# ELABORATION OF A TENDENCY MODEL AND DETERMINATION OF OPTIMAL FEED RATE PROFILES OF STYRENE / BUTYL ACRYLATE SEMI-BATCH EMULSION COPOLYMERIZATION REACTOR

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# SUMMARY

- INTRODUCTION
- PROCESS MODEL
- EXPERIMENTAL SET-UP
- PARAMETRS IDENTIFICATION
- MODEL VALIDATION
- MULTICRITERIA OPTIMIZATION
- CONCLUSIONS AND FUTURE TRENDS

## Emulsion polymerization

paints, adhesives, coatings, varnishes….

Heat removal

Viscosity control

High molecular weights

High versatility of the products

# Position of the problem

**Tendency model**

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**Molecular weight distribution (MWD)**
**Glass transition temperature ($T_g$)**
**Particle size distribution (PSD)…**

⇓

**The end-use properties of the products**

⇓

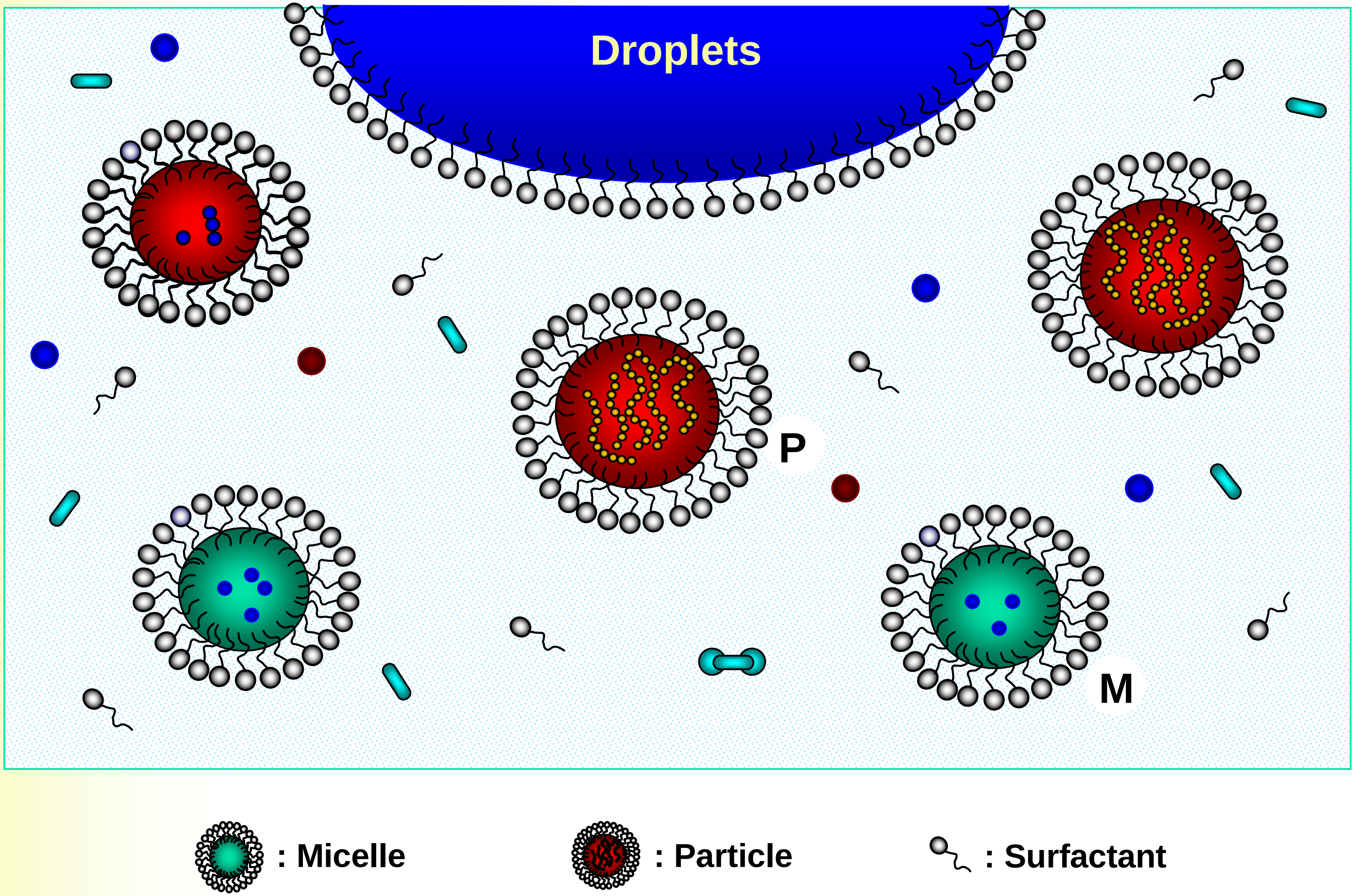
- *Rheological properties*
- *Adhesion and film-forming properties*
- *Elasticity, strength, toughness, and solvent resistance*

Parameter identification and model validation

Multiobjective optimization

B. Benyahia

# PRINCIPLE : Harkins' theory



## Step 1 : Nucleation

Micellar or homogeneous
Number of particles Np ↑

*Conversion : 0 - 10 %*

**Few minutes**

Micelles disappearance

## Step 2 : Particles growth

Np : constant
Particles saturated with monomer

*Conversion : 10 - 40 %*

Droplets disappearance

## Step 3 : End of polymerization

Particles unsaturated

*Conversion : 40-100 %*

# Main assumptions

- Only micellar nucleation is considered.
- Propagation, chain transfer to monomer, transfer chain transfer agent to monomers, and termination reactions in the aqueuse phase are neglected (weak solubility in water).
- Radical desorption is considered
- Droplets and particles diameters are considered as monodisperse
- The reactor is perfectly mixed and isothermal

