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Case study: Solution Free Radical Polymerization (FRP)

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Polymerization Process	Ingredients	Remarks
Bulk	Monomer, Initiator	Homogeneous & heterogeneous Very pure product Mixing and heat removal difficult because of the increasing viscosity
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

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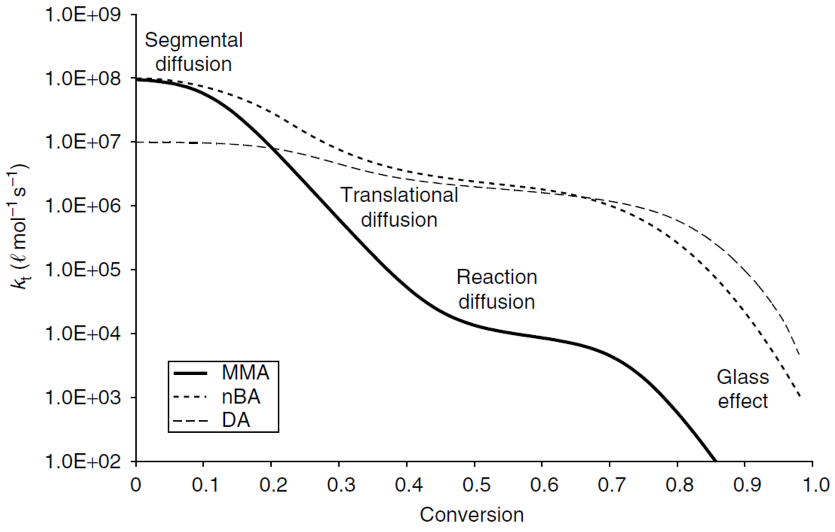
- At increasing conversion, the rate coefficients are affected not only by pressure and temperature but also by viscosity – this is especially true for long chains, i.e. for bimolecular termination



Exercise of the day:

Fraction of polymer

We'll consider these constants

$$k_P = \left(\frac{1}{k_{p,0}} + \frac{exp\left(C_\eta \boldsymbol{w_p}\right)}{k_{pD,0}}\right)^{-1}$$

$$k_t = \left(\frac{1}{k_{t,0}} + \frac{exp\left(C_\eta \boldsymbol{w_p}\right)}{k_{tD,0}}\right)^{-1} + C_{RD} k_p \left(1 - \boldsymbol{w_p}\right)$$

$$with \quad w_p = \frac{m_p}{m_p + m_M + m_S + m_I + m_{CTA}}$$

- **Segmental diffusion** – affected by chain flexibility and ability of internal re-organization, chain length is not yet crucial
- **Translational diffusion** – the two chains have to diffuse through the tangle of preformed polymer, chain lengths become important
- **Reaction diffusion** – the system is so viscous that the polymer radicals move by unit addition, i.e. by propagation
- **Glass effect** – when Tg becomes equal to T, all reactions are affected

Active chains with length *n*:

Propagation $\frac{dR_n^\bullet}{dt} = -k_p M R_n^\bullet$ → $\tau_p = \frac{1}{k_p M}$ (example : 10^{-3} s)

Terminations $\frac{dR_n^\bullet}{dt} = -\left(k_{fM} M + k_t R^\bullet\right) R_n^\bullet$ → $\tau_t = \frac{1}{k_{fM} M + k_t R^\bullet}$ (example : 3.2 s) Characteristic time of termination

Instantaneous chain length of active chains:

$$\lambda = \frac{\tau_t}{\tau_p} = \frac{k_p M}{k_{fM} M + k_t R^\bullet} =$$

$$= \frac{10^3}{1\ 10^{-2} + 3\ 10^{-1}} = 3,226 \quad \text{monomer units}$$

If Chain Transfer Agents are used (to regulate polymer Molecular weigths) :

Chain transfer can happen between monomer, solvent or chain transfer agent

Chain transfer agent can end the polymeric chain before termination

$$\lambda = \frac{\tau_t}{\tau_p} = \frac{k_p M}{k_{fX} X}$$

With X = Chain transfer agent concentration

We have accumulative features of our polymer

What about polymer MWs and distributions in FRP ?

