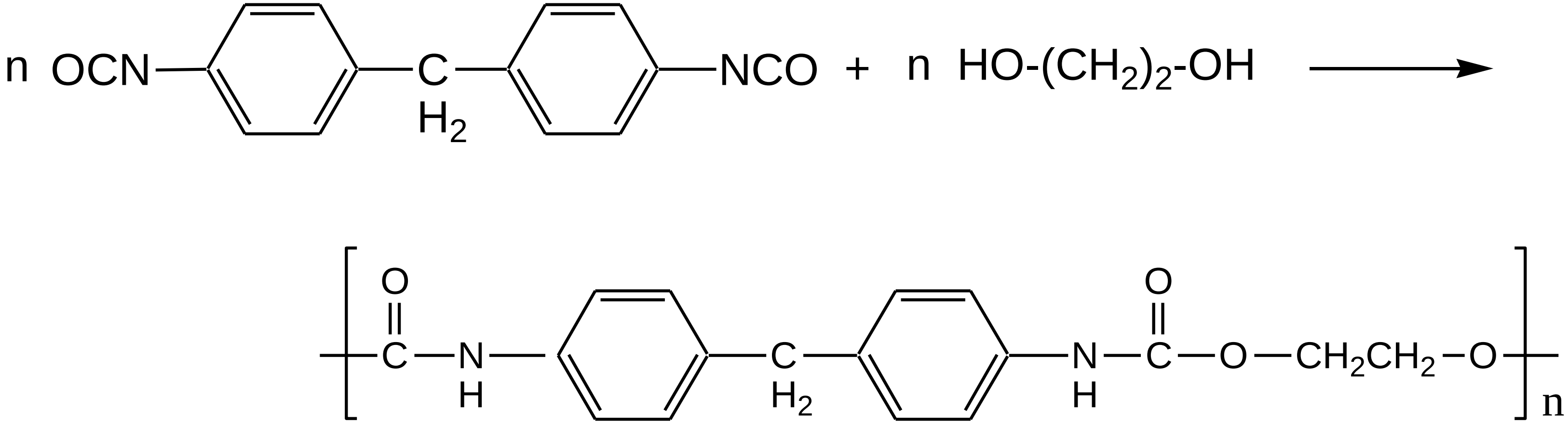
Polymer

- Synthesis of polyamides (e.g. Nylon 6,6



$$n\ HOOC\text{-}(CH_2)_4\text{-}COOH + n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 \longrightarrow H\!\left[\underset{H}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\right]_n OH + (2n-1)\ H_2O$$

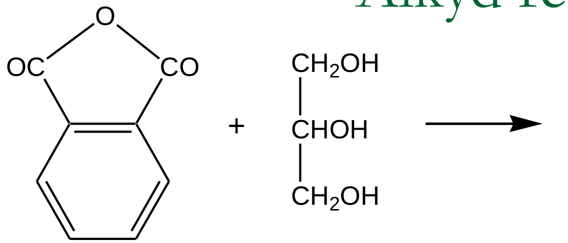
- Synthesis of polyurethanes

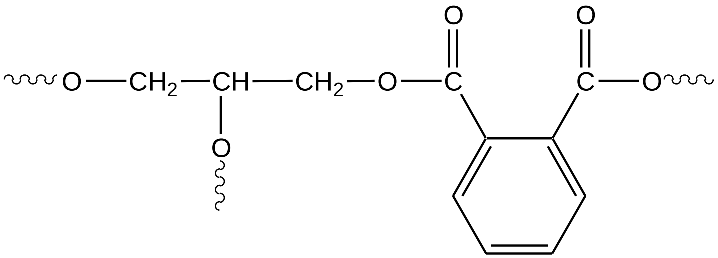


Formation of crosslinked networks when one of the reacting monomers have more than 2 reacting terminal groups (e.g. using glycerin instead of a diol)

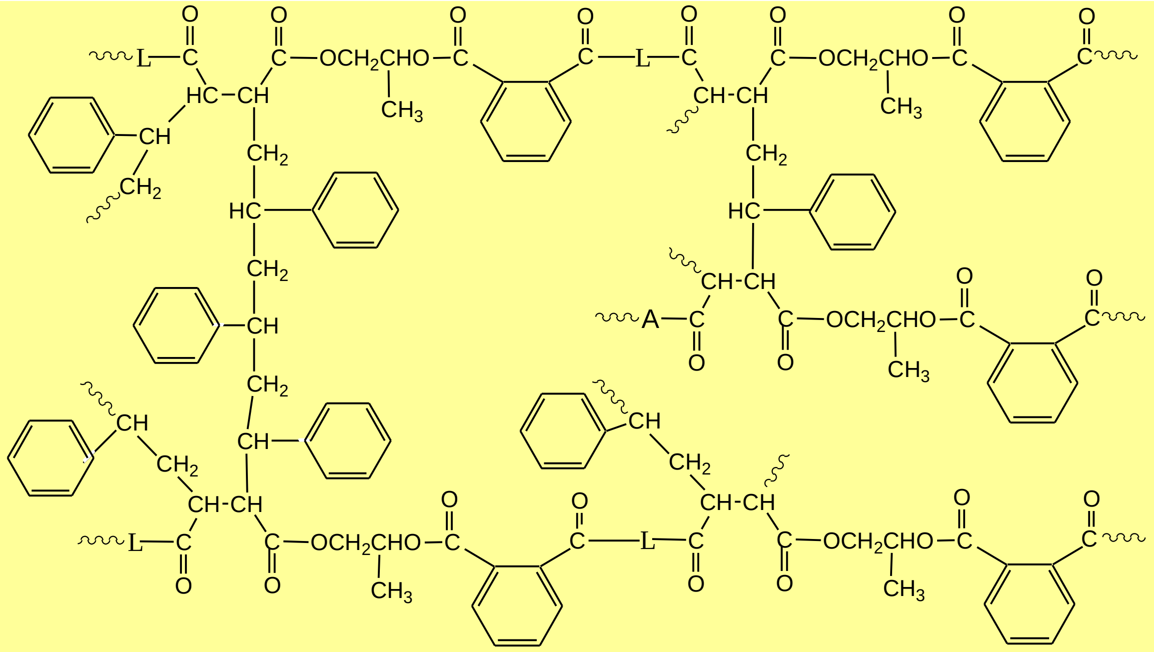
Examples

Alkyd resins



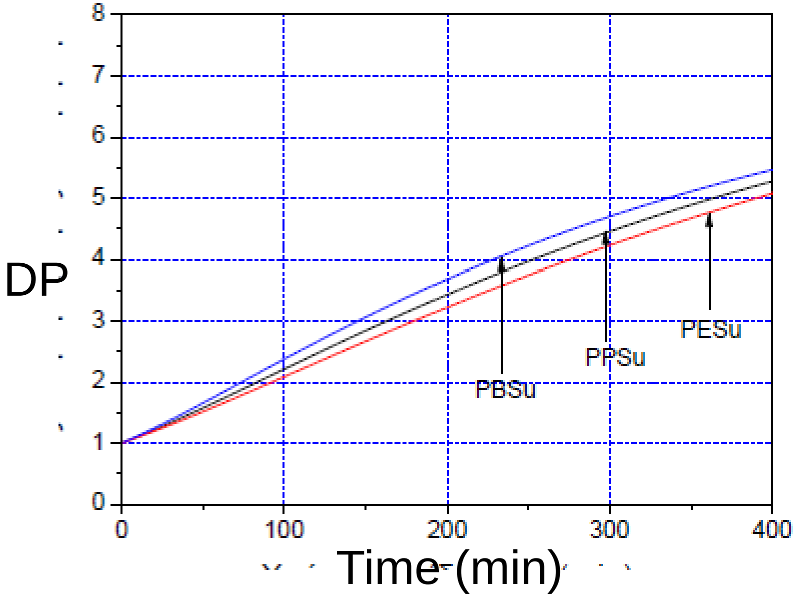


Unsaturated polyester resins

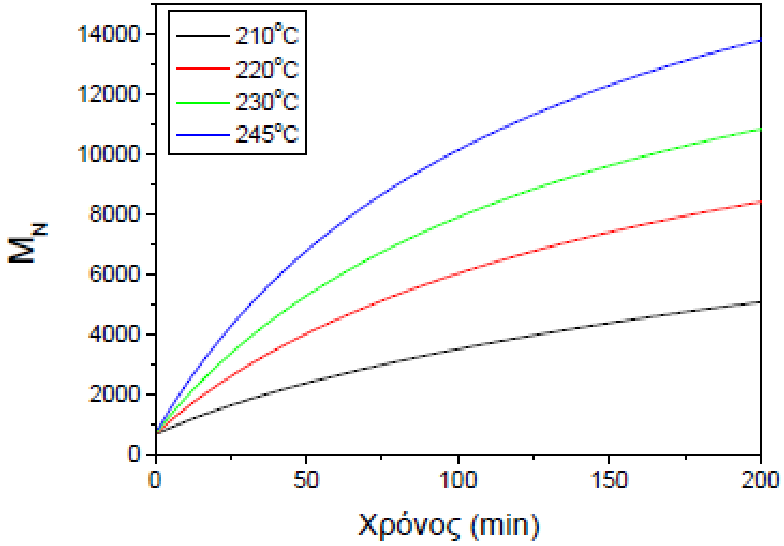


Step polymerization kinetics

- 1st step esterification



- 2nd step polycondensation

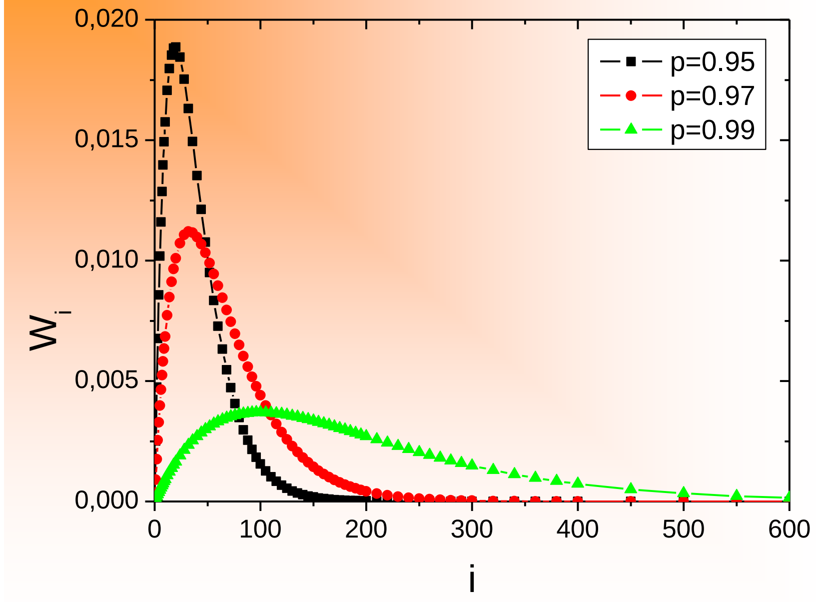


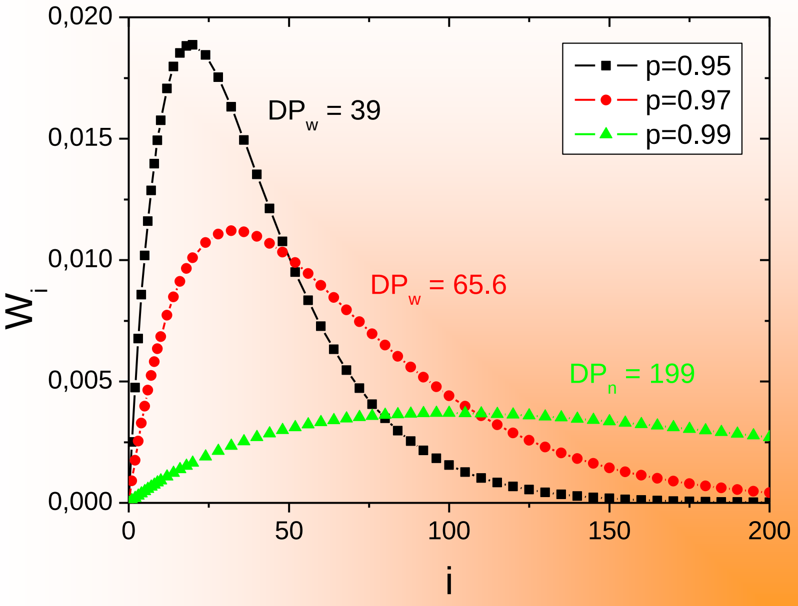
Variation of the MWD with monomer conversion in step polymerization

- Mass fraction of macromolecules with i structural units W_i
- $W_i = i\,p^{i-1}(1-p)^2$
- p is the reaction extent t.

$$DP_n = \frac{\sum_i iN_i}{\sum_i N_i} = \frac{\sum_i ip^{i-1}}{\sum_i p^{i-1}} = \frac{1+2p+3p^2+\ldots}{1+p+p^2+\ldots} = \frac{\frac{1}{(1-p)^2}}{\frac{1}{(1-p)}} = \frac{1}{(1-p)}$$

$$DP_w = \frac{\sum_i iW_i}{\sum_i W_i} = \frac{\sum_i i^2p^{i-1}}{\sum_i ip^{i-1}} = \frac{1+4p+9p^2+\ldots}{1+2p+3p^2+\ldots} = \frac{2}{(1-p)} - 1 = \frac{1+p}{1-p}$$