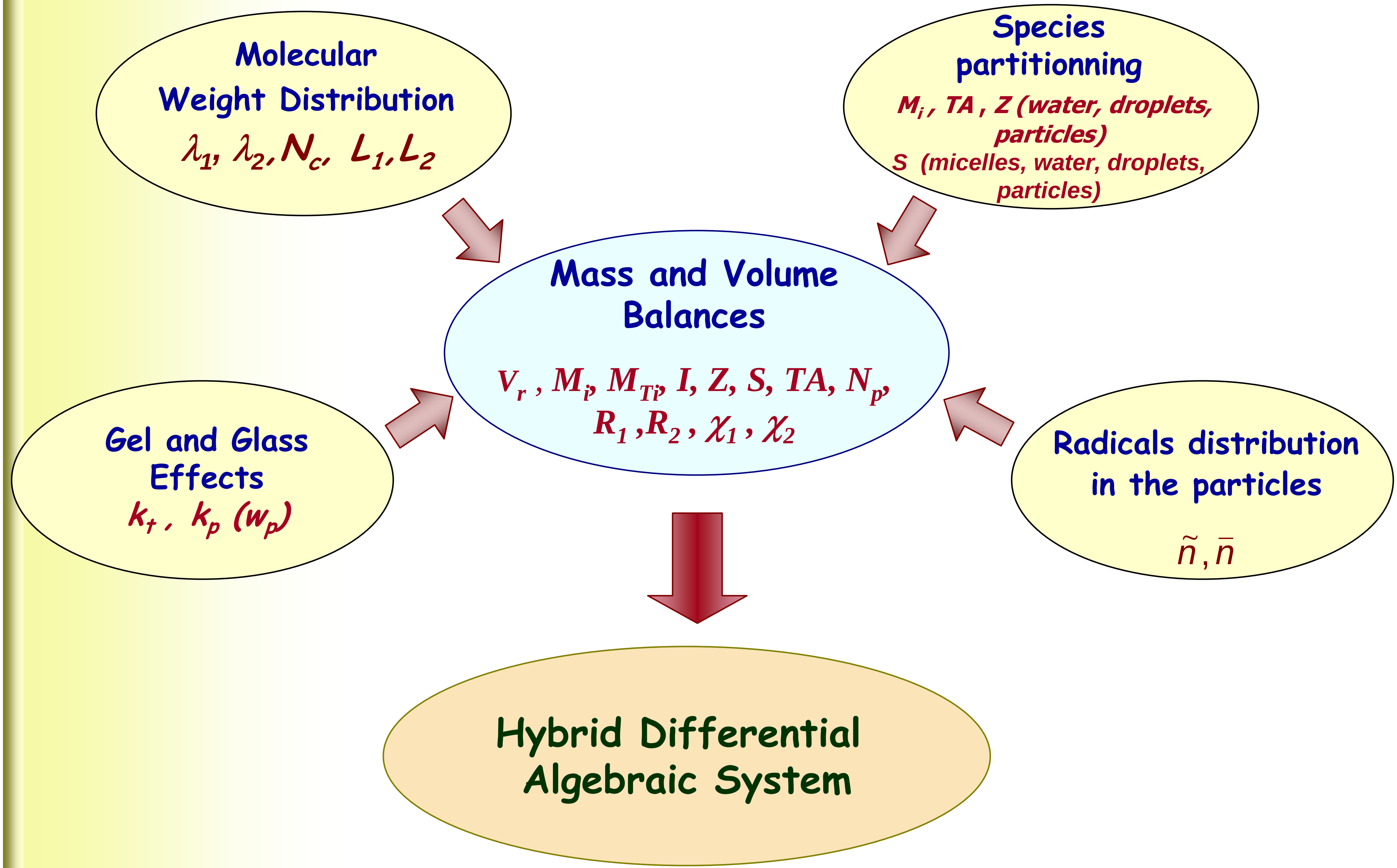
# Reactions Scheme

## Aqueous phase

| | |
|---|---|
| Initiation | $I_2 \xrightarrow{k_d} 2\, I^{\bullet}_{aq}$ |
| | $I^{\bullet}_{aq} + M_{iaq} \longrightarrow R^{\bullet}_{iaq}$ |
| Inihibition | $R^{\bullet}_{iaq} + Z_{aq} \xrightarrow{k_{zaqi}} P + Z^{\bullet}_{aq}$ |
| Nucleation | $R^{\bullet}_{iaq} + micelle \longrightarrow particle + R^{\bullet}_{i}$ |
| Radical absorption | $R^{\bullet}_{iaq} + particle \longrightarrow particle + R^{\bullet}_{i}$ |
| Radical desorption | $R^{\bullet}_{i} \xrightarrow{k_{desi}} R^{\bullet}_{iaq}$ |