Alpha, beta and gamma introduction

(passing through the characteristic times)

Mass Balance on $R_1^\bullet$

$$\frac{dR_1^\bullet}{dt} = 0 \qquad R_I + (k_{fm}M + k_{fs}S)(R^\bullet - R_1^\bullet) = k_p M R_1^\bullet + (k_{tc} + k_{td}) R^\bullet R_1^\bullet$$

$$R_1^\bullet = \frac{R_I + (k_{fm}M + k_{fs}S) R^\bullet}{k_p M + (k_{tc} + k_{td}) R^\bullet + (k_{fm}M + k_{fs}S)}$$

$$R_I = (k_{tc} + k_{td}) R^{\bullet 2}$$

$$R_1^\bullet = R^\bullet \frac{\alpha}{1+\alpha}$$

$$\boxed{\alpha = \frac{\tau_p}{\tau_{tc}} + \frac{\tau_p}{\tau_{td}} + \frac{\tau_p}{\tau_{fm}} + \frac{\tau_p}{\tau_{fs}}}$$

Mass Balance on $R_n^\bullet$

$$\frac{dR_n^\bullet}{dt} = 0 \qquad R_n^\bullet = \frac{1}{(1+\alpha)^{n-1}} R^\bullet \frac{\alpha}{1+\alpha} = R^\bullet \frac{\alpha}{(1+\alpha)^n}$$

$$I_2 \rightarrow 2R_1^\bullet \qquad r = 2 f k_d I_2$$

$$R_n^\bullet + M \rightarrow R_{n+1}^\bullet \qquad r = k_p M R_n^\bullet$$

$$R_n^\bullet + M \rightarrow P_n + R_1^\bullet \qquad r = k_{fM} M R_n^\bullet$$

$$R_n^\bullet + S \rightarrow P_n + R_1^\bullet \qquad r = k_{fS} S R_n^\bullet$$

$$R_n^\bullet + CTA \cancel{\rightarrow P_n + R_1^\bullet \qquad r = k_{fCTA}(CTA)} R_n^\bullet$$

$$R_n^\bullet + R_m^\bullet \rightarrow P_{n+m} \qquad r = k_{tc} R_n^\bullet R_m^\bullet$$

$$R_n^\bullet + R_m^\bullet \rightarrow P_n + P_m \qquad r = k_{td} R_n^\bullet R_m^\bullet$$

$$n, m = [1 \ldots \infty]$$

Main assumptions:

1) **SSA** for all active species
2) **(CLA)** Chain length-independent rate coefficients
3) **Irreversible reactions**
4) **No Chain transfer to CTA** – chain transfer to monomer and solvent

****** See also 'APC lecture notes – Prof. Massimo Morbidelli' – on We Beep***

I) $I_2 \xrightarrow{K_d} R_1$

P) $R_n^\bullet + M \xrightarrow{K_p} R^\bullet_{n+1}$

CT) $R_n^\bullet + M \xrightarrow{K_{fm}} P_n + R_1^\bullet$

$R_n^\bullet + S \xrightarrow{K_{fs}} P_n + R_1^\bullet$

T) $R_n^\bullet + R_m^\bullet \xrightarrow{K_{tc}} P_{n+m}$

$\xrightarrow{K_{td}} P_n + P_m$

population balance on $R_1^\bullet$

$\frac{dR_1}{dt} = 0$ (SSA for all active species)

$$\frac{dR^\bullet}{dt} = \underset{(\mathcal{R}_I)}{2fK_d I} + K_{fM} M R^\bullet + K_{fs} S R^\bullet - K_{fm} M R_1^\bullet - K_{fs} S R_1^\bullet - K_{tc} R_1^\bullet R^\bullet - K_{td} R_1^\bullet R = 0$$

$$R_1^\bullet = \frac{\mathcal{R}_I + K_{fM} M R^\bullet + K_{fs} S R^\bullet}{K_{fm} M + K_{fs} S + K_{tc} R^\bullet + K_{td} R^\bullet}$$