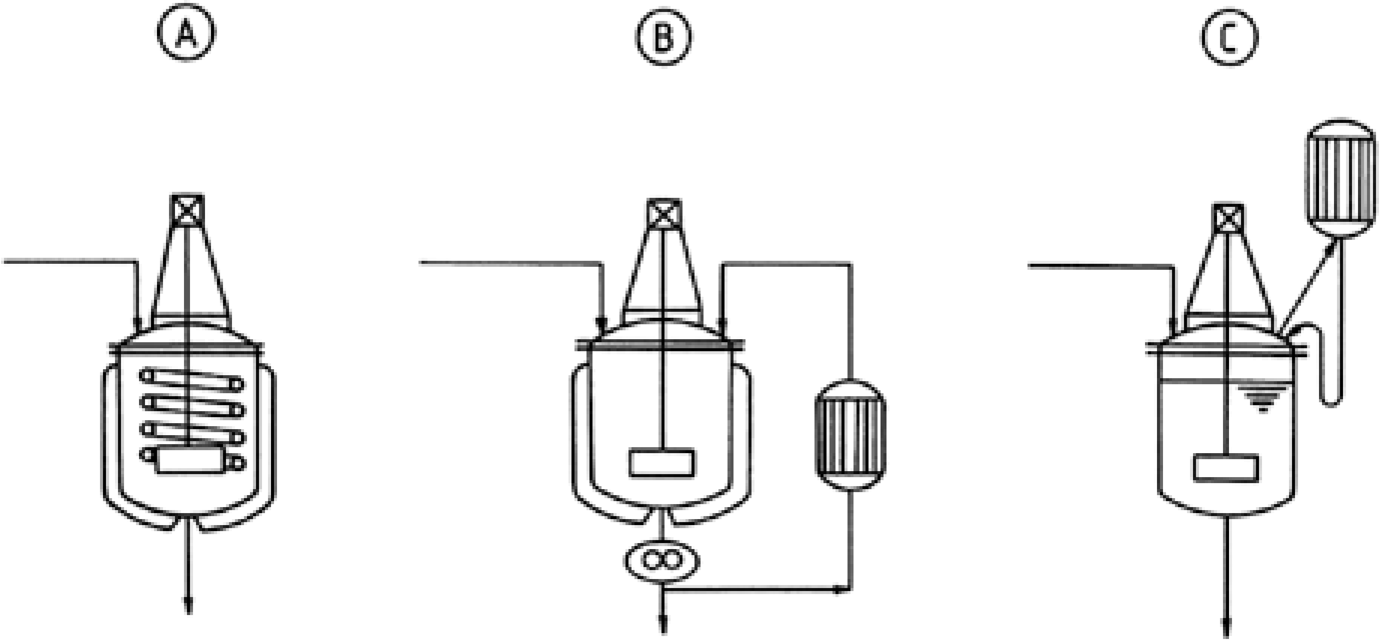
The maximum of the distribution is the number average degree of polymerization,DP_n

POLYMERIZATION TECHNIQUES

Problems that attend mechanical design of polymerization systems

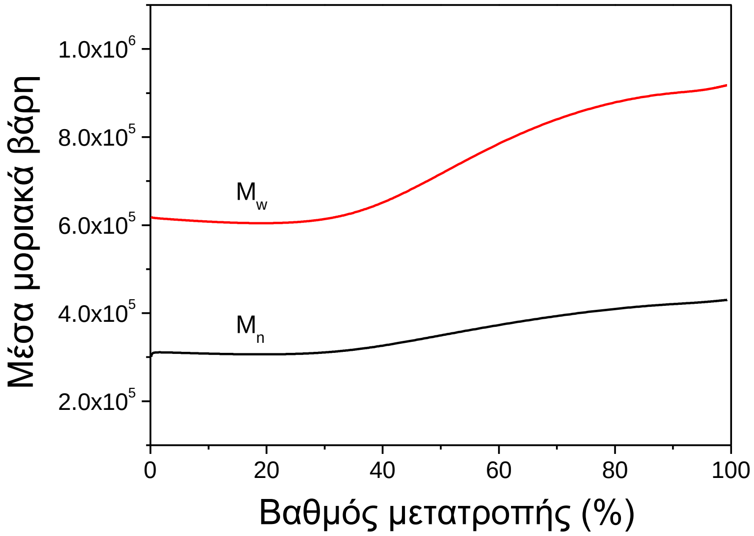
- **Hazardous monomers, solvents, catalysts, Toxicity (acrylonitrile), potential carcinogen (VCM)**, Flammability (Ziegler-Natta catalysts-PP production-involve aluminum triethyl, which is pyrophoric-bursts spontaneously into flames on exposure to air), odors (lower acrylates).
- Chain polymerization reactions since they are addition reactions produce a significant amount of heat (reaction enthalpy). This is not the case in step polymerizations.
- Great care should be taken to remove this high amount of heat produced during the reaction, which results in adiabatic temperature increase as high as 730, 320 and 270 (^{o}C) during polymerization of VCM, styrene and methyl methacrylate, respectively.

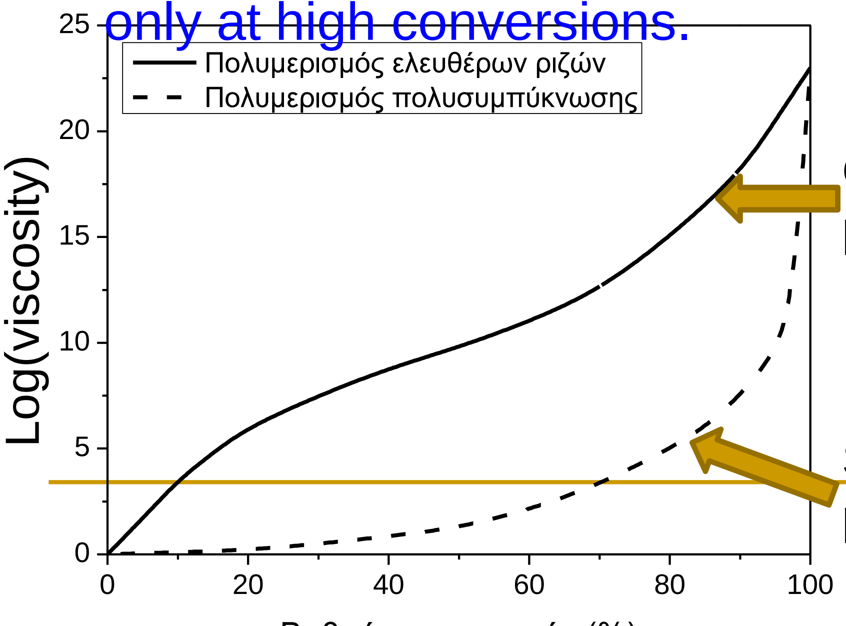
Processes for the removal of the amount of heat produced during chain polymerization (A) jacket and cooling coil, (B) jacket and external cooling (C) cooling condenser



Increase of the mixture viscosity during polymerization

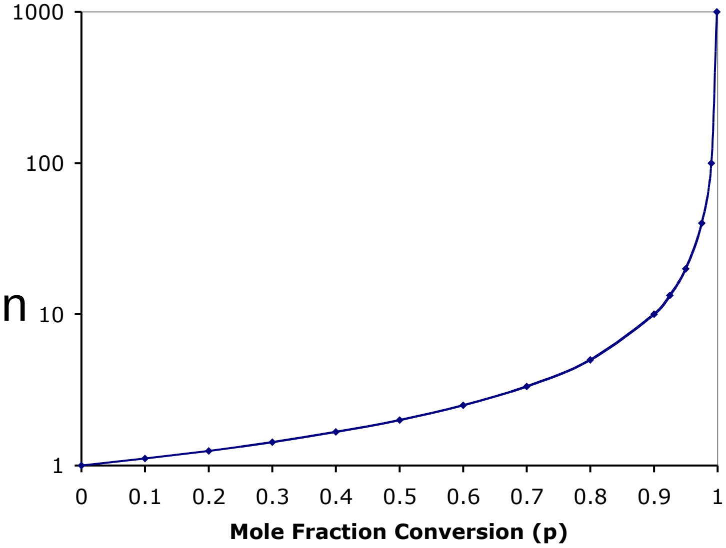
- Typical monomer viscosity 0.5 cp, while polymer melt viscosity 10^5 p (PS, 160^oC) to 10^6 p (PE, 150^oC).
- In chain, radical polymerization, long chain macromolecules are produced from the beginning of polymerization. Therefore, the mixture viscosity increases from the early stages of the reaction.
- In step-polycondensation reactions long chain macromolecules are produced at conversions higher than 90%. Therefore, significant viscosity increase is observed only at high conversions.



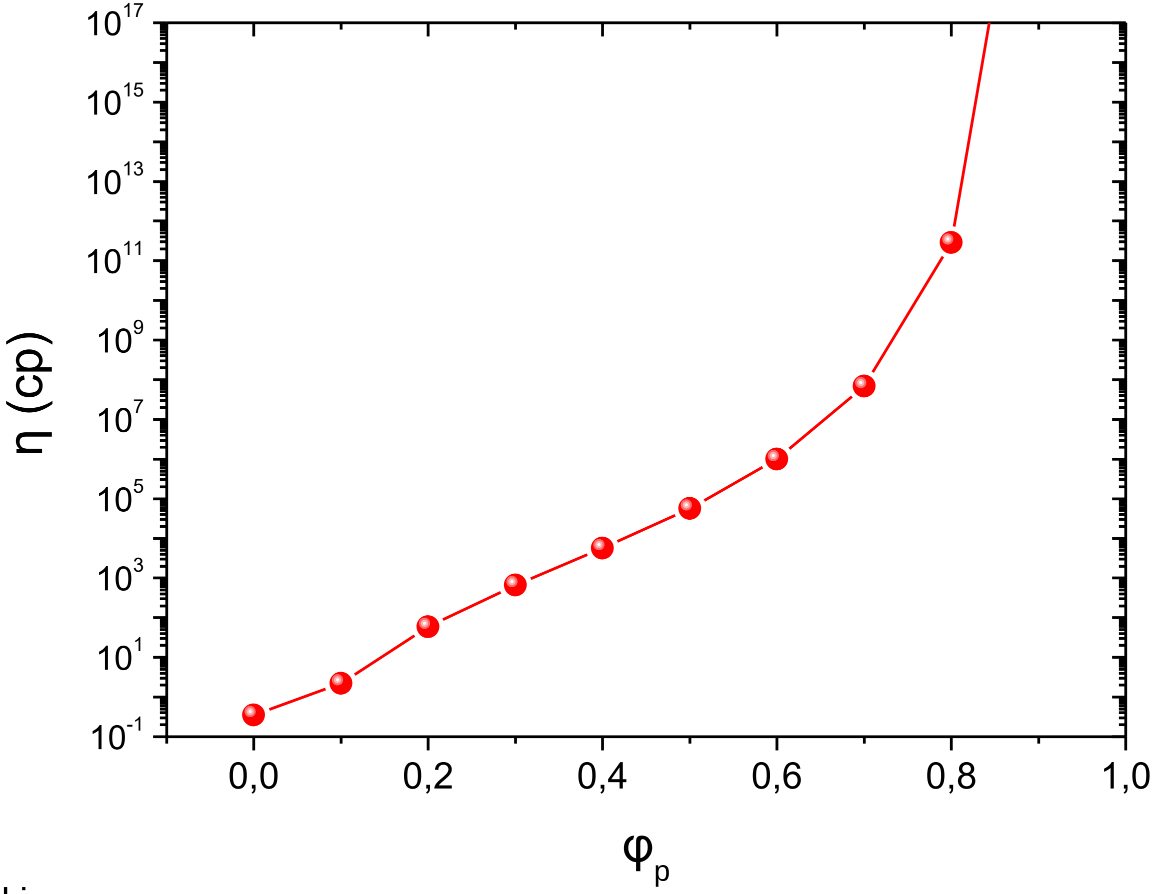


Chain polymerization

Step polymerization



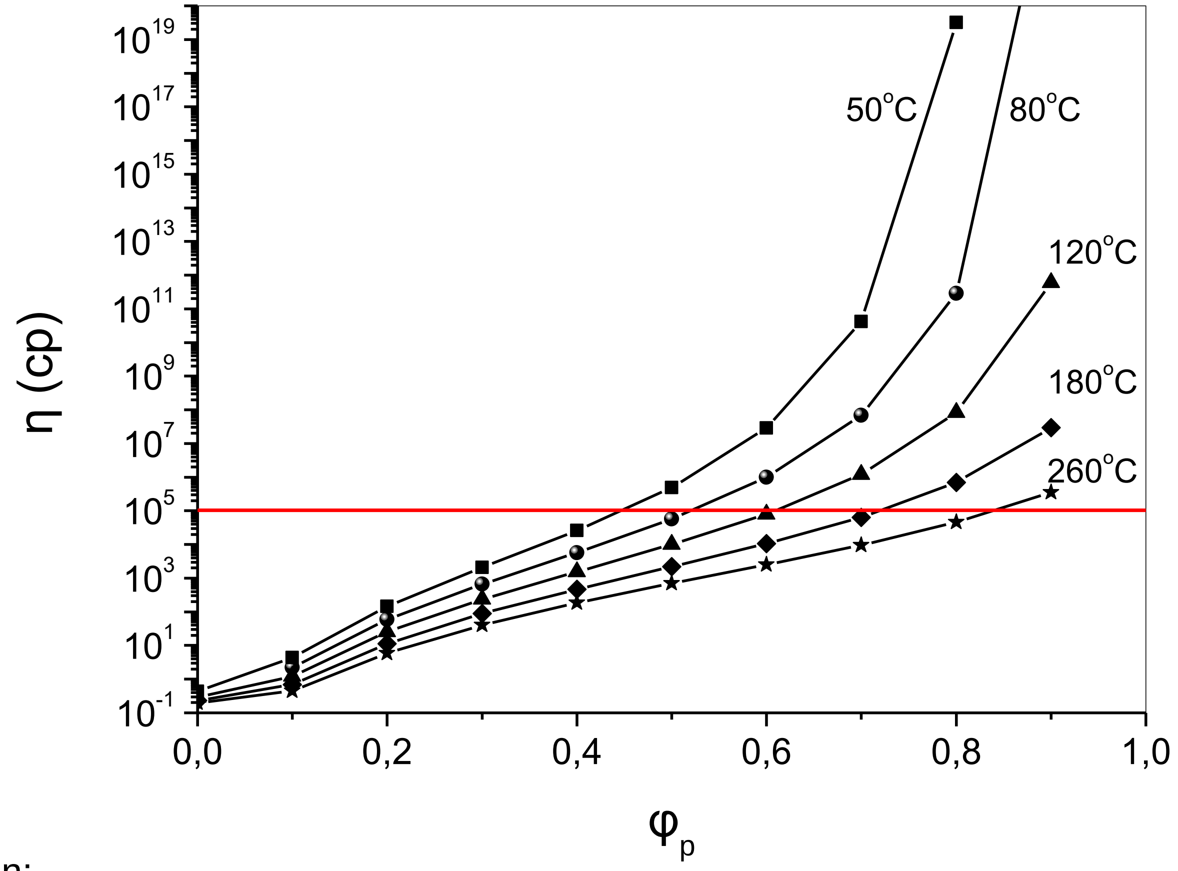
Variation of the reaction mixture viscosity with the volume fraction of the polymer during bulk radical polymerization of methyl methacrylate