## Organic phase

| | |
|---|---|
| Propagation | $R^{\bullet}_{i} + M_j \xrightarrow{k_{pij}} R^{\bullet}_{j}$ |
| Term. by combination | $R^{\bullet}_{i} + R^{\bullet}_{j} \xrightarrow{k_{tcij}} P$ |
| Term.by disproportionation | $R^{\bullet}_{i} + R^{\bullet}_{j} \xrightarrow{k_{tdij}} 2P$ |
| Inihibition | $R^{\bullet}_{i} + Z_P \xrightarrow{k_{zpi}} P + Z^{\bullet}_{P}$ |
| Transfer to monomers | $R^{\bullet}_{i} + M_j \xrightarrow{k_{trmonij}} P + R^{\bullet}_{j}$ |
| Transfer CTA-monomers | $R^{\bullet}_{i} + TA_P \xrightarrow{k_{trpi}} P + TA^{\bullet}_{P}$ |


Molecular
Weight Distribution
λ1, λ2, Nc, L1, L2
Species
partitionning
Mi, TA, Z (water, droplets, particles)
S (micelles, water, droplets, particles)
Mass and Volume
Balances
Vr, Mi, MTi, I, Z, S, TA, Np, R1, R2, χ1, χ2
Gel and Glass
Effects
kt, kp (wp)
Radicals distribution
in the particles
ñ, n̄
Hybrid Differential
Algebraic System

## Material balance

$$\frac{dV_{aq}}{dt} = Q_{aqf}$$

$$\frac{dV_R}{dt} = Q_f + \sum_{i=1,2} \left( \frac{1}{\rho_{pi}} - \frac{1}{\rho_i} \right) M_M^i \left( \Re_{pi} + \Re_{trmi} \right)$$

$$\frac{dM_i}{dt} = -\Re_{pi} - \Re_{trmi} + Q_{Mif}$$

$$\frac{dM_{Ti}}{dt} = Q_{Mif}$$

$$\frac{dI}{dt} = -\Re_d + Q_{If}$$

$$\frac{dZ}{dt} = -\Re_{Zaq} - \left( \Re_{Zp1} + \Re_{Zp2} \right) + Q_{Zf}$$

$$\frac{dTA}{dt} = -\Re_{TAp1} - \Re_{TAp2} + Q_{TAf}$$

$$\frac{dS}{dt} = Q_{Sf}$$

$$\frac{dN_p}{dt} = \Re_N$$

$$\frac{dR_1}{dt} = \left( \Re_N + \Re_{cp} \right) \frac{M_1}{M_1 + M_2} - \Re_{p12} + \Re_{p21} - \Re_{trm12} + \Re_{trm21} - \Re_{Zp1} - \Re_{des1} - \Re_{TAp1} - \left( \Re_{T11} + \Re_{T12} \right)$$

$$\frac{d\left(N_P \bar{n} \chi_1\right)}{dt} = \left( \Re_N + \Re_{cp} \right) \frac{M_1}{M_1 + M_2} - \Re_{trm21} + \Re_{trm11} - \Re_{des1} - \left( \Re_{trm11} + \Re_{trm12} + \Re_{p11} + \Re_{p12} + \Re_{TAp1} + \Re_{Zp1} \right) \chi_1 - \left( \Re_{T11} - \Re_{T12} \right) \chi_1$$

## Populations balance

$$\frac{d\left(N_P \bar{n}\right)}{dt} = \Re_N + \Re_{cp} - \left( \Re_T + \Re_{Zp} + \Re_{des} + \Re_{TAp} \right)$$

$$\frac{d\left(N_P \tilde{n}\right)}{dt} = 2\Re_{cp} \bar{n} + \left( \frac{2\tilde{\tilde{n}}}{\tilde{n}} + 1 \right) \Re_T - 2 \frac{\tilde{n}}{\bar{n}} \left( \Re_{Zp} + \Re_{des} + \Re_{TAp} \right)$$

## Equations of Moments

$$\frac{d\left(N_P \bar{n} \lambda_1\right)}{dt} = \Re_N + \Re_{cp} - \Re_{des} + \Re_P + \Re_{trm} \left(1 - \lambda_2\right) - \left( \Re_{Zp} + \Re_T + \Re_{TAp} \right) \lambda_1$$

$$\frac{d\left(N_P \bar{n} \lambda_2\right)}{dt} = \Re_N + \Re_{cp} - \Re_{des} + \Re_P \left(1 - 2\lambda_1\right) + \Re_{trm} \left(1 - \lambda_2\right) - \left( \Re_{Zp} + \Re_T + \Re_{TAp} \right) \lambda_2$$

$$\frac{d\left(N_C\right)}{dt} = \Re_N + \Re_{cp} + \Re_{trm} - \Re_{des} + \frac{\Re_{TC}}{2}$$

$$\frac{d\left(N_C L_1\right)}{dt} = \Re_N + \Re_{cp} + \Re_{trm} + \Re_P - \Re_{des}$$

$$\frac{d\left(N_C L_2\right)}{dt} = \Re_N + \Re_{cp} + \Re_{trm} + \Re_P \left(1 - 2\lambda_1\right) - \Re_{TC} \lambda_1^2 - \Re_{des}$$

## Algebraic equations

$$V_P = \frac{\sigma}{\sigma - 1} V_{pol}$$

$$\frac{1}{\sigma} = \frac{Z\, M_M^Z}{\rho_Z \left( V_p + V_d \sigma + V_{aq} K_{pZ} \right)} + \frac{TA\, M_M^{TA}}{\rho_{TA} \left( V_p + V_d \sigma + V_{aq} K_{pTA} \right)} + \sum_{j=A,B} \frac{M_j M_M^j}{\rho_j \left( V_p + V_d \sigma + V_{aq} K_{aq-p}^j \right)}$$