$$\frac{dR^\bullet}{dt} = \mathcal{R}_I - K_t R^{\bullet 2} = 0$$

$$\mathcal{R}_I = K_t R^2$$

$$\frac{1}{K_p M} = \tau_p$$

$$R_1^\bullet = \frac{\frac{K_t R^{\bullet 2}}{K_p M} + \frac{K_{fm} M R^\bullet}{K_p M} + \frac{K_{fs} S R^\bullet}{K_p M}}{\left(\frac{K_{fm} M}{K_p M} + \frac{K_{fs} S}{K_p M} + \frac{K_{tc} R^\bullet}{K_p M} + \frac{K_{td} R^\bullet}{K_p \cdot M}\right) + 1}$$

controlla

$$\boxed{\alpha = \frac{\tau_p}{\tau_{tc}} + \frac{\tau_p}{\tau_{td}} + \frac{\tau_p}{\tau_{fm}} + \frac{\tau_p}{\tau_{fs}}}$$

What about polymer MWs and distributions in FRP ?

Alpha, beta and gamma introduction (passing through the characteristic times)

Mass Balance on R_1·

$$\frac{dR_1^\bullet}{dt} = 0 \qquad R_I + (k_{fm}M + k_{fs}S)(R^\bullet - R_1^\bullet) = k_p M R_1^\bullet + (k_{tc} + k_{td}) R^\bullet R_1^\bullet$$

$$R_1^\bullet = \frac{R_I + (k_{fm}M + k_{fs}S) R^\bullet}{k_p M + (k_{tc} + k_{td}) R^\bullet + (k_{fm}M + k_{fs}S)}$$

$$R_I = (k_{tc} + k_{td}) R^{\bullet 2}$$

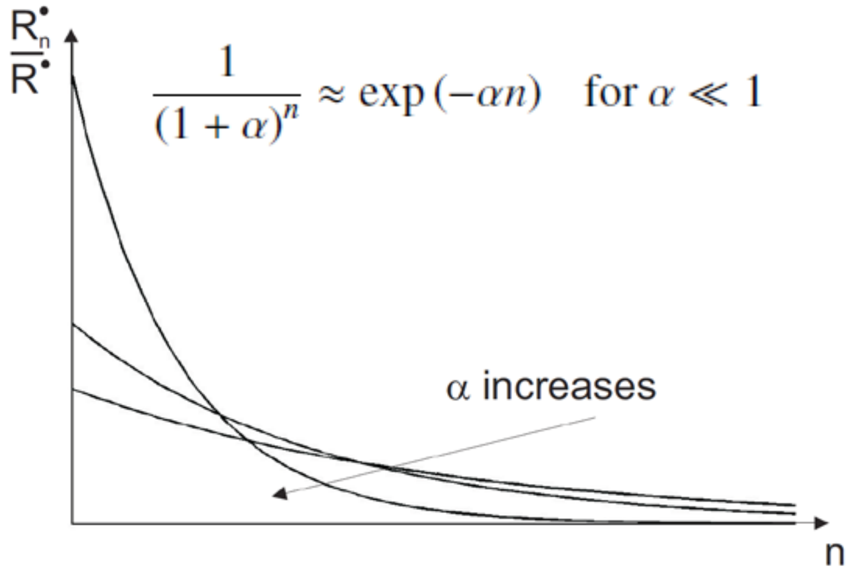
$$R_1^\bullet = R^\bullet \frac{\alpha}{1+\alpha}$$

$$\boxed{\alpha = \frac{\tau_p}{\tau_{tc}} + \frac{\tau_p}{\tau_{td}} + \frac{\tau_p}{\tau_{fm}} + \frac{\tau_p}{\tau_{fs}}}$$

Mass Balance on R_n·

$$\frac{dR_n^\bullet}{dt} = 0 \qquad R_n^\bullet = \frac{1}{(1+\alpha)^{n-1}} R^\bullet \frac{\alpha}{1+\alpha} = R^\bullet \frac{\alpha}{(1+\alpha)^n}$$

For long chains (alpha <<1):



***Remark:** This is the **MWD** of the active chains **at a given instant time**: it is representing the **instantaneous** property of the active polymer*

Knowing Rn* we can evaluate the fractons of radicals with length 'n', so their number (and weigth) distributions, passing through alpha and the characteristic times