Equation provided in:

PIERRE E. BAILLAGOU & DAVID S. SOONG (1985) A VISCOSITY CONSTITUTIVE EQUATION FOR PMMA—MMA SOLUTIONS, Chemical Engineering Communications, 33:1-4, 125-134, DOI: 10.1080/00986448508911164

Carrying out the reaction at higher temperatures results in reduced viscosity of the mixture. Data from the bulk radical polymerization of MMA to PMMA



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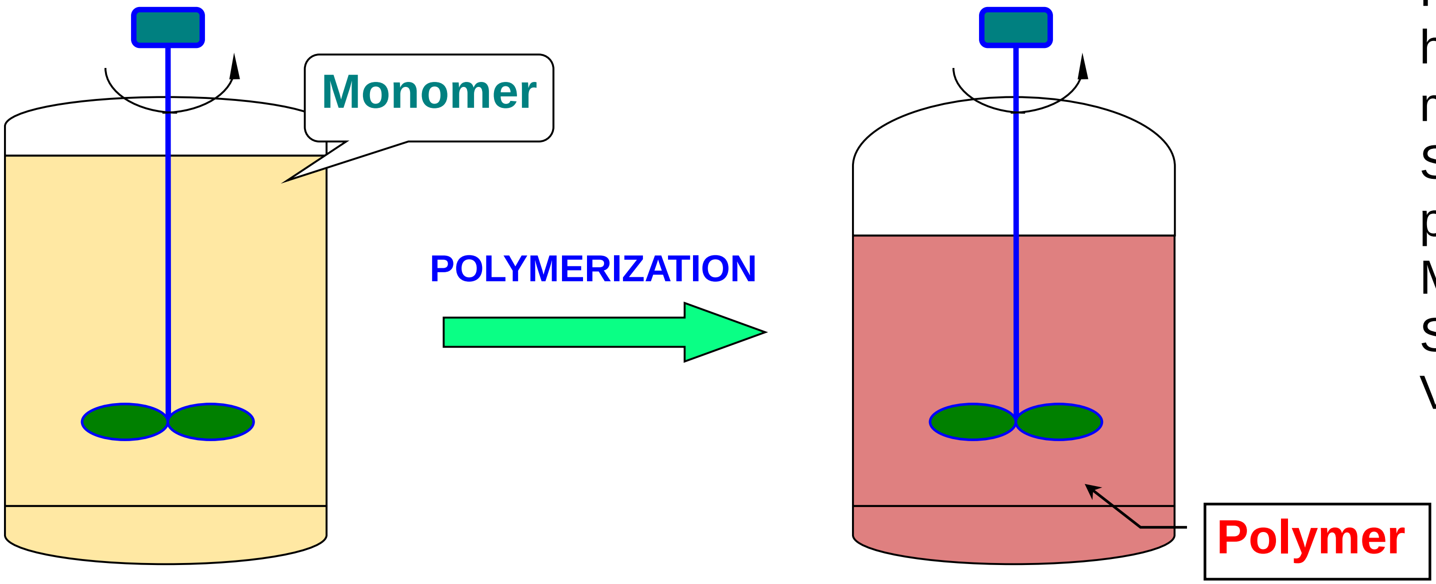
Volume shrinkage during polymerization



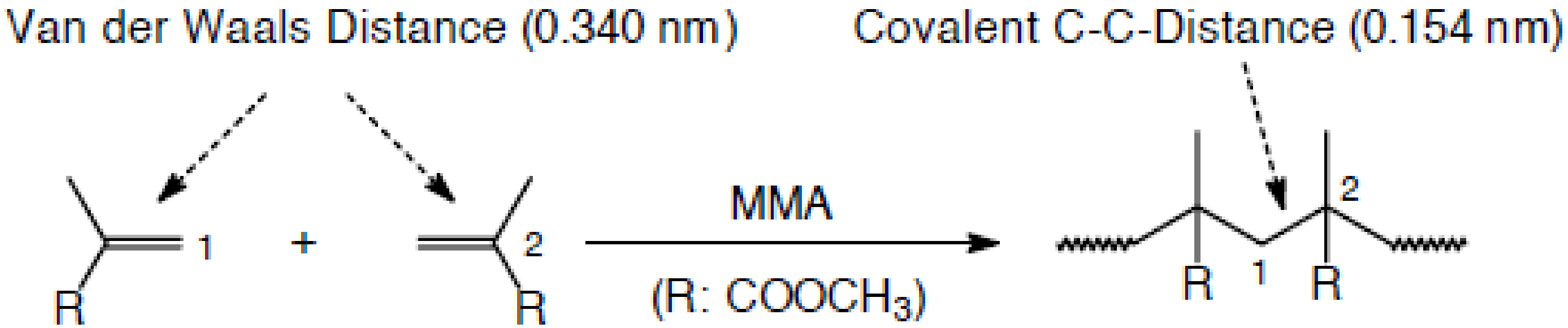
Polymer density higher than the monomer density

Shrinkage during polymerization of

MMA : 23%

Styrene: 15%

VCM: 34%



Issues in step-polycondensation reactions

- In polycondensation it is very important to achieve during the reaction the necessary stoichiometry between the two reacting monomers
- Since the reactions are two-way, in order to be able to shift the reaction in the direction of producing high molecular weight macromolecules, it is very important to remove the by-products of the reaction, especially towards the end of it.
- This removal is achieved either with condensers at the top of the reactor or by applying a very high vacuum.

Polymerization techniques

- Homogeneous
  - Bulk (mass) polymerization)
  - Solution polymerization (polymer dissolved in solvent and monomer)
- Hybrid processes
  - Precipitation polymerization (polymer not dissolved in its monomer
- Heterogeneous polymerization
  - Suspension polymerization
  - Emulsion polymerization
  - Slurry polymerization
  - Gas phase polymerization

Polymerization techniques

- A technique is not unique for the production of a specific polymer. Polystyrene can be produced from bulk, solution, suspension or emulsion polymerization.
- A polymer is not produced only by a specific technique: HDPE can be produced by gas phase, or slurry polymerization.
- Different types of reactors can be used (i.e. batch, semi-batch, continuous in stirred tanks, tubular, etc.)

Bulk polymerization

- Only monomer(s) and initiator in the reactor
- Application to the polymerization of PMMA sheets, PS, LDPE in tubular reactors, etc.
- Can be carried out in batch or continuous reactors.
- Advantages
  - Polymer without any contaminants
- Disadvatages
  - Large amount of heat is released during the reaction leading to increased temperature, higher reaction rates and broader molecular weight distribution.
  - Viscosity increases as conversion increases, making heat removal and processing more difficult.
- Process scheme
  - Carry out the reaction at low monomer conversions in continuous reactors and separate and recycle the unreacted monomer

Solution polymerization

- Monomer(s), initiator and solvent in the reaction mixture
- If the polymer produced is soluble in the solvent and the monomer then the process is homogeneous (Vinyl acetate in toluene, styrene in ethylbenzene, etc.)
- If the polymer is insoluble in the solvent or the monomer then we have the precipitation polymerization (heterogeneous mixture) (acrylonitrile in aqueous solution).
- Advantages:
  - Solvent acts as a diluent and aids in removal of heat of polymerization.
  - Solvent reduces viscosity, making processing easier.
  - Thermal control is easier than in the bulk.
- Disadvantages:
  - Chain transfer to solvent occurs, leading to low molecular weights.
  - Difficult to remove solvent from final form, causing degradation of bulk properties.
  - Environmental pollution due to solvent release.

New trends in solution polymerization

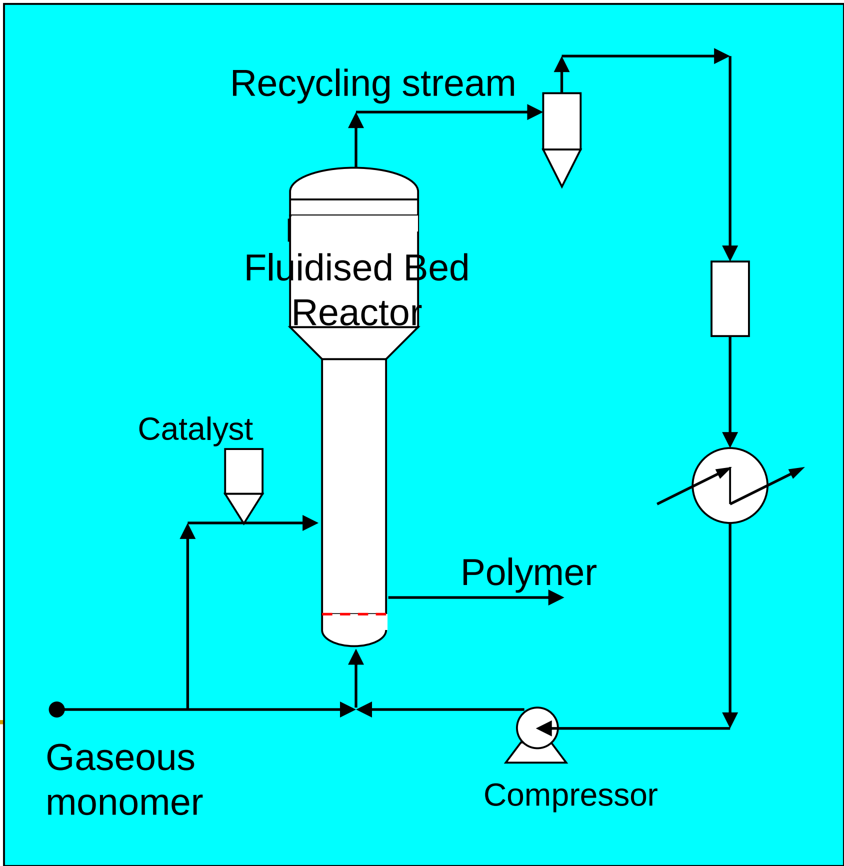
- Replace typical organic, potentially harmful, solvents with other more environmentally friendly.
- One way is to use supercritical fluids
- Fluids being in temperature and pressure above their thermodynamic critical values.
- Supercritical fluids combine properties of liquids and gases, such as low viscosity, high diffusion coefficient and density of a liquid.
- Supercritical fluids due to their ability to have several different densities depending on T and P they have been also used in polymer recycling.
- Best representative CO_2 with critical temperature 31^{o}C and pressure 73 atm. Low cost, low toxicity.
- (critical temperature and pressure for water 374^{o}C and 218 atm).
- Polymerization takes place in solution whereas after the reaction CO_2 becomes gas and is easily separated.
- Polymers: Polystyrene, Poly(methyl methacrylate), Poly(vinyl acetate), etc..

Heterogeneous polymerization

- Slurry polymerization.
- Production of polyolefins in continuous autoclaves
- Production of polypropylene in continuous loop reactors (Spheripol process)
- Reaction temperature 70-100°C, pressure 3 -4 Mpa, solvent isobutane.
- Catalyst triethyl aluminum
- Production of HDPE with Ziegler-Natta catalysts in continuous reactors and solvent (e.g. hexane)

- Gas-phase polymerization
- Production of HDPE with the Union Carbide UNIPOL method in Fluidized bed reactors.

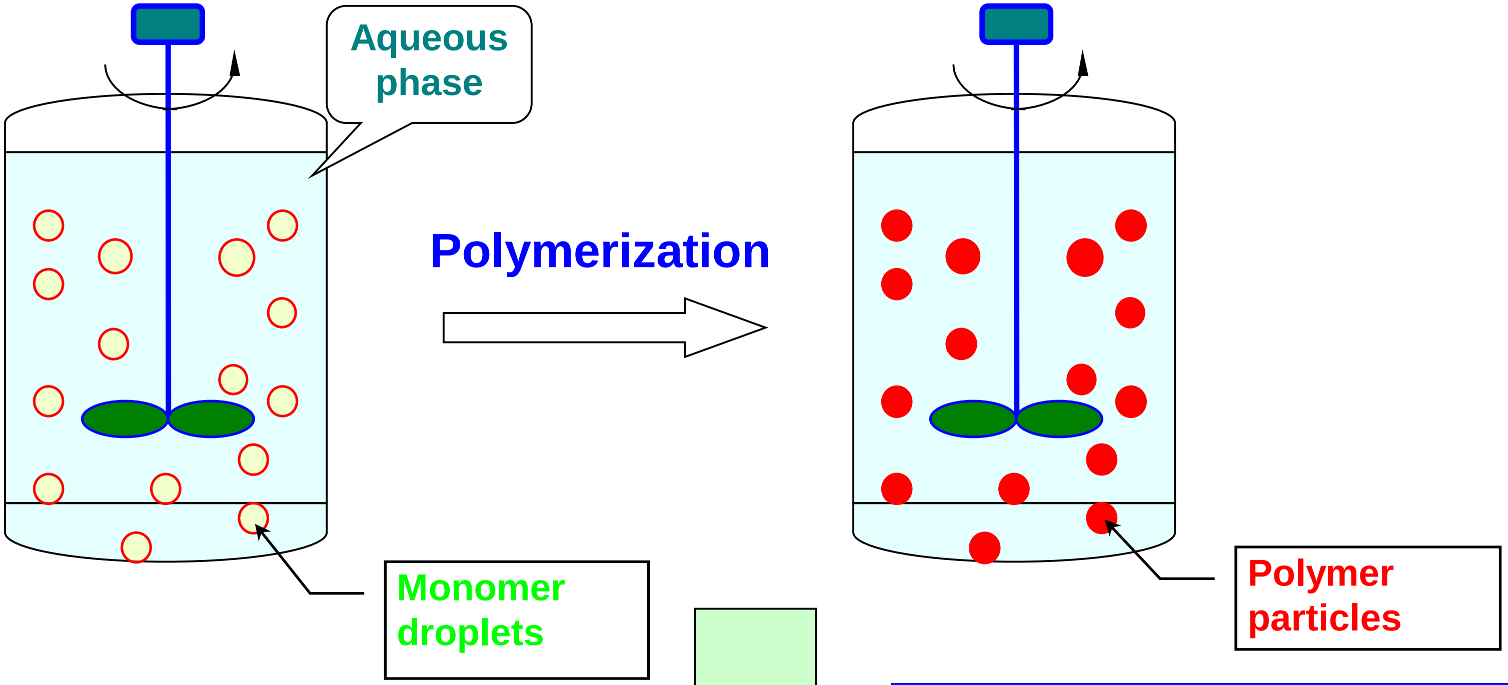
Unit at Hellenic Petroleum, Greece



Heterogeneous polymerization

Suspension polymerization

- Polymerization taking place inside the monomer droplets stabilized with surfactants and agitation. Use of oil soluble initiators. Formation of polymer particles.