# Application : Styrene / Butyl acrylate

***Recipe :***

| | | | |
|---|---|---|---|
| Dispersion medium | : | Water | 68 % |
| Monomer 1 (M1) | : | Butyl Acrylate | 29.8 % (M1 + M2) |
| Monomer 2 (M2) | : | Styrene | |
| Surfactant (S) | : | REWOPOL SBFA 50 | 2 % |
| Initiator (I) | : | Ammonium persulfate | 0.1 % |
| Chain Transfer Agent (TA) | : | n-C12 mercaptan | 0.1 % |

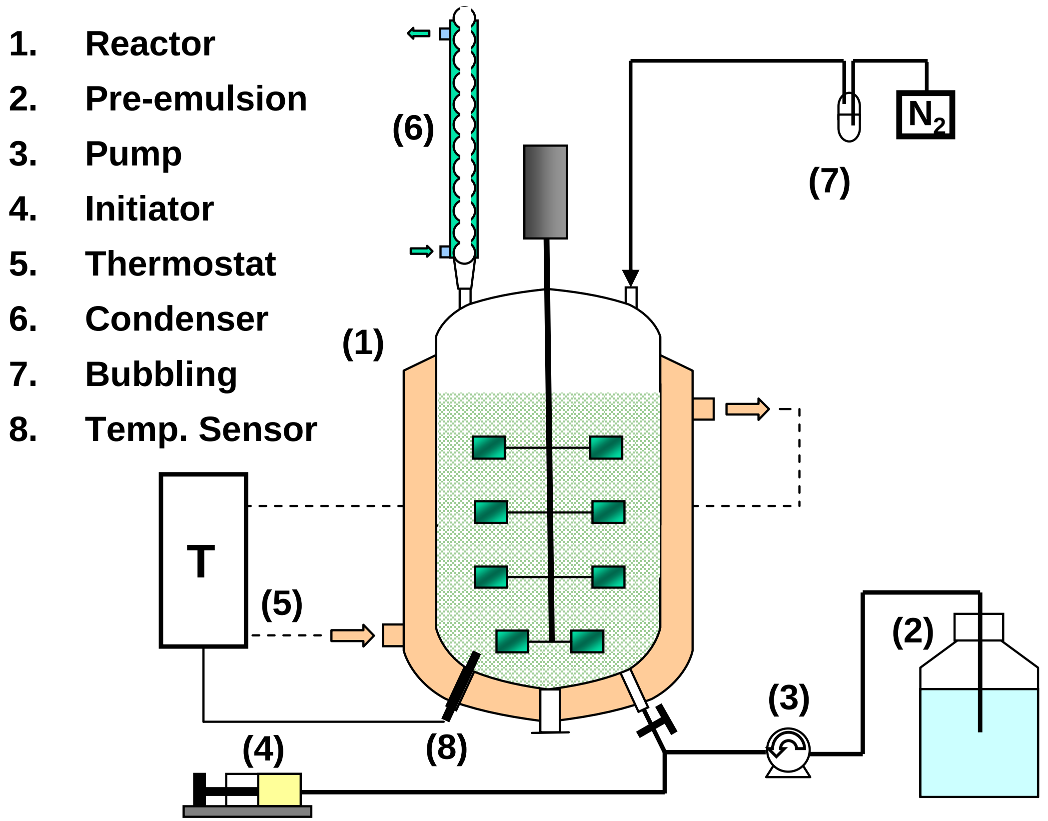
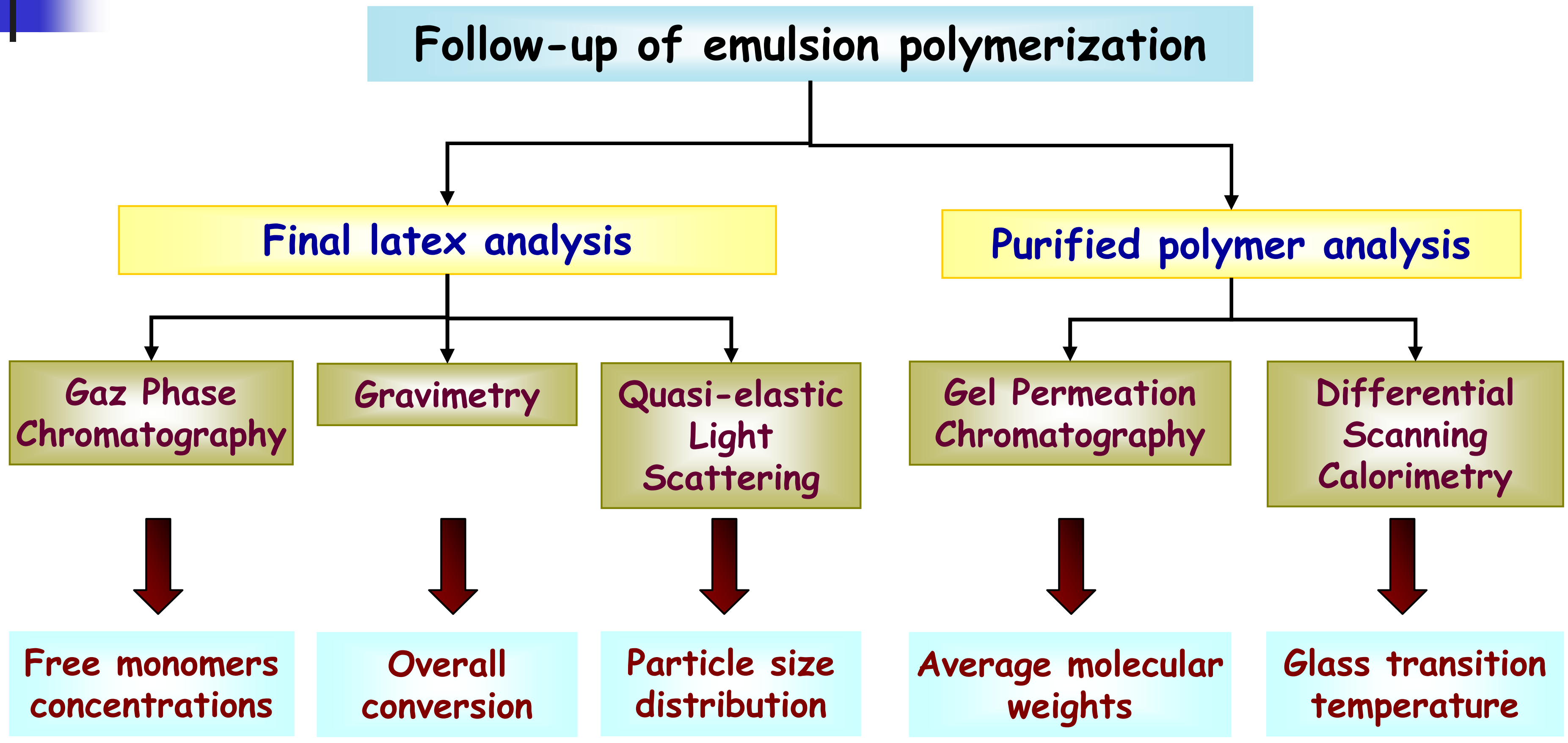