****** See also 'APC lecture notes – Prof. Massimo Morbidelli' – on We Beep***

- ***From the population balance on the primary radical 'Alpha' has been defined***
- ***From the population balance on dead polymer chains it is necessary to define 'Beta' and 'Gamma', also function of the characteristic times,*** *to describe the whole polymer distribution (alpha alone is not sufficient this time)*

Mass Balance on P_n

general balance on a polymer

$$\frac{dP_n}{dt} = (k_{fm}M + k_{fs}S + k_{td}R^\bullet)R_n^\bullet + \frac{1}{2}k_{tc}\sum_{j=1}^{n-1} R_j^\bullet R_{n-j}^\bullet$$

$$\frac{dP_n}{dt} = (k_pMR^\bullet)\left[\left(\frac{k_{fm}}{k_p} + \frac{k_{fs}S}{k_pM} + \frac{k_{td}R^\bullet}{k_pM}\right)\frac{\alpha}{(1+\alpha)^n} + \left(\frac{k_{tc}R^\bullet}{k_pM}\right)\frac{1}{2}\frac{\alpha^2(n-1)}{(1+\alpha)^n}\right]$$

$$\frac{dP_n}{dt} = R_p\frac{\alpha}{(1+\alpha)^n}\left[\gamma + \frac{1}{2}(n-1)\alpha\beta\right]$$

$$\boxed{\gamma = \frac{k_{fm}}{k_p} + \frac{k_{fs}S}{k_pM} + \frac{k_{td}R^\bullet}{k_pM} = \frac{\tau_p}{\tau_{fm}} + \frac{\tau_p}{\tau_{fs}} + \frac{\tau_p}{\tau_{td}}}$$

$$\boxed{\beta = \frac{k_{tc}R^\bullet}{k_pM} = \frac{\tau_p}{\tau_{tc}}}$$

$$\boxed{\alpha = \beta + \gamma}$$

INSTANTANEOUS PROPERTIES

Instantaneous normalized number distribution : Number fraction of polymer (dead) chains at time t

$$x_n^{Inst}(t) = \frac{\text{polymer chains of length } n}{\text{total number of polymer chains}} = \frac{\dfrac{dP_n}{dt}}{\displaystyle\sum_{n=1}^{\infty}\frac{dP_n}{dt}} = \frac{\alpha}{(1+\alpha)^n}\left[\frac{\gamma + \frac{1}{2}(n-1)\beta(\beta+\gamma)}{\gamma+\frac{1}{2}\beta}\right]$$

summation of all the balances

$$\sum_{n=1}^{\infty} x_n^{Inst}(t) = 1$$

Instantaneous normalized weight distribution : Weigth fraction of polymer (dead) chains at time t

$$x_w^{Inst}(t) = \frac{\text{number of monomer units in the chains of length } n}{\text{total amount of consumed monomer}} = \frac{\dfrac{n \cdot dP_n}{dt}}{R_p} \quad \textit{(Definition)}$$

$$x_w^{Inst}(t) = \frac{n * x_n^{Inst}(t)}{\sum_{n=1}^{\infty} n * x_n^{Inst}(t)} = \frac{n * x_n^{Inst}(t)}{\mu_1^{Inst}(t)} \quad \textit{(Expressed in terms of } x_n^{Inst}(t)\textit{)}$$

*** Also for the distributions it is possible to define the moment of j^th order**

$$\left(\bar{\mu}_j^{inst} = \sum_{n=1}^{\infty} n^j x_n^{inst} \right)$$

$$\bar{\mu}_0^{inst} = 1$$

$$\bar{\mu}_1^{inst} = \frac{\alpha + 1}{\gamma + \beta / 2} \xrightarrow{\alpha << 1} \frac{1}{\gamma + \beta / 2}$$

$$\bar{\mu}_2^{inst} = \frac{\alpha^2 (\gamma + 2\beta) + \alpha(3\gamma + 5\beta) + (2\gamma + 3\beta)}{\alpha^2 (\gamma + \beta / 2)} \xrightarrow{\alpha << 1} \frac{2\gamma + 3\beta}{\alpha^2 (\gamma + \beta / 2)}$$