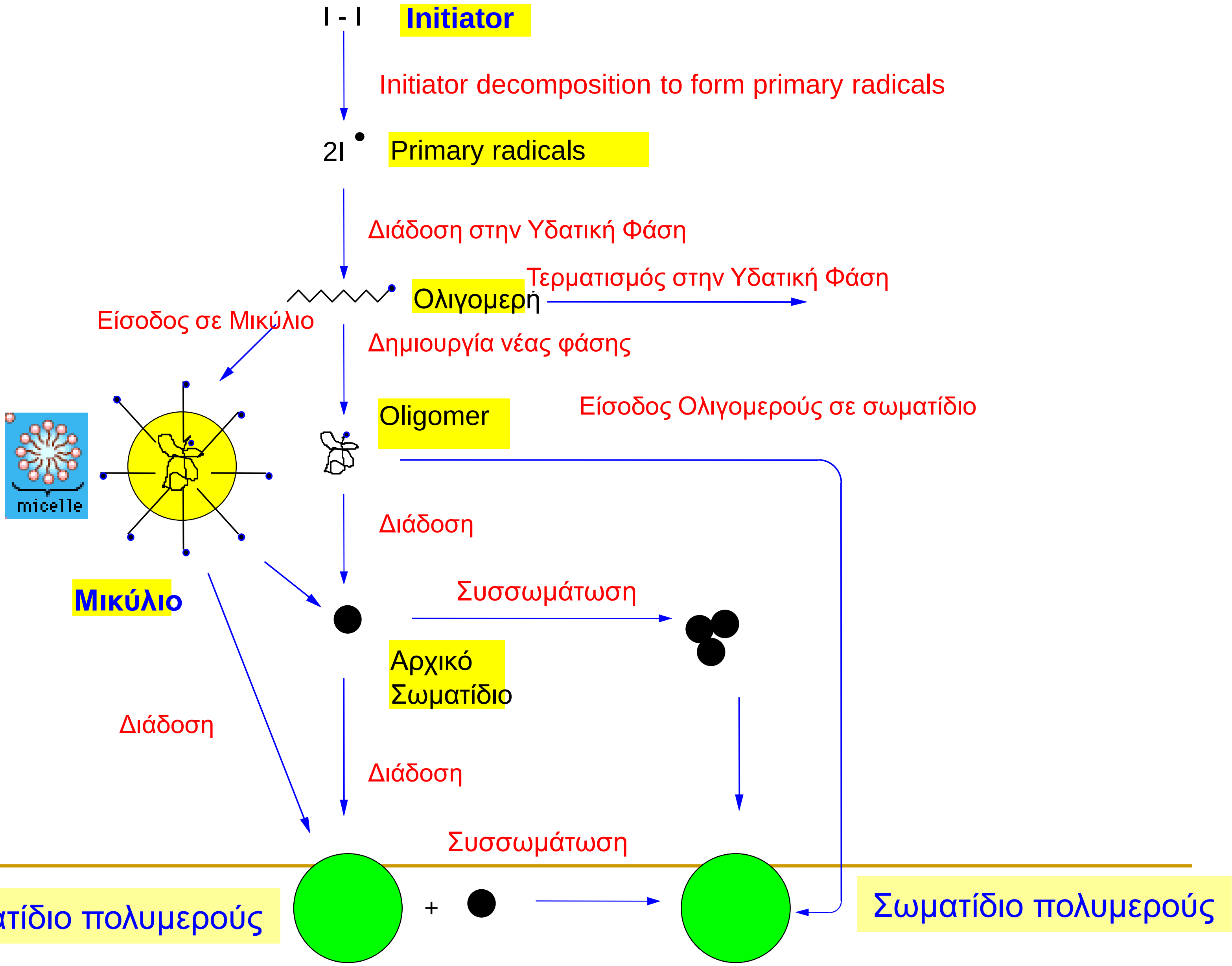
Polymer soluble in its monomer.
Formation of compact particles pearls or beads.   PMMA, PS

Polymer particles

Polymer insoluble in its monomer
Formation of, *porous powder*
PVC

Πολυμερισμός Γαλακτώματος
Μηχανισμός Σχηματισμού Σωματιδίων

Ομογενής – Μικύλια - Συσσωματώσεις



I - I **Initiator**

Initiator decomposition to form primary radicals

$2I^{\bullet}$ Primary radicals

Διάδοση στην Υδατική Φάση

Ολιγομερή

Τερματισμός στην Υδατική Φάση

Είσοδος σε Μικύλιο

Δημιουργία νέας φάσης

Oligomer

Είσοδος Ολιγομερούς σε σωματίδιο

Μικύλιο

Διάδοση

Συσσωμάτωση

Αρχικό Σωματίδιο

Διάδοση

Διάδοση

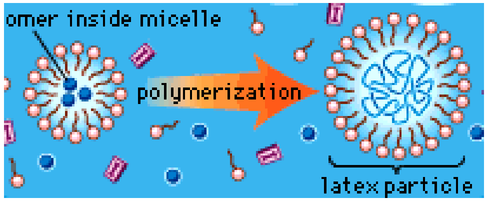
Συσσωμάτωση

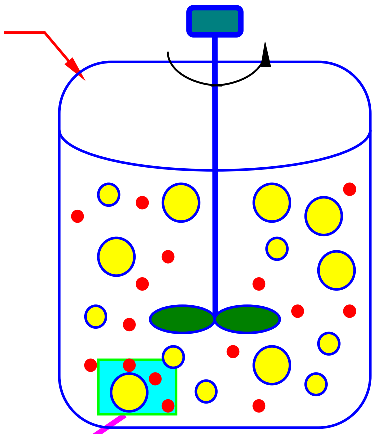
Σωματίδιο πολυμερούς

Σωματίδιο πολυμερούς

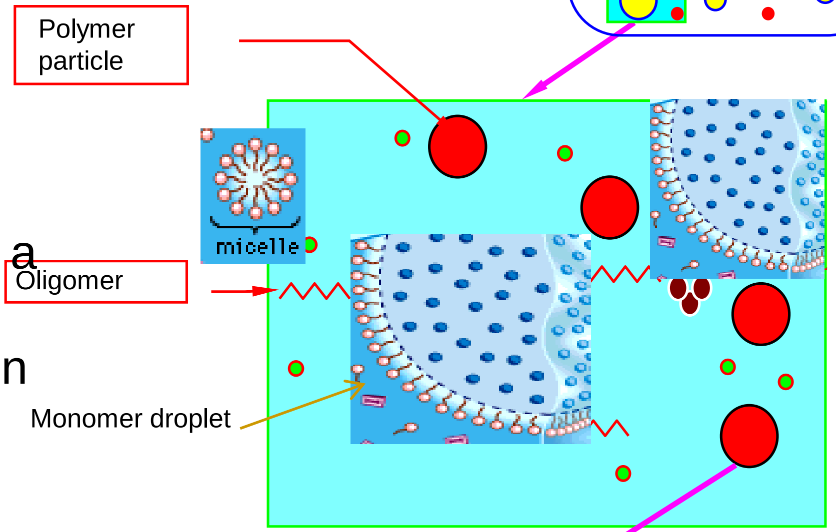
Emulsion polymerization

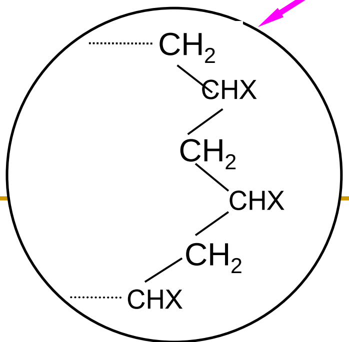
Addition of water-soluble initiator(s)
Addition of monomer and emulsifier
Initiator decomposition starts in the aqueous phase.
Emulsifier in concentration higher than CMC results in the formation of micelles
Nucleation based on micelles
Monomer molecules enter the micelle and start polymerization
Each micelle molecule is transformed into a polymer particle
Homogeneous nucleation: nucleation when emulsifier concentration is less than CMC
Particle growth through polymerization
Exhaustion of monomer droplets (all monomer molecules in monomer droplets have reacted).
Formation of the final polymer latex





Emulsion polymerization reactor

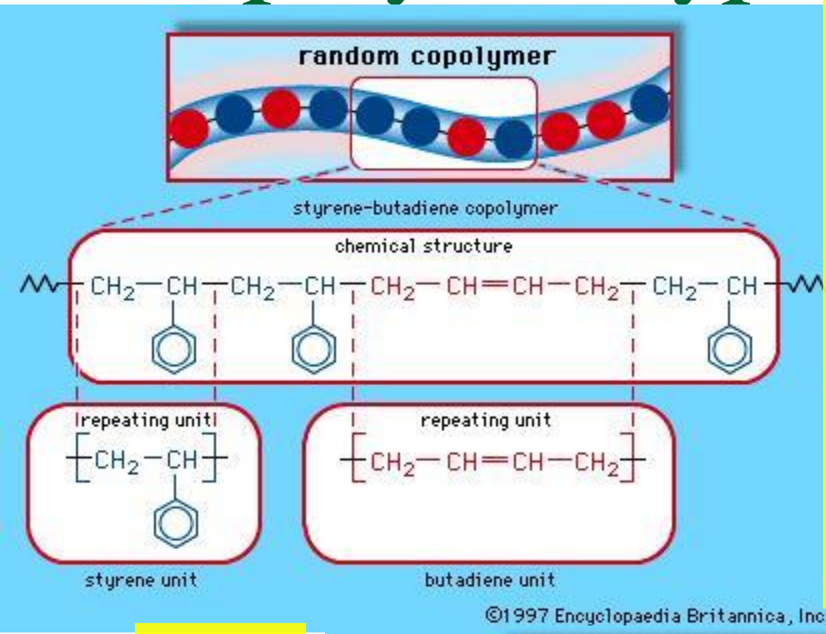




Some schemes are taken from Encyclopedia Brittanica

COPOLYMERIZATION

Copolymer types



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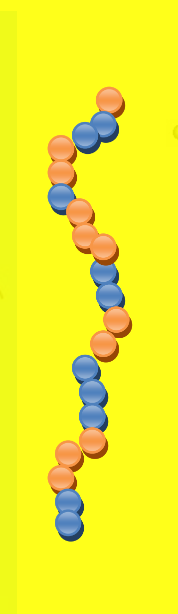

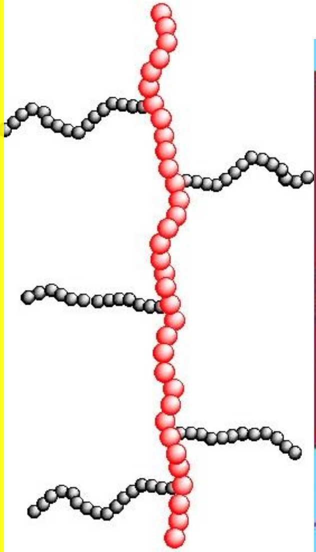

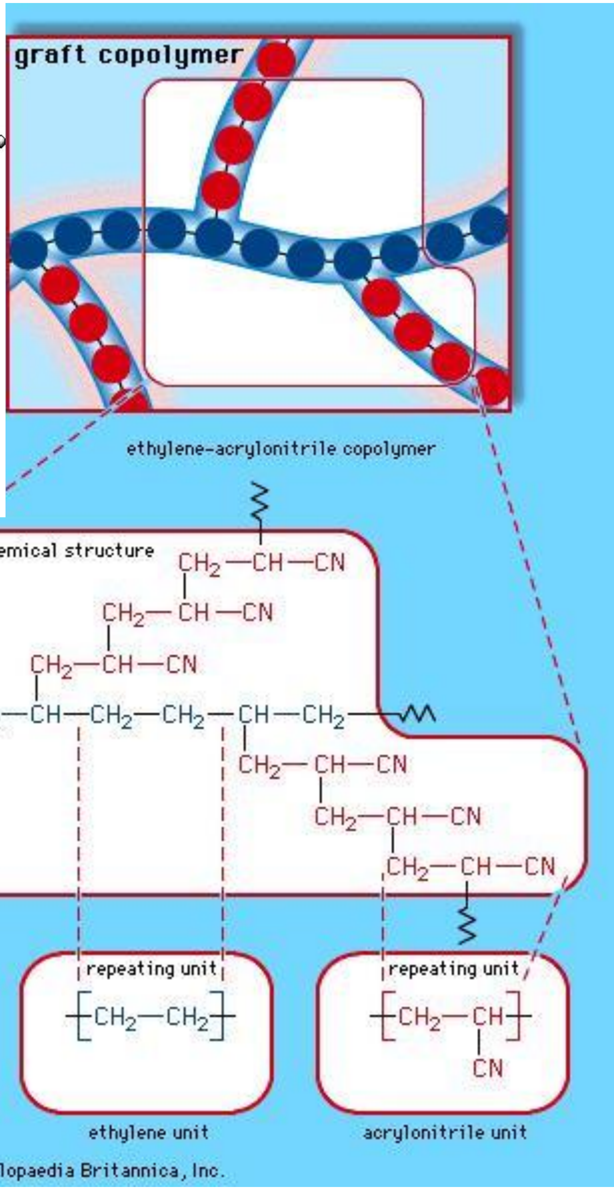

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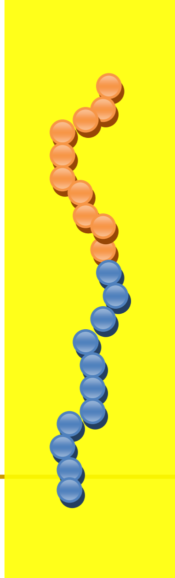