Diagram of the reactor

# Experimental investigation



Number of parameters to be determined: 38

Identified parameters : 18 parameters from an estimability ranking technique (Zhen et al., 2003) (the other parameters were taken from literature)

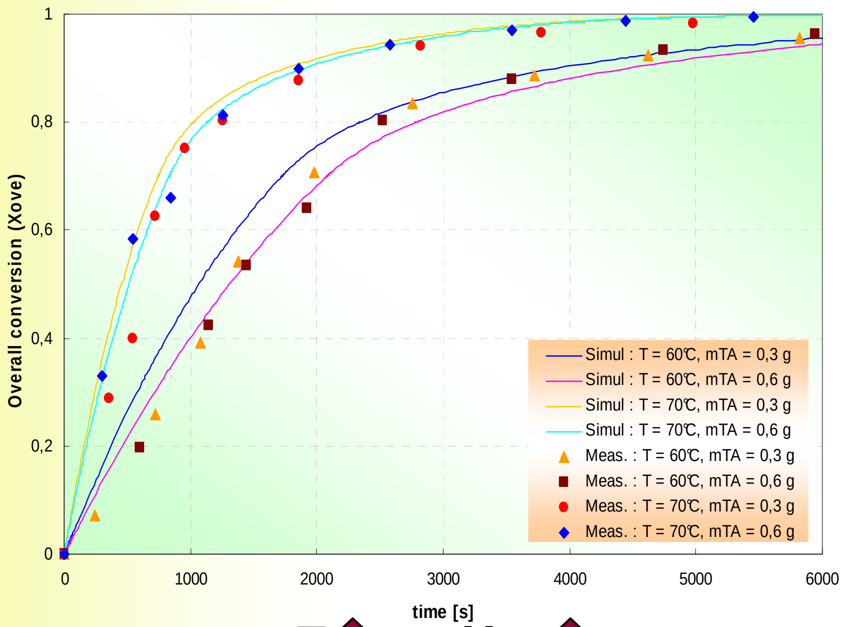
Experimental data : X, Mn, Mw, dp, Res. Monomers

Criteria of optimization : maximum likehood

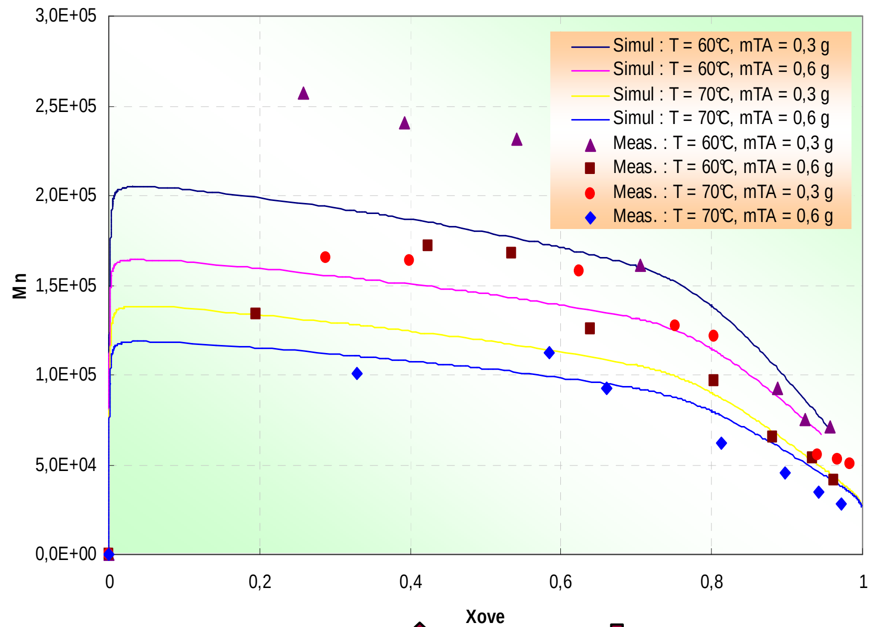
Objective function :