Instantaneous Number average Molecular weight

$$\bar{M}_n^{inst} = \frac{\bar{\mu}_1^{inst}}{\bar{\mu}_0^{inst}} M_M = \frac{1}{\gamma + \frac{1}{2}\beta} M_M$$

Instantaneous Weight average Molecular weight

$$\bar{M}_w^{inst} = \frac{\bar{\mu}_2^{inst}}{\bar{\mu}_1^{inst}} M_M = \frac{2(\gamma + \frac{3}{2}\beta)}{(\gamma + \beta)^2} M_M$$

Instantaneous Polydispersity index

$$P_d^{inst} = \frac{\bar{M}_w^{inst}}{\bar{M}_n^{inst}} = \frac{2(\gamma + \frac{3}{2}\beta)(\gamma + \frac{1}{2}\beta)}{(\gamma + \beta)^2}$$

Instantaneous Number Average Degree of polymerization

$$DP_n^{inst} = \frac{\bar{M}_n^{inst}}{M_M} = \frac{1}{\gamma + \frac{1}{2}\beta} = \frac{k_p M}{k_{fM} M + k_{fS} S + k_{td} R^{\bullet} + \frac{1}{2} k_{tc} R^{\bullet}}$$

Instantaneous Weight Average Degree of polymerization

$$DP_w^{inst} = \frac{\overline{M_w^{inst}}}{M_m}$$

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E3 polymerisation mechanisms (Chain-growth) : Solution FRP

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		Reaction rates	
Initiation	$I_2 \rightarrow 2R_1^\bullet$	$r = 2fk_d I_2$	
Propagation	$R_n^\bullet + M \rightarrow R_{n+1}^\bullet$	$r = k_p M R_n^\bullet$	
Chain Transfer	$R_n^\bullet + M \rightarrow P_n + R_1^\bullet$	$r = k_{fM} M R_n^\bullet$	***(CT to Monomer)***
	$R_n^\bullet + \cancel{S \rightarrow P_n + R_1^\bullet}$	$\cancel{r = k_{fS} S R_n^\bullet}$	***(CT to Solvent)***
	$R_n^\bullet + \cancel{CTA \rightarrow P_n + R_1^\bullet}$	$\cancel{r = k_{fCTA} (CTA) R_n^\bullet}$	***(CT to CTA)***
Termination	$R_n^\bullet + R_m^\bullet \rightarrow P_{n+m}$	$r = k_{tc} R_n^\bullet R_m^\bullet$	***(Combination)***
	$R_n^\bullet + R_m^\bullet \rightarrow P_n + P_m$	$r = k_{td} R_n^\bullet R_m^\bullet$	***(Disproportionation)***

$\boldsymbol{Initiation}$: $I_2 \xrightarrow{k_d, f} 2R_1^{\cdot}$

$\boldsymbol{Propagation}$: $R_n^{\cdot} + M \xrightarrow{k_p} R_{n+1}^{\cdot}$

$\boldsymbol{Chain\ transfer\ to\ monomer}$: $R_n^{\cdot} + M \xrightarrow{k_{fm}} P_n + R_1^{\cdot}$

$\boldsymbol{Termination}$: $R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{tC}} P_{n+m}$

$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{tD}} P_n + P_m$

Main assumptions:

1) **SSA** for all active species
2) **(CLA)** Chain length-independent rate coefficients
3) **Constant volume**, isothermal, well-mixed Batch reactor
4) **Irreversible reactions** –neglect reverse reaction such as depropagation at high temperature
5) **No Chain transfer to solvent** – chain transfer to monomer only

Requests:

1) For 4 different values of conversion:

x_n^{Inst}, x_w^{Inst}, DP_N^{Inst}, DP_w^{Inst}, M_n^{Inst}, M_w^{Inst}, PDI^{Inst}

With

a) Dominant termination by disproportionation (C_{fm}=0,C_t=1000)

b) Dominant termination by combination (C_{fm}=0,C_t=0.001)

c) Dominant chain transfer to monomer and negligible termination by combination (C_{fm}=0.01,C_t=1000)

2) Same quantities neglecting the diffusion limitations