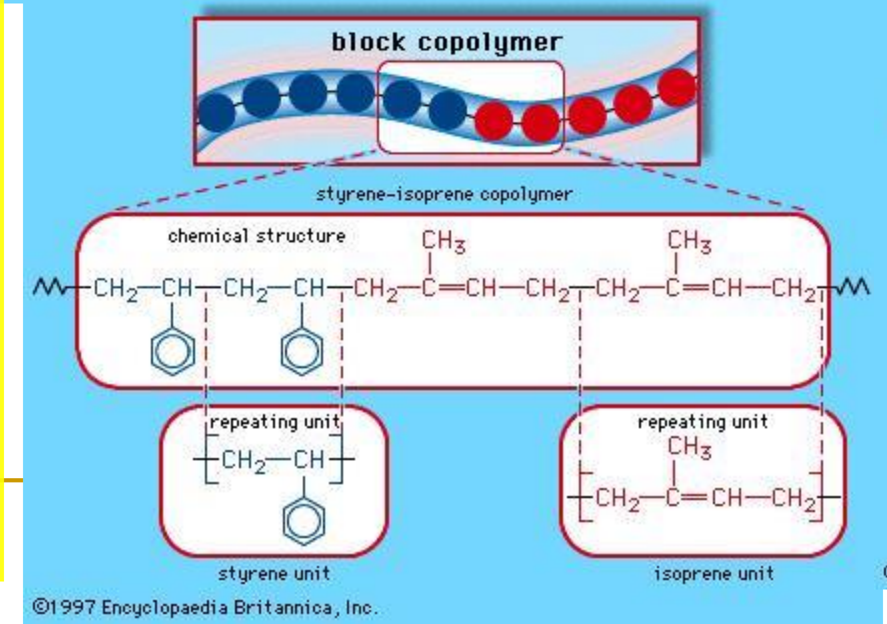

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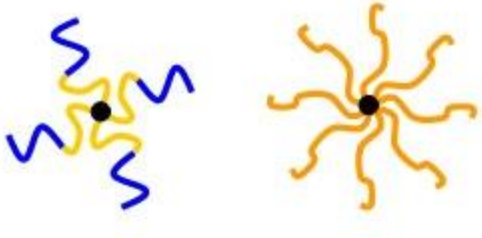
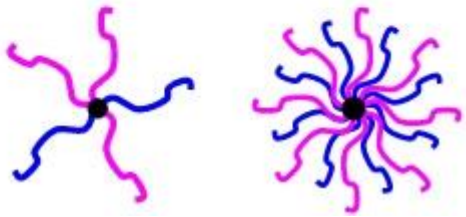
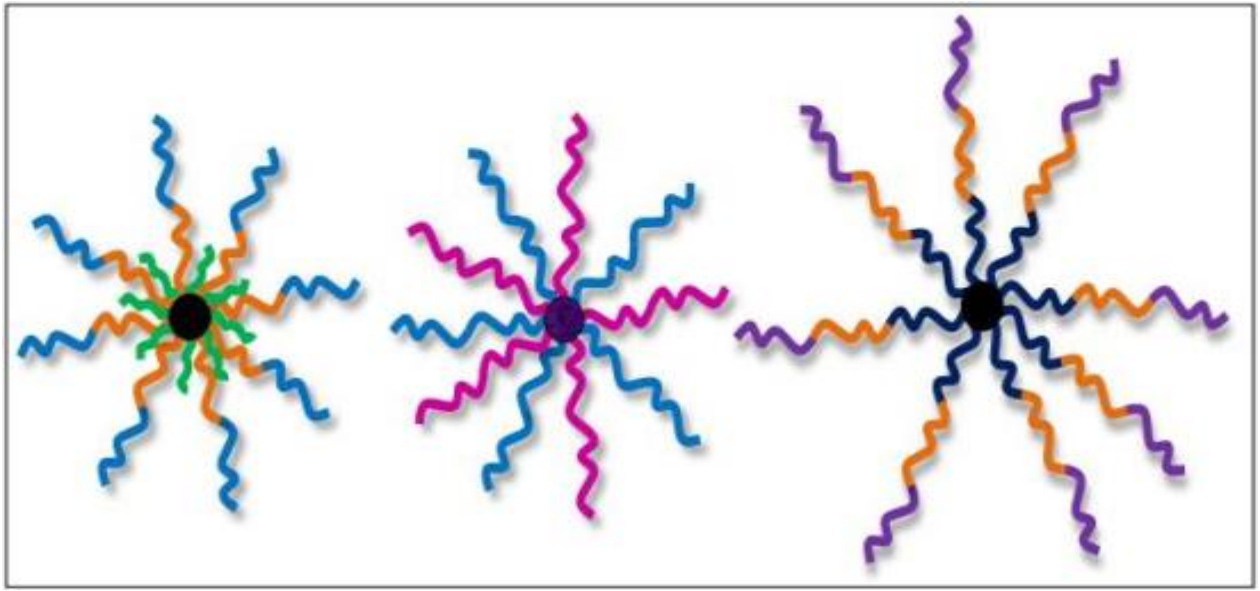
Star copolymers



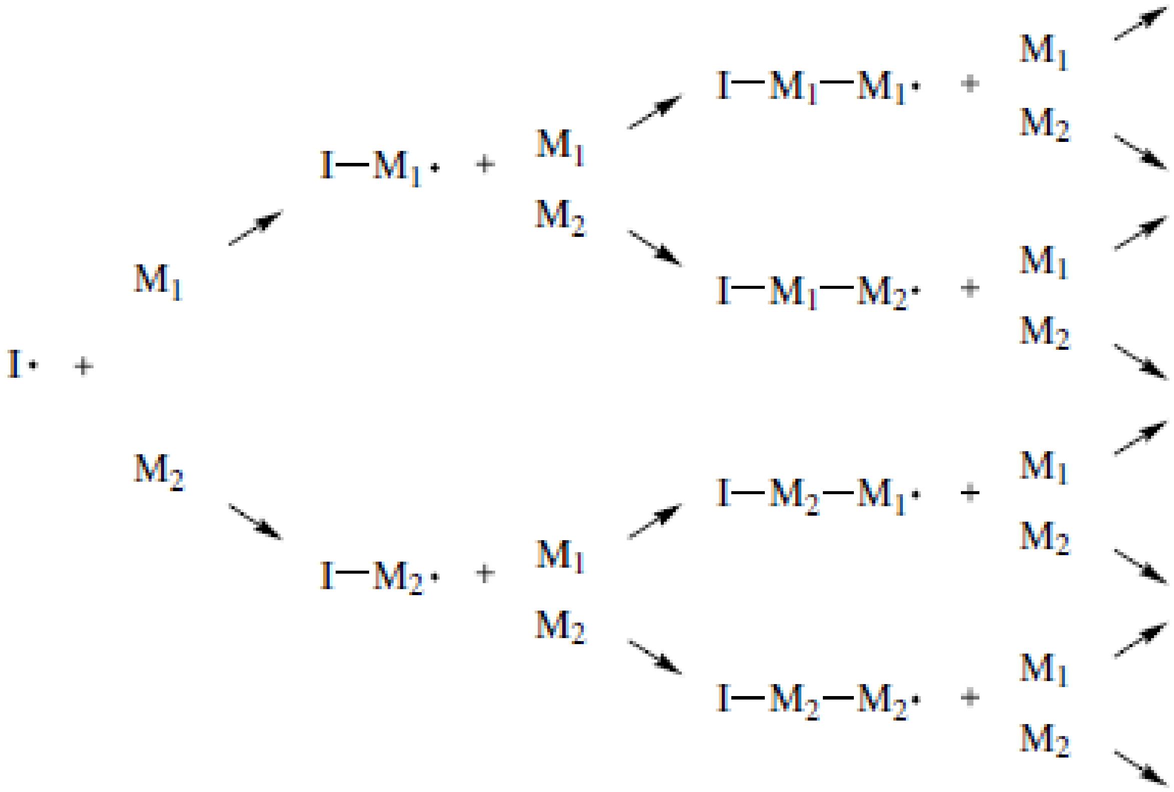
Star polymer



Miktoarm star polymer



Complex reaction mechanism



$\mathrm{I}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_1}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_2}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_1{-}M_1}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_1{-}M_2}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_2{-}M_1}\cdot + \mathrm{M}_1$, M_2

$\mathrm{I{-}M_2{-}M_2}\cdot + \mathrm{M}_1$, M_2

Copolymerization features

- Copolymer composition is different than the initial monomer mole fraction.
- The same only when the azeotropic composition is used
- Composition drift during the reaction

Instantaneous composition

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

Azeotropic composition

$$F_1 = f_1$$

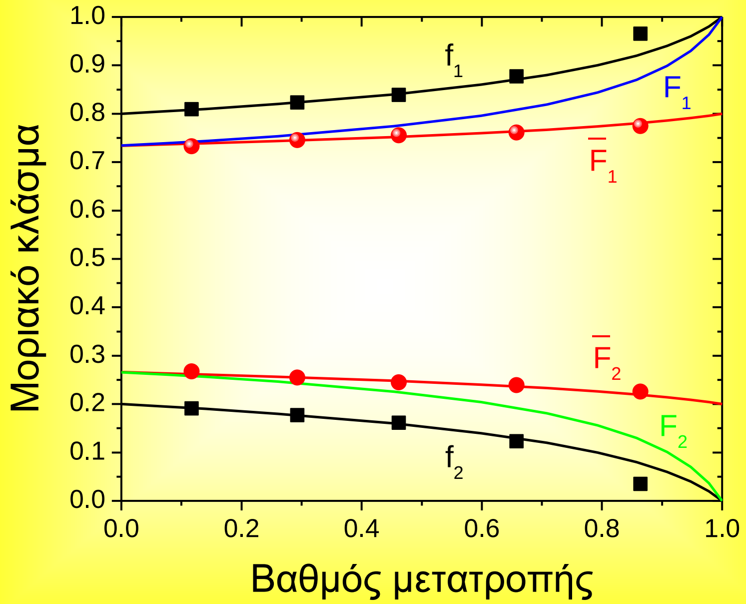
$$f_1 = \frac{(1-r_2)}{(2-r_1-r_2)}$$

Cumulative composition

$$\bar{F}_1 = \frac{f_{10} - f_1(1-X)}{X}$$

$$X = 1 - \frac{N}{N_0} = 1 - \left[\frac{f_1}{f_{10}}\right]^{\alpha} \left[\frac{f_2}{f_{20}}\right]^{\beta} \left[\frac{f_{10}-\delta}{f_1-\delta}\right]^{\gamma}$$

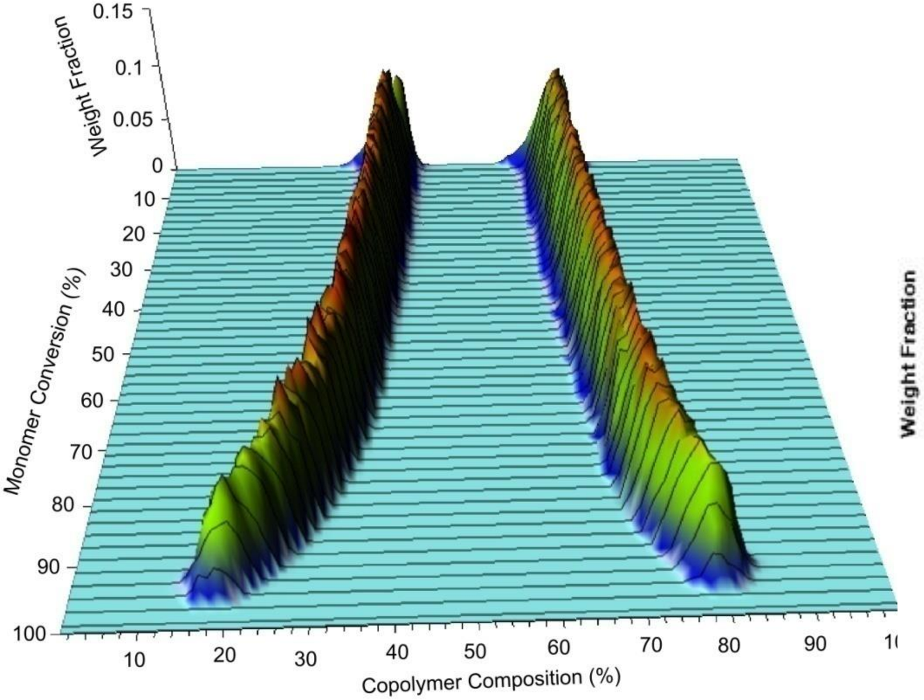
$$a = \frac{r_2}{(1-r_2)}, \quad \beta = \frac{r_1}{(1-r_1)}, \quad \gamma = \frac{(1-r_1 r_2)}{(1-r_1)(1-r_2)}, \quad \delta = \frac{(1-r_2)}{(2-r_1-r_2)}$$

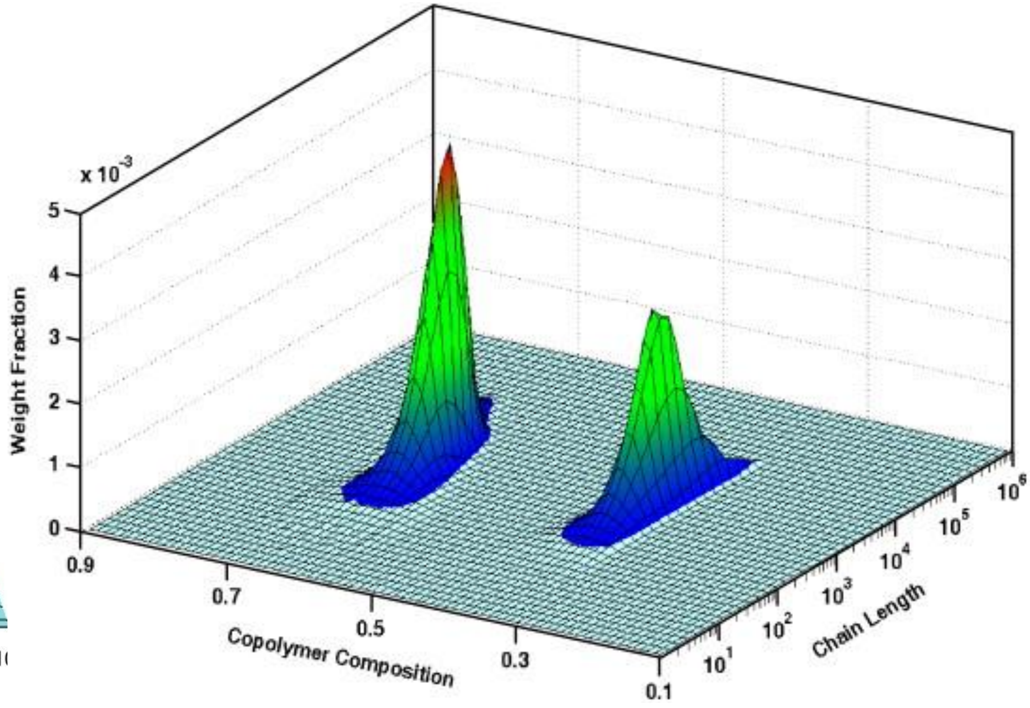


Dynamic prediction of the bivariate molecular weight–copolymer composition distribution using sectional-grid and stochastic numerical methods