$$J = w_X.\ln\left(\sum_{data}\left(X_{exp}-X_{mod}\right)^2\right) + w_{d_p}.\ln\left(\sum_{data}\left(d_{pexp}-d_{pmod}\right)^2\right)$$
$$+ w_{\overline{M}_n}.\ln\left(\sum_{data}\left(\overline{M}_{nexp}-\overline{M}_{nmod}\right)^2\right) + w_{\overline{M}_w}.\ln\left(\sum_{data}\left(\overline{M}_{wexp}-\overline{M}_{wmod}\right)^2\right) +$$
$$w_{Fr_1}.\ln\left(\sum_{data}\left(Fr_{1exp}-Fr_{1mod}\right)^2\right)$$

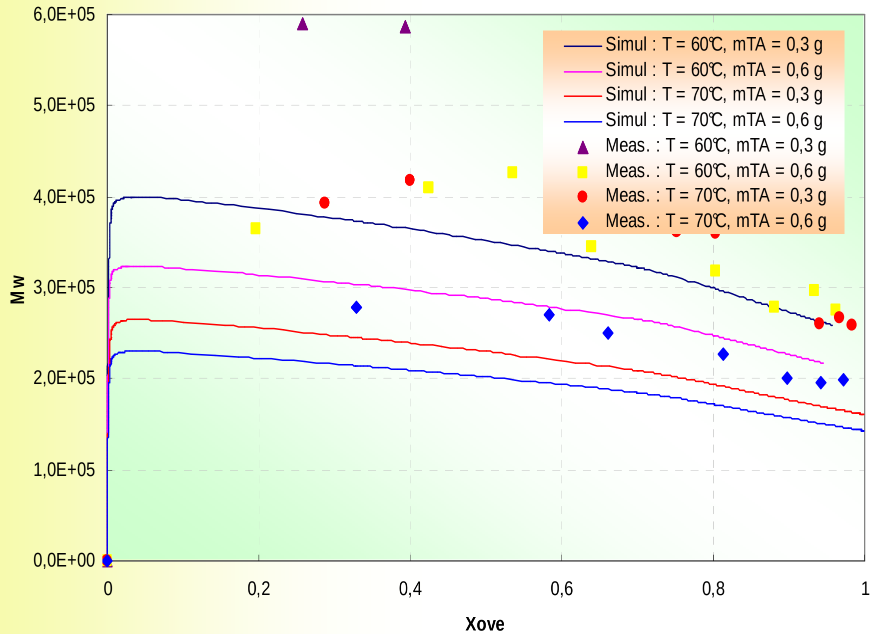
# *Parameter identification results*



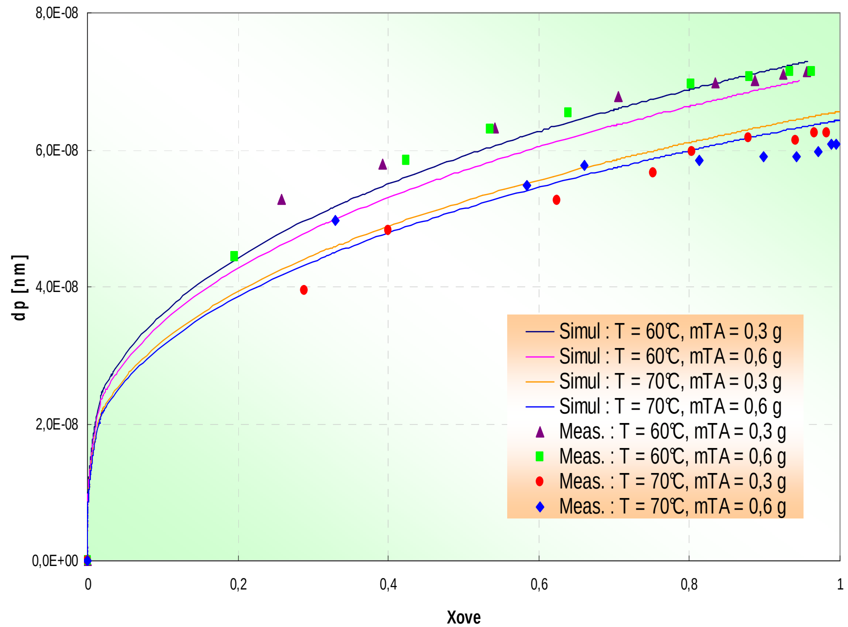

**T ↑ ⇒ $X_{ove}$ ↑**




**$m_{CTA}$ ↑ ⇒ $M_n$ ↓**

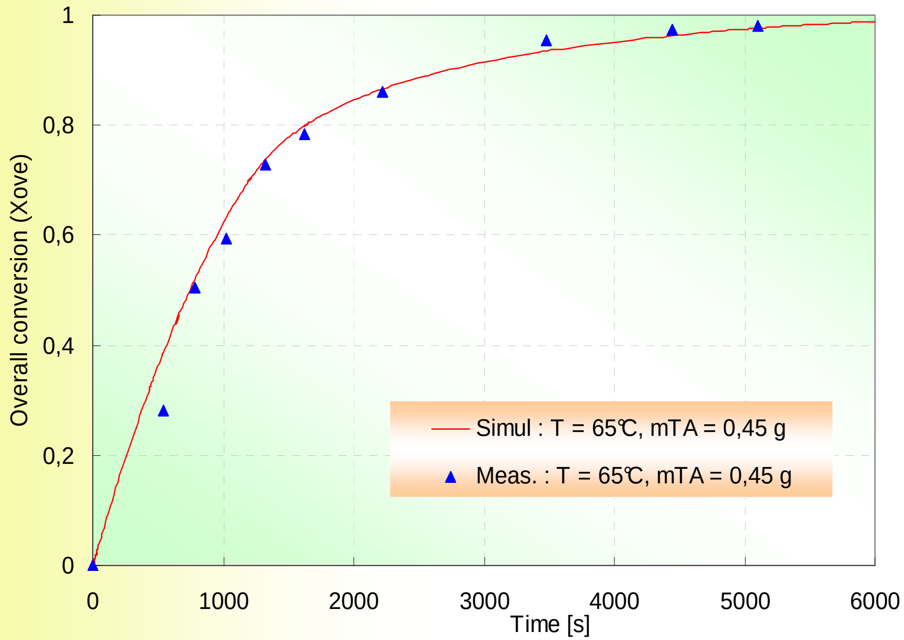


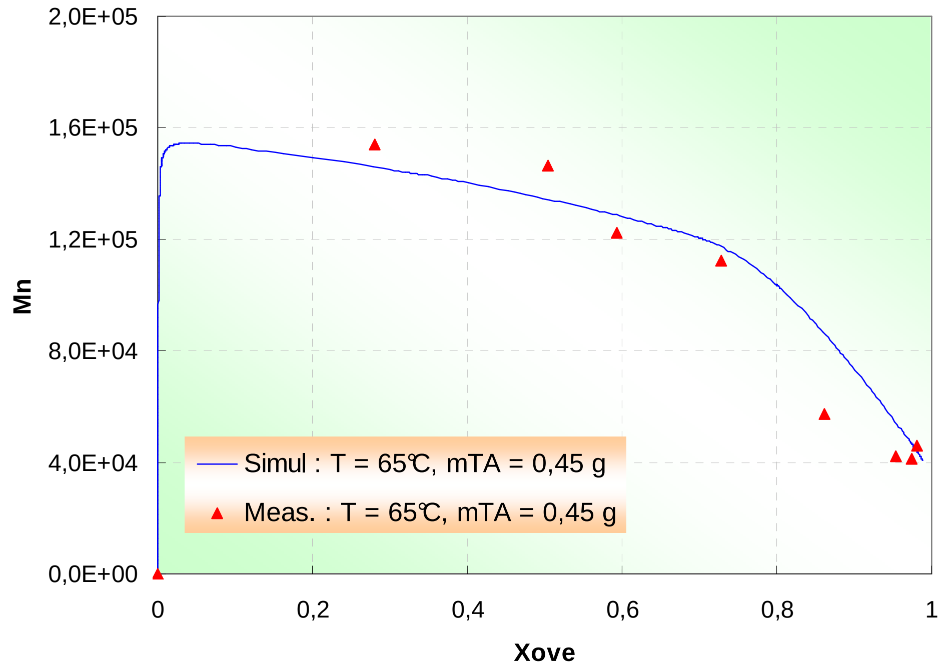

**$m_{CTA}$ ↑ ⇒ $M_n$ ↓**

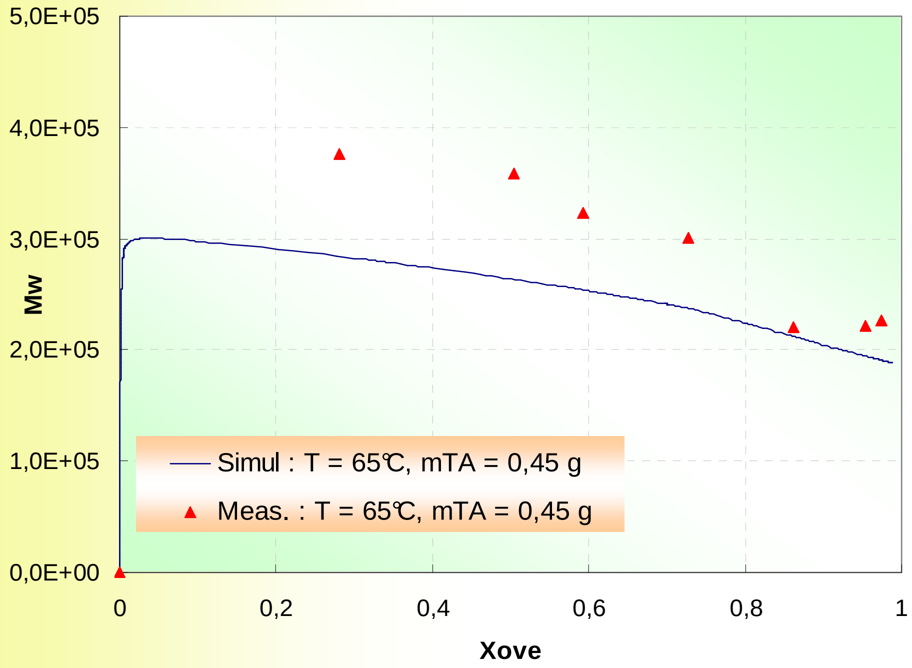


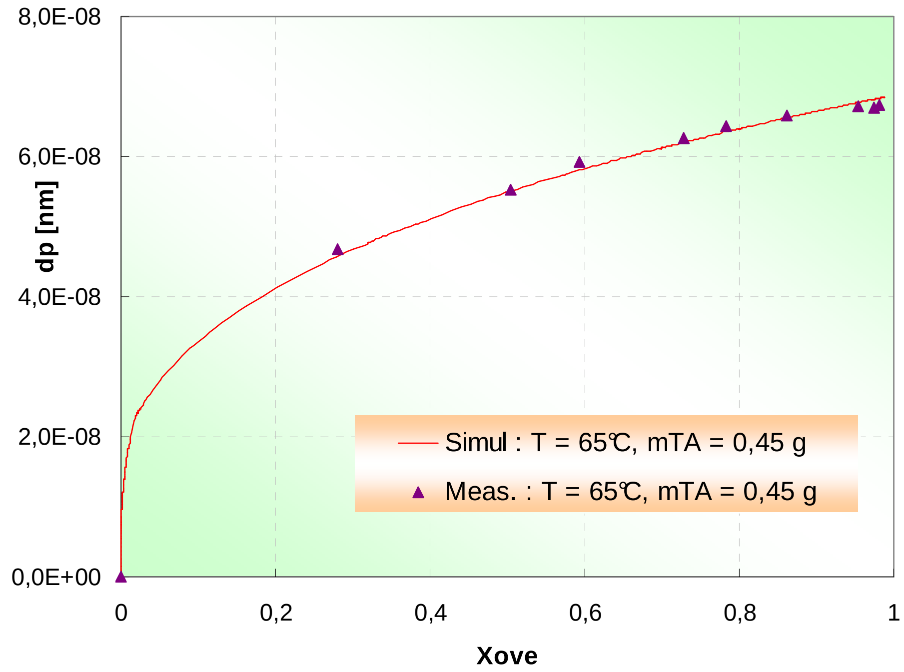

