

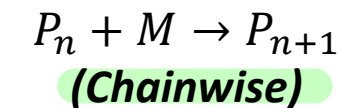
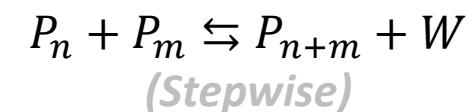
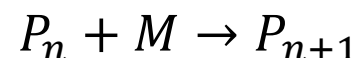
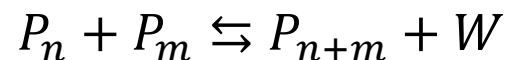


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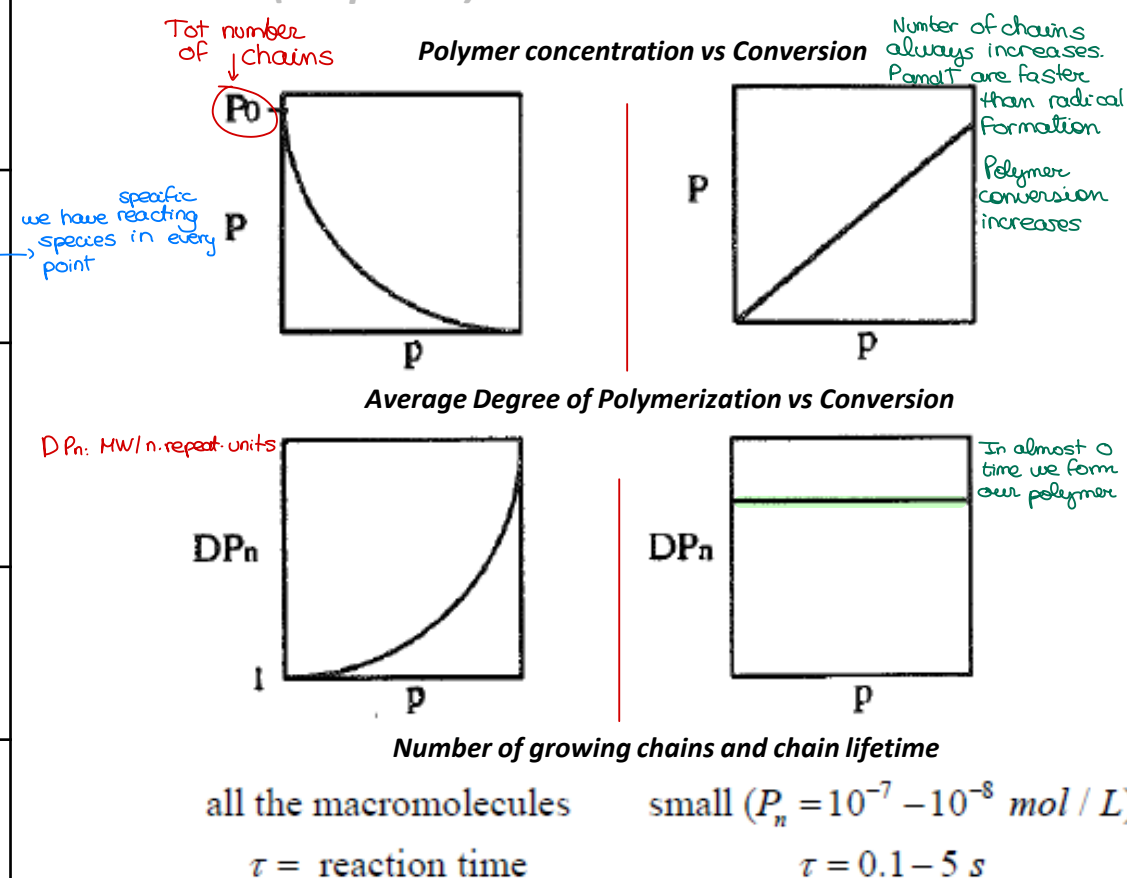
# Case study: Bulk Free Radical Polymerization (FRP)