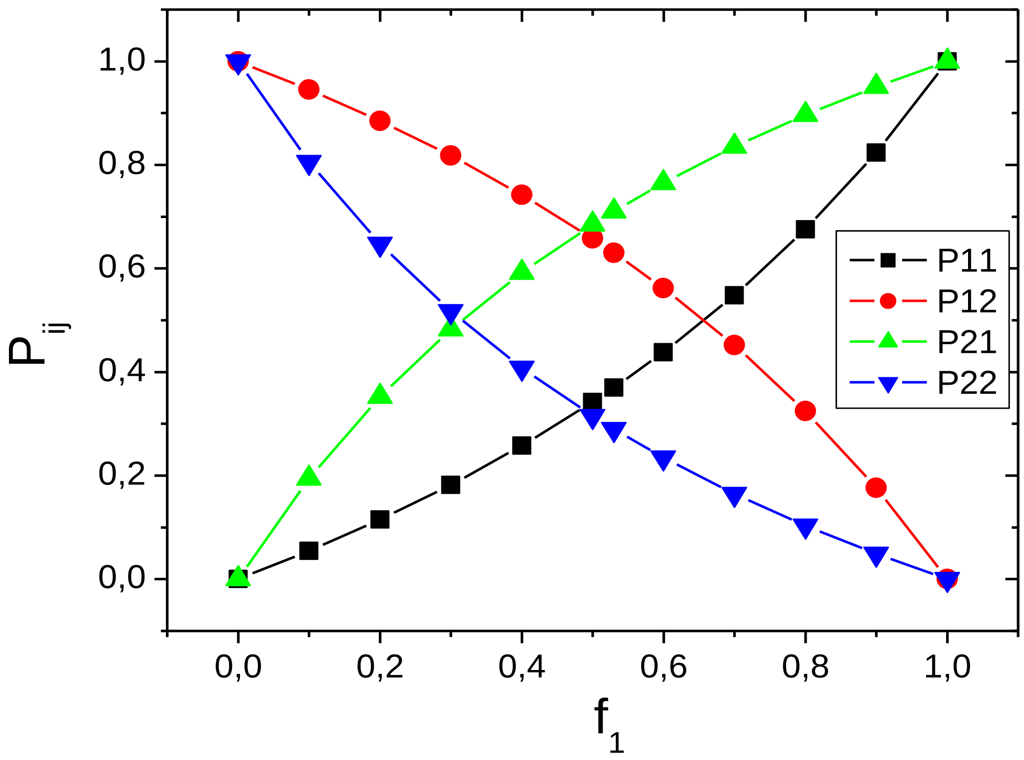
(A. Krallis, D. Meimaroglou, C. Kiparissides, Chemical Engineering Science, 63(17), 2008, 4342-4360)

- Dynamic evolution of the instantaneous CCD calculated by the MC algorithm for two different initial styrene mole fractions (T=60∘C, [I0]=0.01M AIBME).
- Bivariate MW–CC distributions calculated by the MC algorithm at a 93% total monomer conversion for two initial styrene mole fractions of 0.3 and 0.7





Sequence distribution - microstructure probability of monomer M_i followed by monomer M_j for several initial monomer mol fractions, f_1



...penultimate effect

$$\sim\sim\sim\sim M_1M_1^{\bullet} + M_1 \xrightarrow{k_{p111}} \sim\sim\sim\sim M_1M_1M_1^{\bullet}$$

$$\sim\sim\sim\sim M_1M_1^{\bullet} + M_2 \xrightarrow{k_{p112}} \sim\sim\sim\sim M_1M_1M_2^{\bullet}$$

$$\sim\sim\sim\sim M_1M_2^{\bullet} + M_1 \xrightarrow{k_{p121}} \sim\sim\sim\sim M_1M_2M_1^{\bullet}$$

$$\sim\sim\sim\sim M_1M_2^{\bullet} + M_2 \xrightarrow{k_{p122}} \sim\sim\sim\sim M_1M_2M_2^{\bullet}$$

$$\sim\sim\sim\sim M_2M_1^{\bullet} + M_1 \xrightarrow{k_{p211}} \sim\sim\sim\sim M_2M_1M_1^{\bullet}$$

$$\sim\sim\sim\sim M_2M_1^{\bullet} + M_2 \xrightarrow{k_{p212}} \sim\sim\sim\sim M_2M_1M_2^{\bullet}$$

$$\sim\sim\sim\sim M_2M_2^{\bullet} + M_1 \xrightarrow{k_{p221}} \sim\sim\sim\sim M_2M_2M_1^{\bullet}$$

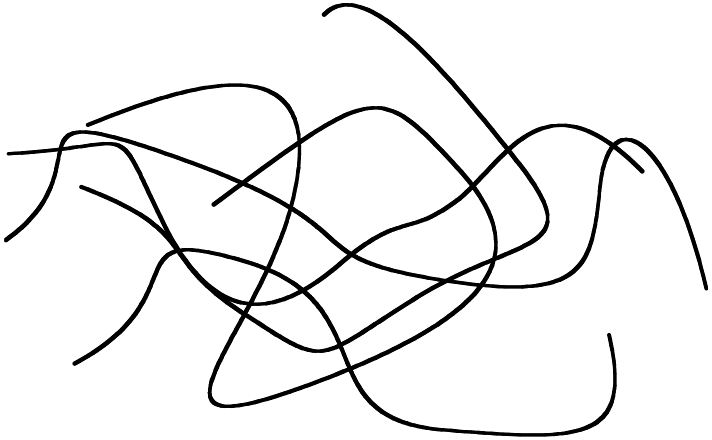
$$\sim\sim\sim\sim M_2M_2^{\bullet} + M_2 \xrightarrow{k_{p222}} \sim\sim\sim\sim M_2M_2M_2^{\bullet}$$

$$F_1 = \frac{1 + r_{21}(f_1/f_2)(r_{11}f_1 + f_2)/(r_{21}f_1 + f_2)}{2 + r_{21}(f_1/f_2)(r_{11}f_1 + f_2)/(r_{21}f_1 + f_2) + r_{12}(f_2/f_1)(r_{22}f_2 + f_1)/(r_{21}f_1 + f_2)}$$

BASIC POLYMER PROPERTIES

What makes polymers unique?

- Very high molecular weight
  - Chains wrapped in space



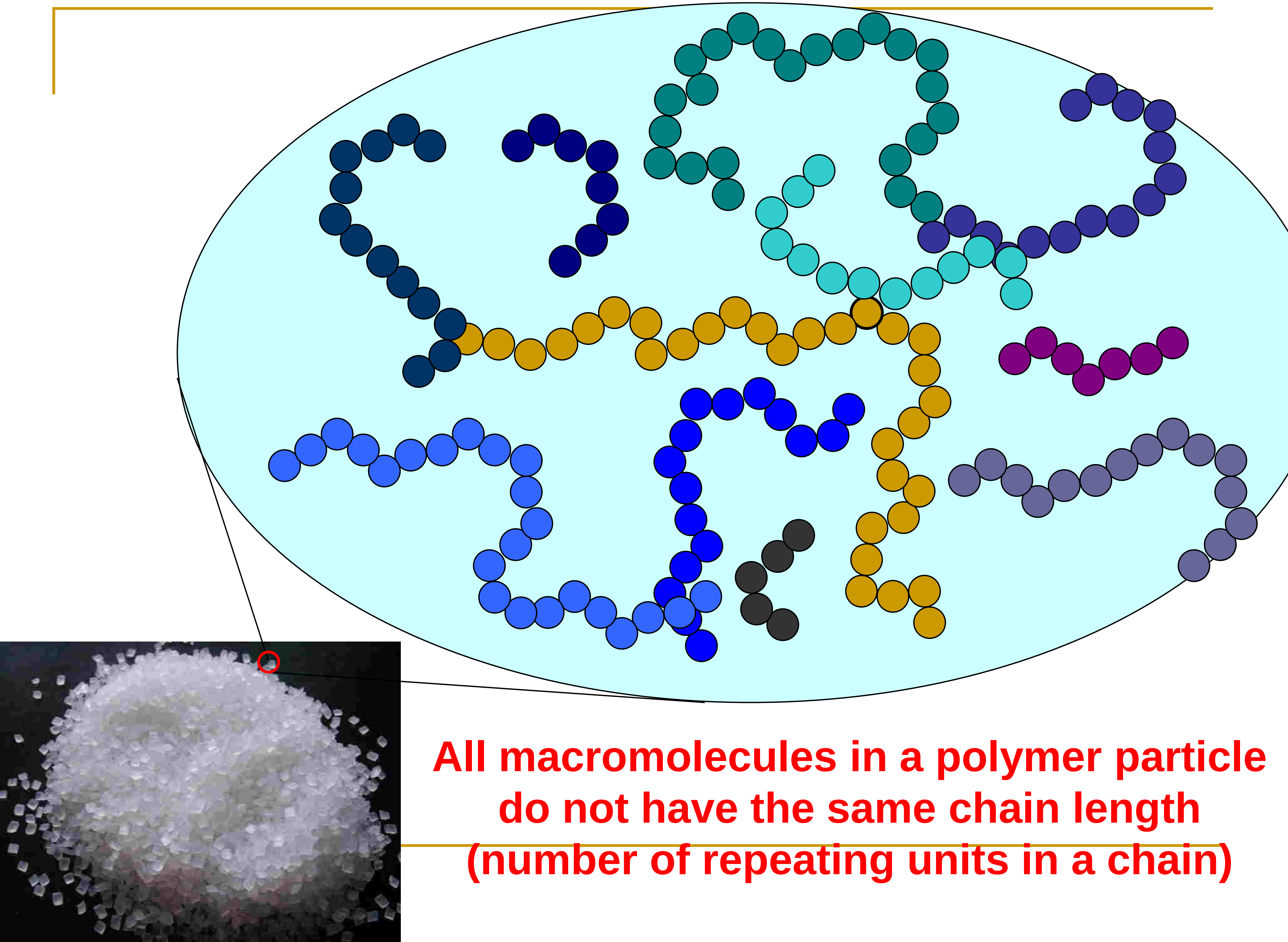
- Glass transition temperature
  - Transition from glass to elastomeric state

Polymer molecular weight (mass)

- Question: What is the molecular weight of polyethylene?
- Answer:

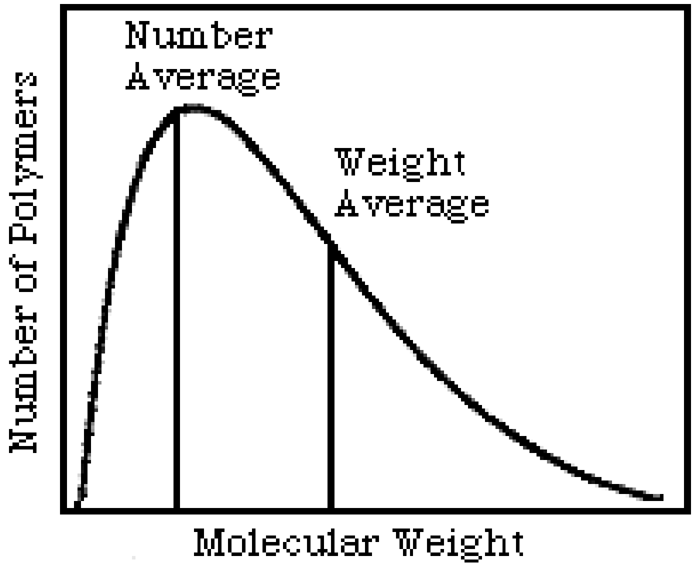
The question does not have a straight answer, because:

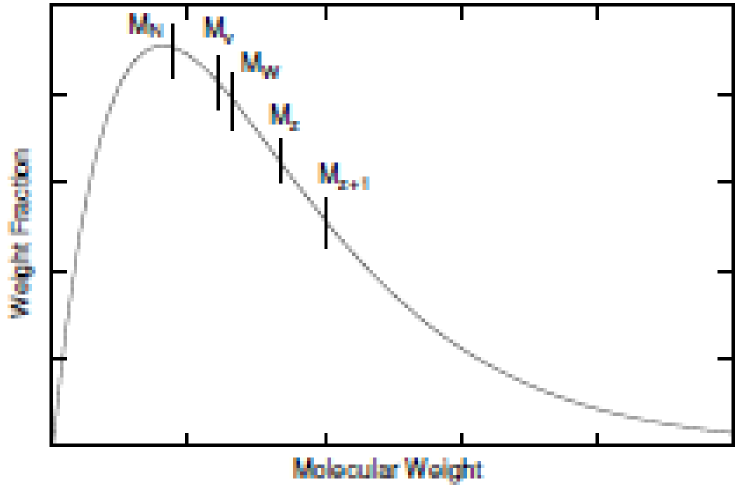
- All the macromolecules in a polymer do not have the same molecular weight.
- It is better to use the term average molecular weight estimated from the molecular weight distribution.
- The average molecular weight of a polymer is not unique. It depends on the reaction mechanism, the polymerization technique, the reaction conditions, thermal or chemical treatment, mechanical stress, etc.



All macromolecules in a polymer particle do not have the same chain length (number of repeating units in a chain)

Molecular Weight Distribution





- What is the average of the distribution?
- How one can define the dispersity of the distribution?
- How the skewness of the distribution can be estimated?