**T ↑ ⇒ $d_p$ ↓**

# *Validation results*



# General Context

**Problematics : Simultaneous optimization of criteria often conflicting** *(productivity, cost, quality, security, environment…)*

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***No optimal solution***

↓

**Search for a group of compromises**

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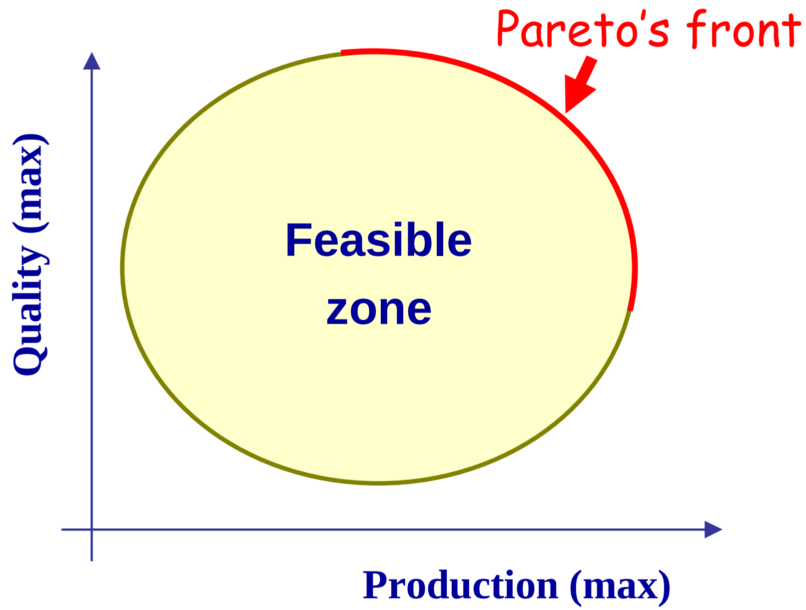
**Choice of the best compromise**



## Definition of the problem :

$$
\begin{cases}
Min & f = [f_1, f_2] \\
 & f_1 = \dfrac{1}{t_{fc} - t_0} \displaystyle\int_{t_{fc}}^{t_0} \left| T_g - T_{g1} \right| dt + \dfrac{1}{t_{fs} - t_{fc}} \displaystyle\int_{t_{fs}}^{t_{fc}} \left| T_g - T_{g2} \right| dt \\
 & f_2 = -X(t_f) \\
s.t & \dot{x} = f(\boldsymbol{x}(t), \boldsymbol{u}(t), \boldsymbol{p}, t) \\
 & \dfrac{1}{t_{fc} - t_0} \displaystyle\int_{t_{fc}}^{t_0} (X_a - X(t))^2 dt \le \varepsilon^2 \\
 & \boldsymbol{u}_{\inf} \le \boldsymbol{u} \le \boldsymbol{u}_{\sup}
\end{cases}
$$

⇩

***u: feed rate ($Q_f$)***

# Conclusions

Elaboration and validation of a tendency model able to predict :

*Overall and partial conversions*

*Residual monomers*

*Number and weight average molecular weights*

*Particles diameters*

Development of a methodology to solve multiobjective decision problems :

*Simultaneous optimization of several criteria*

*Productivity*

*Quality*

# Futur trends

Decision-making support

Implementation of a solution from Pareto's front

Dynamic optimization (one criterium)

*THANK YOU*

*DAKUJEM*