Prof. Davide Moscatelli, Eng. Gabriele Galbo  
Milano, 22/11/2023



Polymerization Mechanisms: *Stepwise* vs. *Chainwise* Polymerization

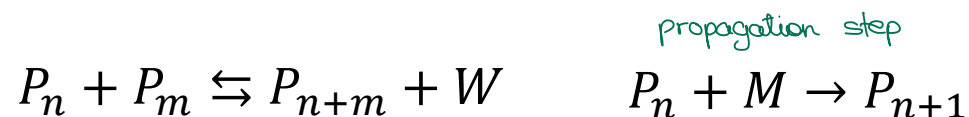
	Step Growth	Chain Growth Free-Radical Polymerization (Conventional *)
Number and kind of reactions	Only one necessary, that between two functional (usually different) groups	At least three: <b>Initiation</b> , <b>Propagation</b> , <b>Termination</b> <small>Prop and term are very fast processes</small>
Reacting Species	Two dissimilar functional groups: species of any size react with one another	<b>Active species (free-radical) with monomer</b> ; active species can react only with monomer to further grow
What is considered polymer	All species	Unreacted monomer is not considered polymer
MWD Composition	PolyDisperisityIndex (PDI) near to 2	Relatively broad; random alternating and graft



we can control the polymer distribution

\* Other chain growth mechanism exist (**Controlled FRP**, **Living FRP**) for a better control of the polymer MWD and architecture

## Polymerization Mechanisms: *Stepwise* vs. *Chainwise* Polymerization

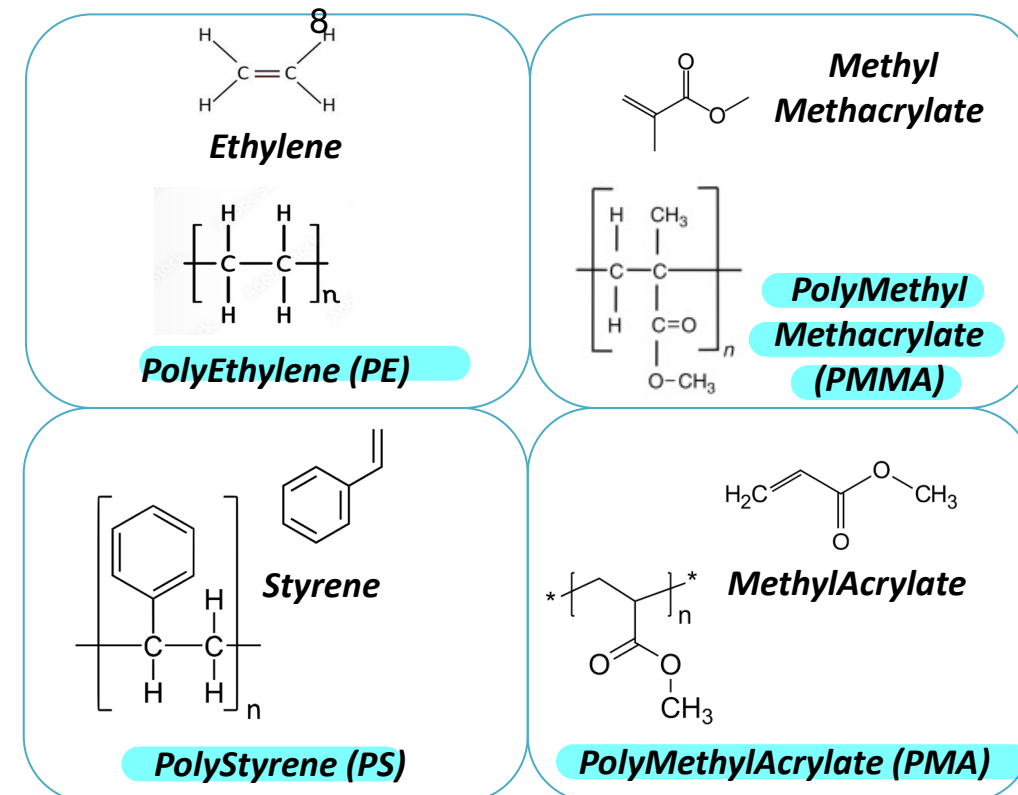


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- The active center is a **free-radical** (a very reactive species containing an unpaired electron **created by an initiator**)

- Very popular Polymerization mechanism

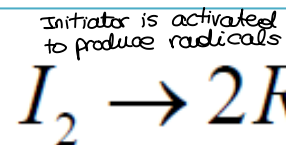
Examples:



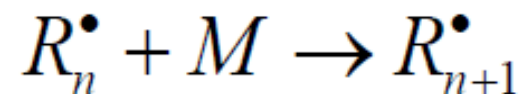
\* Other chain growth mechanism exist (**Controlled FRP**, **Living FRP**) for a better control of the polymer MWD and architecture

Polymerization Process	Ingredients	Remarks
Bulk	Monomer, Initiator (also the catalyst)	Homogeneous & heterogeneous Very pure product <small>→ there are no solvents or other substances</small> <div> <div>explosion run away reactions</div> <div>↖</div> </div> Mixing and heat removal difficult because of the increasing viscosity <small>⇒ mixing problems</small>
Solution	Monomer, Initiator, Solvent	Low viscosity Heat removed by reflux cooling Large amounts of unfriendly solvents
Suspension	Monomer, Initiator, Stabilizer, Water	Low viscosity, easy heat removal Aqueous medium Droplet size controlled by agitation and stabilizers (10 micron – 1 mm)
Emulsion	Monomer, Initiator, Surfactant, Water	Low viscosity, easy heat removal Aqueous medium Particle size controlled by emulsifier (100 nm) Product ready for use (paints, adhesives,...)
Slurry	Monomer, Catalyst, Medium	Monomer and catalyst dispersed or solubilized in the medium Polymer insoluble in the medium
Gas	Monomer, Catalyst	Monomer in gas phase (pure or diluted) Catalyst and polymer dispersed in the gas phase

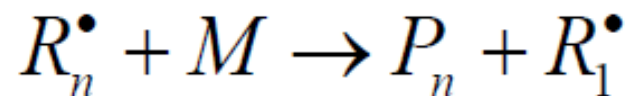
## Reaction rates

**Initiation**

$$r = 2fk_d I_2$$

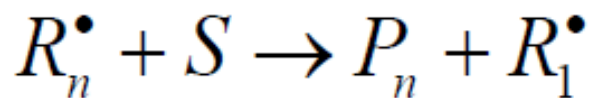
**Propagation**

$$r = k_p MR_n^\bullet$$

**Chain Transfer**

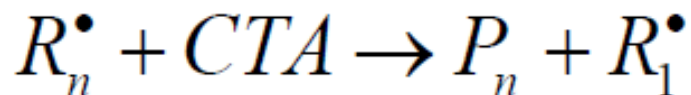
$$r = k_{fM} MR_n^\bullet$$

(CT to Monomer)



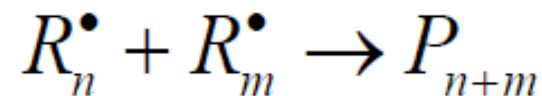
$$r = k_{fS} SR_n^\bullet$$

(CT to Solvent)



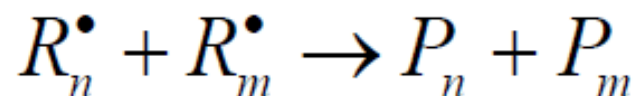
$$r = k_{fCTA} (CTA) R_n^\bullet$$

(CT to CTA)

**Termination**

$$r = k_{tc} R_n^\bullet R_m^\bullet$$

(Combination)



$$r = k_{td} R_n^\bullet R_m^\bullet$$

(Disproportionation)

↳ 2 polymers : 1) length m  
1) length n

to achieve  
polymers

↓  
more homogeneous

- Overall Concentration of active species (notation):**

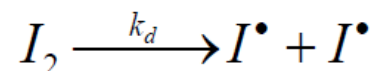
$$R^{\bullet} = \sum_{n=1}^{\infty} R_n^{\bullet}$$

we consider species one by one  
→ summation of all radicals

- Concerning the initiation step:**

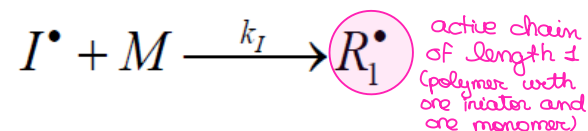
Initiator is activated  
forming two primary radicals  $I^{\bullet}$ .