Definitions

w_i = grams

N_i = moles

M_i = g/mol

$w_i = N_iM_i$

$Z_i = N_iM_i^2$

Number average molecular weight

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \ldots}{N_1 + N_2 + N_3 + \ldots}$$

Average molecular weight

Weight average molecular weight

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} W_i M_i}{\sum_{i=1}^{\infty} W_i} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} = \frac{N_1M_1^2 + N_2M_2^2 + \ldots}{N_1M_1 + N_2M_2 + \ldots}$$

Polydispersity of the MWD

$D = M_w/M_n$

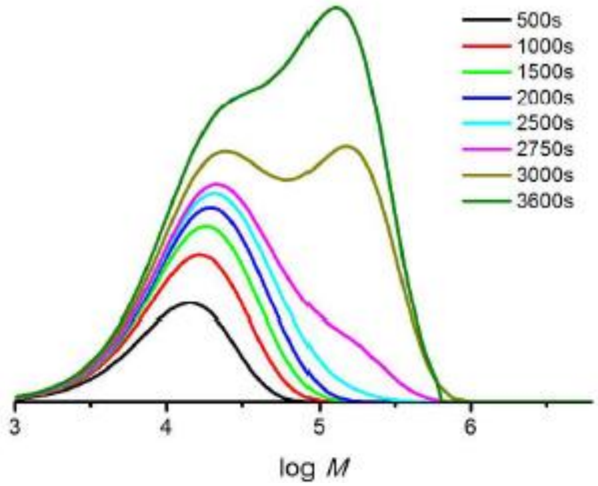
Z-average molecular weight

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} z_i M_i}{\sum_{i=1}^{\infty} z_i} = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{N_1M_1^3 + N_2M_2^3 + \ldots}{N_1M_1^2 + N_2M_2^2 + \ldots}$$

Skewness of the MWD

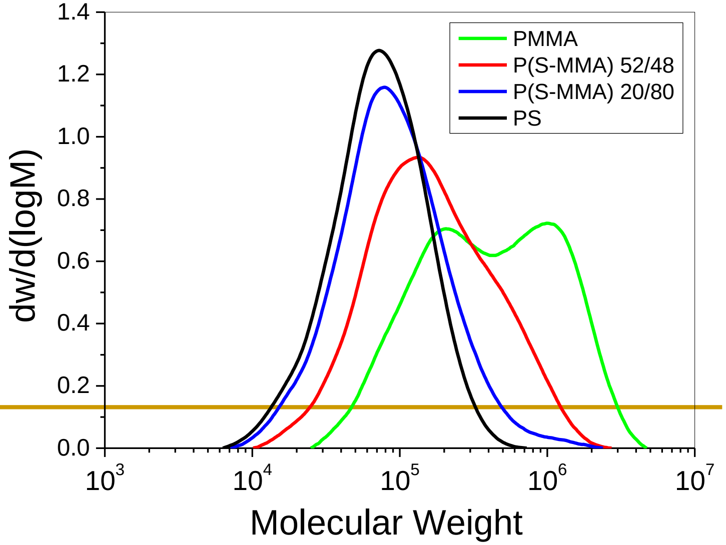
MWD

- is usually measured via Gel Permeation Chromatography with appropriate columns and calibration curves.
- Average molecular weights and the full MWD is changing:
- during polymerization (effect of monomer conversion and existence of diffusion-controlled phenomena)
- with temperature
- Initial initiator concentration
- Copolymer composition



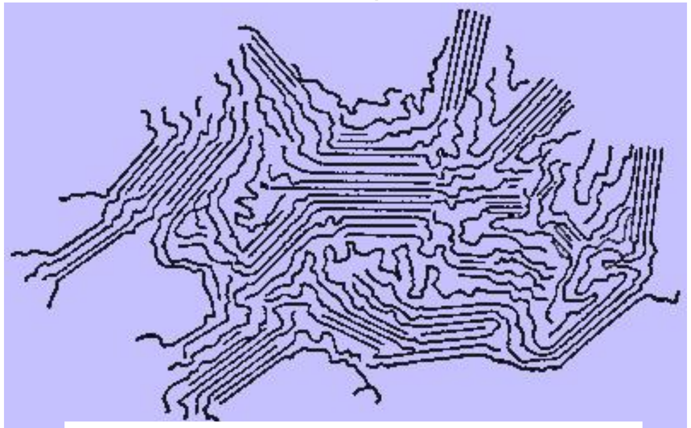
MMA polymerization with BPO/DMT

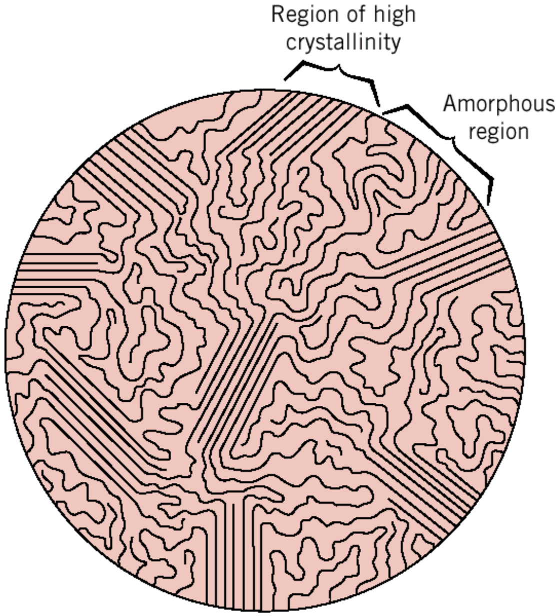
A. Zoller, D. GIGMES and Y. Guillaneuf, *Polym. Chem., 2015, DOI: 10.1039/C5PY00229J.*



Polymers in the solid state

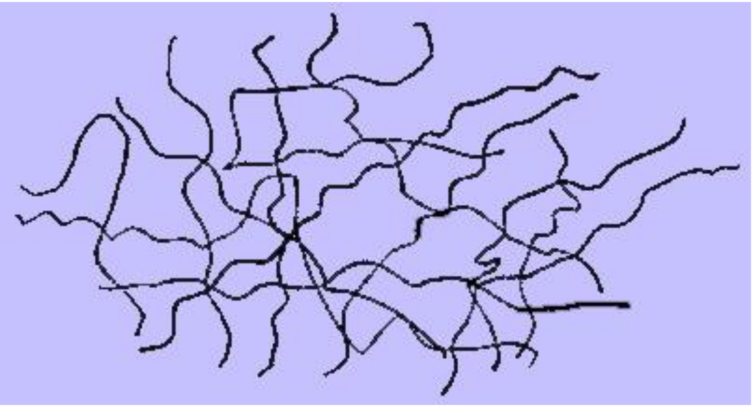
Semi-crystalline





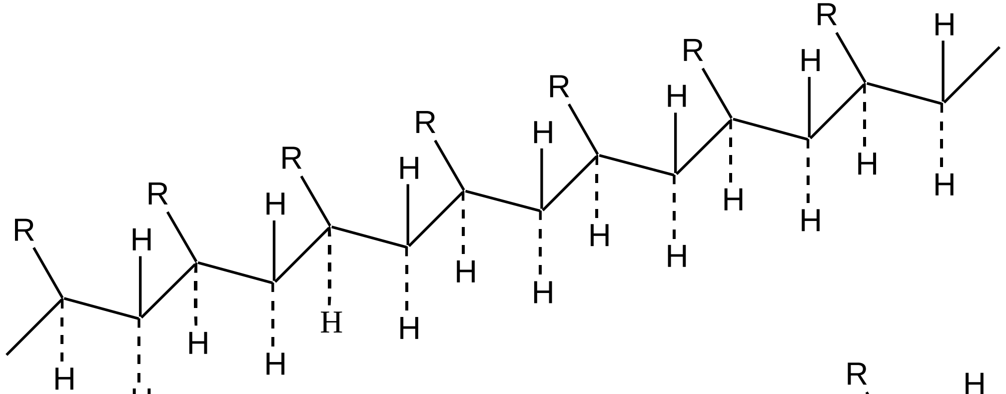
Amorphous

Glassy ⇄ **Rubbery**

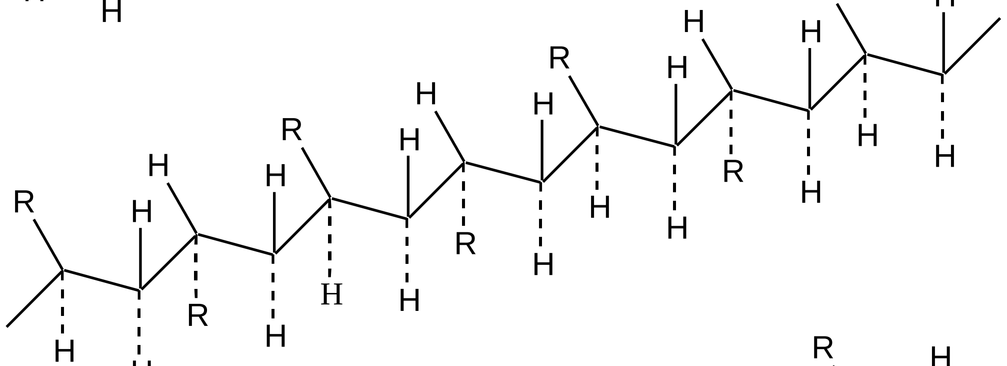


Tacticity of polymers

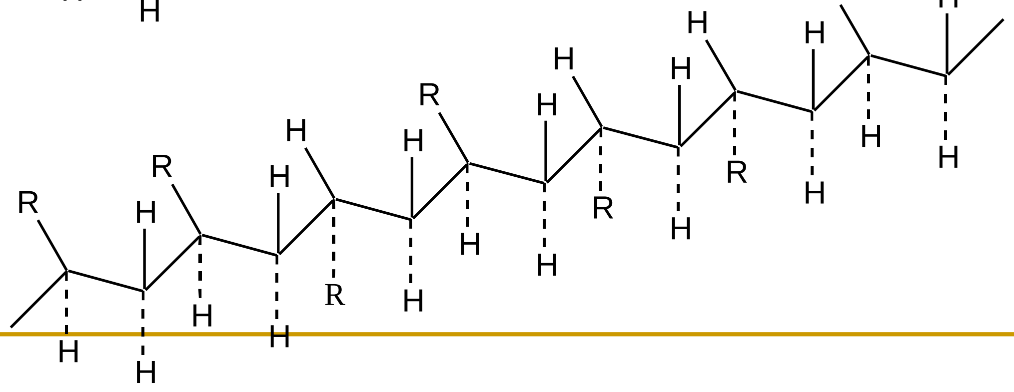
Isotactic



Syndyotactic



Atactic



Glass transition temperature, Tg

- PMMA, Plexiglas,

  T_g=100 °C

  T < Tg

- Polyisoprene, elastomer

  T_g=-40 έως -10 °C

  T > Tg

Poly(lactic acid), PLA Tg=60 °C

cold water hot water

PLA below T_g PLA above T_g

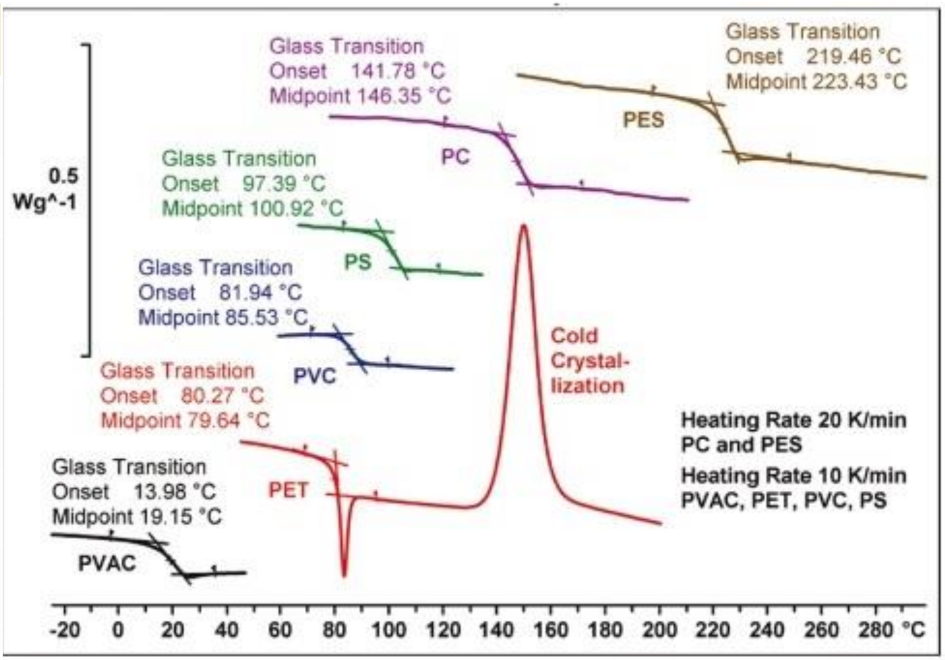
How to remove a chewing gum from clothes. Physical meaning of the glass transition temperature

- You may have experienced the glass tra chewing gum.
- At body temperature the gum is soft and pliable, which is characteristic of an amorphous solid in the rubbery state.
- If you hold an ice cube on the gum, it becomes hard and rigid.
- The glass transition temperature of the gum is somewhere between 0^{o}C and 20^{o}C.

Polymers: Materials with very different properties.