### Reaction scheme



$$r_d = k_d I_2$$

**Primary radical formation**



$$r_1 = k_I M I^{\bullet}$$

**Active chain of length 1 formation**

$I_2$  = initiator       $I^{\bullet}$  = primary radical

$R_1^{\bullet}$  = active chain, length 1

### Mass Balances

stoich. coeff. is inside these relations

$$\frac{dI_2}{dt} = -k_d I_2$$

**Initiator molecule**

$$\frac{dI^{\bullet}}{dt} = 2f k_d I_2 - k_I I^{\bullet} M$$

2 because we form 2  $I^{\bullet}$       one  $I^{\bullet}$  is consumed

**Primary radical**

\* **'f' factor**: it accounts for the possibility, for a primary radical, to recombine with another primary radical and form the initiator molecule

The reactivity of the primary radicals is extremely high → the rate of radical formation is much lower than the rate of radical reaction with the monomer. Accordingly, the concentration of primary radicals remains very small in the system and, neglecting their accumulation inside the reactor, the corresponding material balance becomes:

STEADY STATE  
APPROXIMATION  
(accumulation term  
equal to zero)

$$\frac{dI^{\bullet}}{dt} = 2f k_d I_2 - k_I I^{\bullet} M \approx 0 \quad \Rightarrow \quad k_I I^{\bullet} M = 2f k_d I_2 \equiv r_I$$

Active chain production rate

Initiation rate

- **Typical Assumptions**

### 1) Long Chain Assumption (LCA):

*Chain-length independent rate constants  
(universally applied when dealing with high  
MW polymers)*

Since we have many polymer with high MW  
we can consider this approximation

Balance made on the active chains \*  
 Radical formed with initiation and ended with termination  
 $R_1^{\bullet}$  consumed to form  $R_2^{\bullet}$ ,  $R_2^{\bullet}$  forms  $R_3^{\bullet}$  ...  
\* we don't consider the propagation term

### **Material balances for I, R' and M**

$$\frac{dI_2}{dt} = -k_d I_2$$

$$\frac{dR^\bullet}{dt} = 2fk_d I_2 - k_t R^{\bullet 2}$$

$$\frac{dM}{dt} = -k_p MR^\bullet - k_{fm} MR^\bullet - k_I MI^\bullet \approx -k_p MR^\bullet$$

↗ higher value

### Long-Chain Hypothesis (LCH)

**2) Steady-state approximation (SSA):**

*The radicals consumptions rate is much higher than the radical formation rate*



### ***No accumulation term in the radicals mass balances***

$$\frac{dI^\bullet}{dt} = 2f k_d I_2 - k_I I^\bullet M \approx 0 \quad \Rightarrow \quad \underbrace{k_I I^\bullet M}_{\text{inactivation}} = \underbrace{2f k_d I_2}_{\text{production}} \equiv r_I$$

### Active chain production rate

### Initiation rate

$$\star \frac{dR^\bullet}{dt} = 2fk_d I_2 - k_t R^{\bullet 2} \approx 0 \quad \Rightarrow$$

$$R^{\bullet} = \sqrt{\frac{2fk_d \bar{I}_2}{k_t}}$$

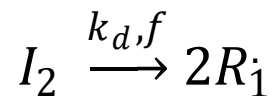
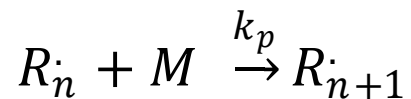
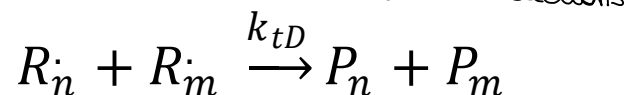
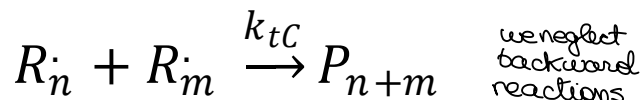




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# E2 polymerisation mechanisms (Chain-growth) : Bulk FRP



**Initiation:****Propagation:****Termination:**we neglect  
backward  
reactions**Main assumptions:**

- 1) **SSA** for all active species
- 2) **(CLA)** Chain length-independent rate coefficients
- 3) **Constant volume**, isothermal, well-mixed ~~batch~~ <sup>PFR or CSTR</sup> reactor
- 4) **Irreversible reactions** –neglect reverse reaction such as depropagation at high temperature
- 5) **No CTA** –chain transfer to monomer and solvent only