- Glass transition and melting temperature

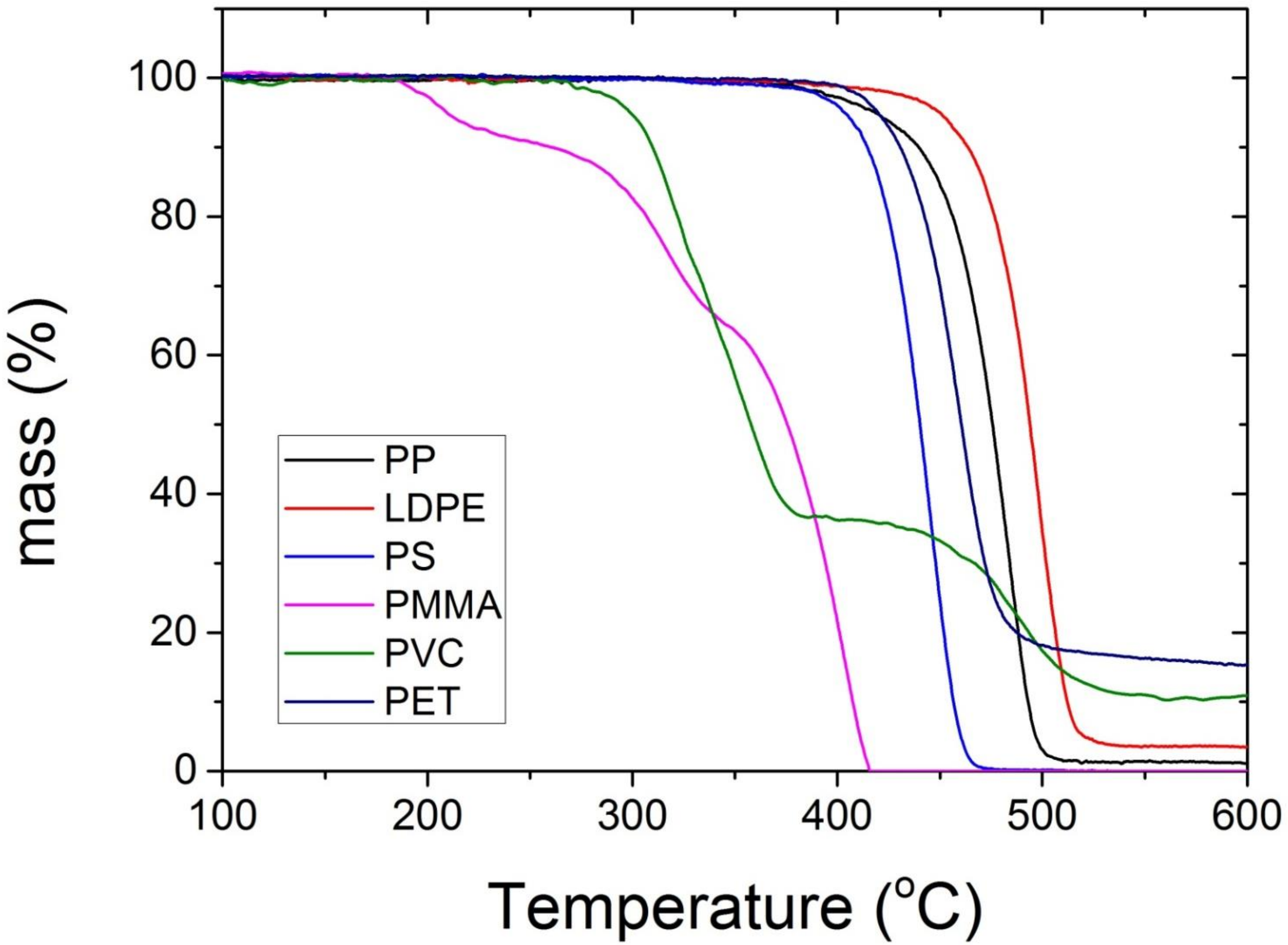
Polymer	T_g (°C)	T_m(°C)
LDPE	< -100	100 to 110
HDPE	< -100	125 to 135
PP	-30 to -20	160 to 165
PVC	80 to 85	-
PS	90 to 105	-
PMMA	100 to 110	-
PC	145	-
PET	70 to 80	250 to 260
PA 6,6	70 to 90	225 to 265



Glass Transition Temp. Measurements of Different Polymers Using DSC
(Source: Mettler-Toledo Analytical)

Polymers: Materials with very different properties.

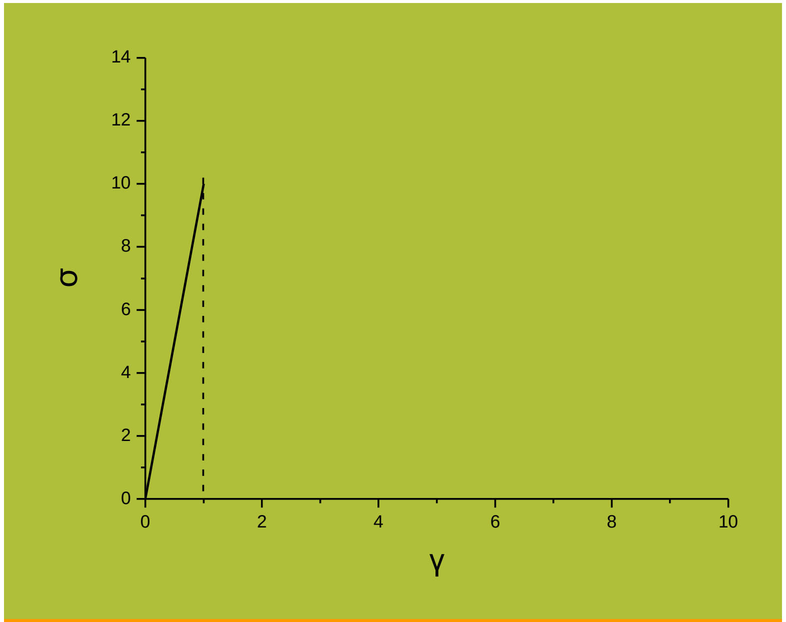
Thermal degradation in inert atmosphere



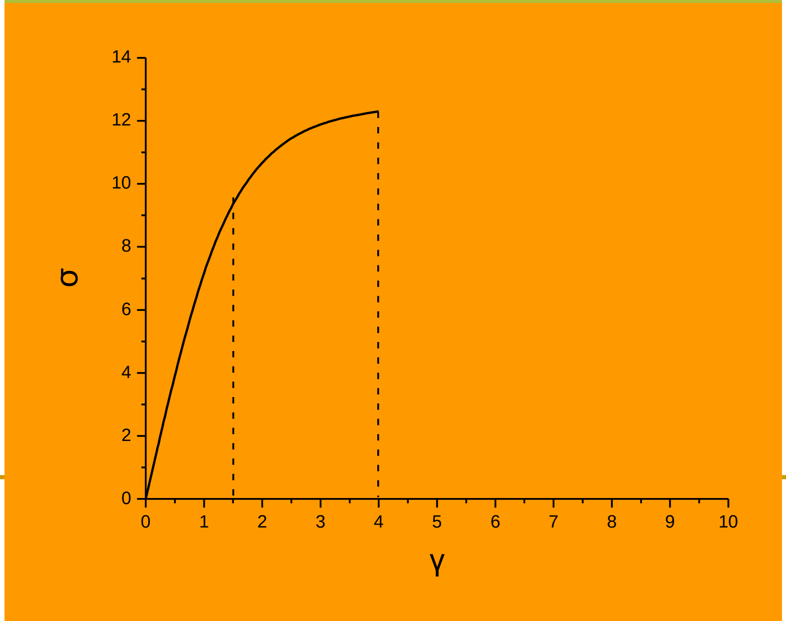
Tensile properties of polymers

Stress – Strain curves

- Brittle, T << Tg
  (PS, Tg=100^{o}C)

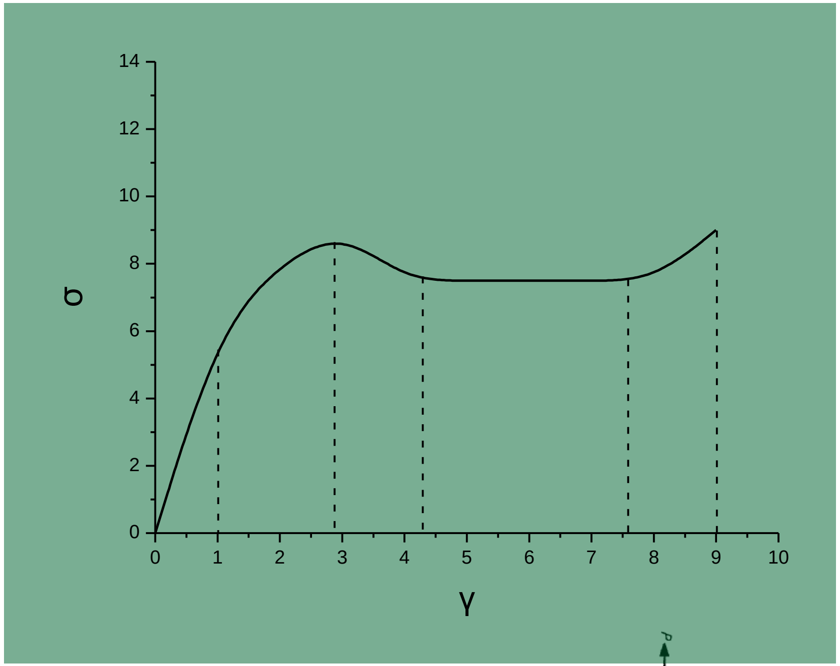


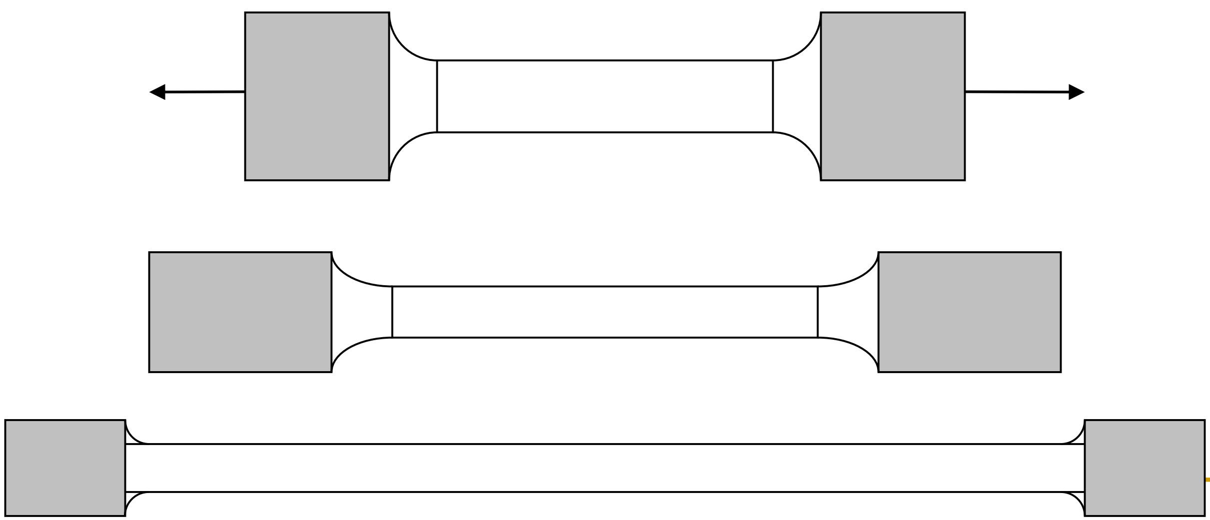
- Tough and strong,
  T < Tg (PVC, Tg=80^{o}C)



Tensile tests

- Hard and Tough
- T ~ Tg, e.g. Nylon, Tg ~ 50^{o}C
- Yield point, formation of neck
- Examples cellulose acetate, ABS





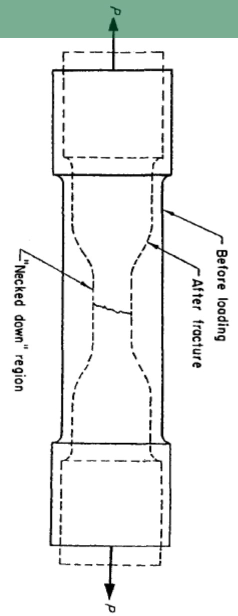
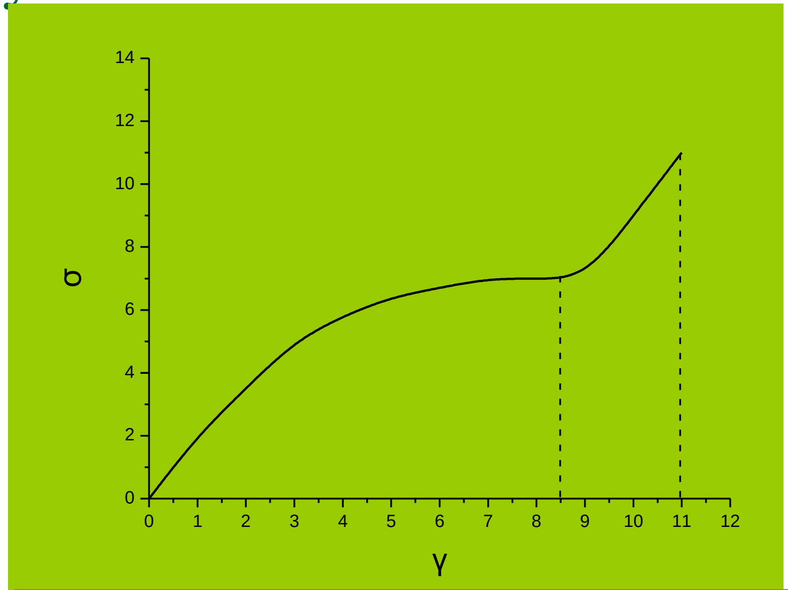


FIGURE 4-26 Necking of a dumbbell

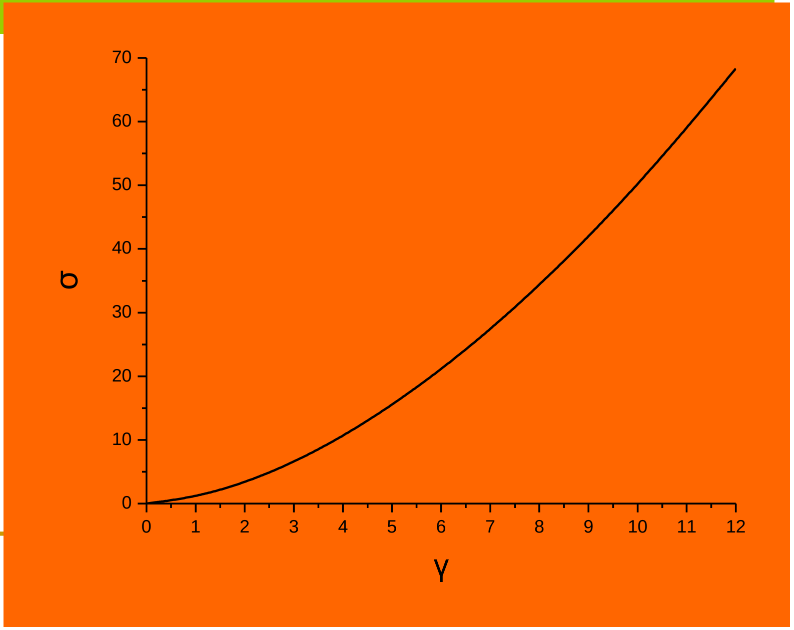
Tensile properties of polymers

Stress – Strain curves

- Soft and tough
  T > Tg,
  e.g. PE (Tg ~ -35^{o}C), plasticized PVC



- T >> Tg,
  Elastomer, natural rubber (polyisoprene), Tg=-70^{o}C, SBR, Tg=-60^{o}C



Summarizing

- All these were just a brief introduction into the wonderful world of polymer science and technology
- Issues not covered:
    - controlled radical polymerization
    - Chain conformation
    - Properties in solution
    - Polymer blends
    - Multi-polymerization
    - Melting and crystallization
    - and so on

- What is very fascinating is that: each polymer has its own properties, each polymerization reaction has its own peculiarities.

Thank you very much for your attention