**Problem DATA****Starting conditions for all monomers:**

- $M_{in} = 4$  [mol/L]
- $I_{in} = 6 \cdot 10^{-3}$  [mol/L]
- $f = 0.5$  [-]

**Kinetic Rate Constants at 50°C, 1 atm**  
related to decomposition of initiation

Monomer	Ethylene	Styrene	Methyl Methacrylate	Methyl Acrylate
$k_d$ [1/s]	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
$k_p$ [L/mol/s]	54	238	648	22900
$k_t$ [L/mol/s]	$2.9 \cdot 10^8$	$2.0 \cdot 10^8$	$9.4 \cdot 10^7$	$5.1 \cdot 10^8$

**Propagation**

Monomer	$E_p$ [kJ/mol]	$\Delta V_p$ [L/mol]	$A_p$ [L/mol/s]
Methyl Acrylate	17.7	$-11.7 \cdot 10^{-3}$	$1.66 \cdot 10^7$

**Termination**

Monomer	$E_t$ [kJ/mol]	$\Delta V_t$ [L/mol]	$A_t$ [L/mol/s]
Methyl Acrylate	6.7	$20.0 \cdot 10^{-3}$	$6.0 \cdot 10^9$

**Requests:****1)  $I(\tau)$ ?  $M(\tau)$ ?  $X(\tau)$ ?**

- For all the 4 monomers

- Both **analytical** and **numerical** resolution

- In PFR and CSTR

**2)  $I(\tau)$ ?  $M(\tau)$ ?  $X(\tau)$ ?**

- For PMA

- In PFR and CSTR in series

**3) Rate constants effect on  $I(\tau)$   $M(\tau)$   $X(\tau)$** 

- For PMA

- In PFR

CSTR (continuous, homogen, NO ACC, Algebraic)

$\dot{F}$  volumetric flow rate

$$F = \text{const} \left[ \frac{\text{m}^3}{\text{s}} \right]$$

$$0 = C_i^{\text{IN}} - C_i^{\text{OUT}} + \sum_{j=1}^{N_{\text{reactions}}} \nu_{ij} R_j \tau \quad \left( \tau = \frac{V}{F} \right)$$

Multiple CSTR

$$\tau_{\text{single CSTR}} = \frac{\tau}{N_{\text{CSTRs}}}$$

$$C_i|_N = \frac{C_{i,\text{IN}}}{(1 + \tau K)^n} \quad n: \text{number of CSTR}$$

PFR (F const, homogeneous...)

$$\frac{dC_i}{d\tau} = \sum_{j=1}^{NR} \nu_{ij} R_j \quad \text{B.C.} \quad C_i(\tau=0) = C_i^{\text{IN}}$$

PFR coordinate is in space

$$d\tau = \frac{dV}{F}$$

CSTR

$$I(\tau) = \frac{I_{\text{IN}}}{1 + K_d \tau} \quad \text{initiator}$$

$$M(\tau) = \frac{M_{\text{IN}}}{1 + K_p R^\bullet \tau} \quad \text{monomer}$$

$$R^\bullet = \sum_{i=1}^{\infty} R_{mi} \longrightarrow R^\bullet = \sqrt{\frac{2fk_d I_{\text{IN}}}{k_t}} \quad \text{radical concentration ??}$$

$$X = 1 - \frac{1}{1 + K_p R^\bullet \tau} \quad \text{conversion}$$

$$X = \frac{M_{\text{IN}} - M(\tau)}{M_{\text{IN}}}$$

PFR

$$I(\tau) = I_{\text{IN}} \cdot \exp(-K_d \tau)$$

$$M(\tau) = M_{\text{IN}} \cdot \exp \left[ \frac{2K_p}{K_d} \sqrt{\frac{2fk_d I_{\text{IN}}}{k_t}} \left( \exp\left(-\frac{K_d \tau}{2}\right) - 1 \right) \right] \quad \left( \frac{dM}{dt} \right)$$

$$X(\tau) = 1 - \exp \left[ \frac{2K_p}{K_d} \sqrt{\frac{2fk_d I_{\text{IN}}}{k_t}} \left( \exp\left(-\frac{K_d \tau}{2}\right) - 1 \right) \right]$$

Inside  $M_{\text{IN}}$  we have  
 $R^\bullet$  inside

## Exercise

