# Modeling of Polymerization Reactors by Coupling of CFD and Reaction Kinetics

A. Daiss, K.D. Hungenberg, W. Loth, S. Müssig
BASF SE

1. Motivation
2. Approach
3. Validation concept
4. Application example

# Motivation

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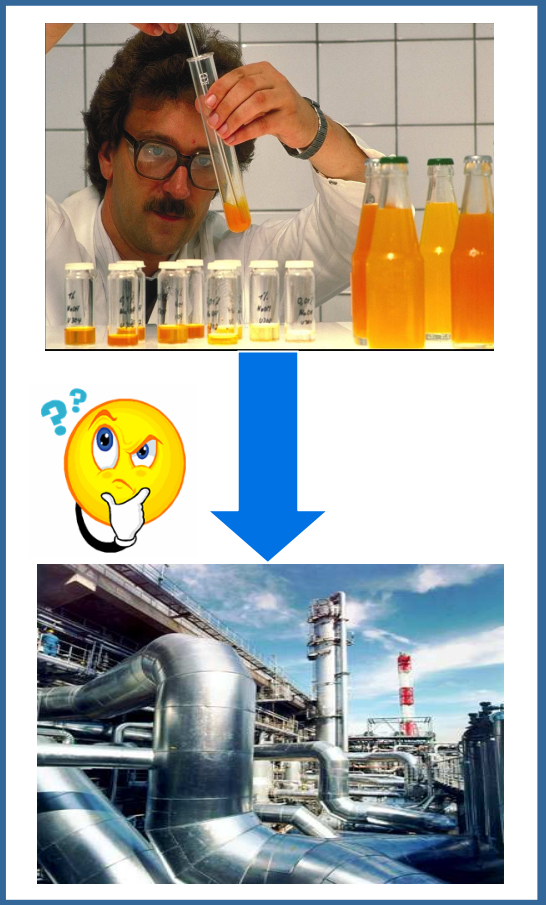
*Scale-up of polymerization reactors is a difficult task:*

- Polymerization reactions are strongly influenced by temperature variations and non-uniform residence time distributions
- Flow properties (e.g. viscosity) may change dramatically due to polymerization and thus process parameters (mixing, heat transfer) may significantly change along the reaction



Usually polymerization processes are calculated and scaled by assuming plug flow conditions in tubular reactors and ideally mixed conditions in batch- or semi-batch reactors or by using simplified reactor cascade models

→ CFD may be a helpful tool for evaluating the effect of non-ideal reaction conditions in polymerization processes and for scale-up

# Approach

## Method of Moments

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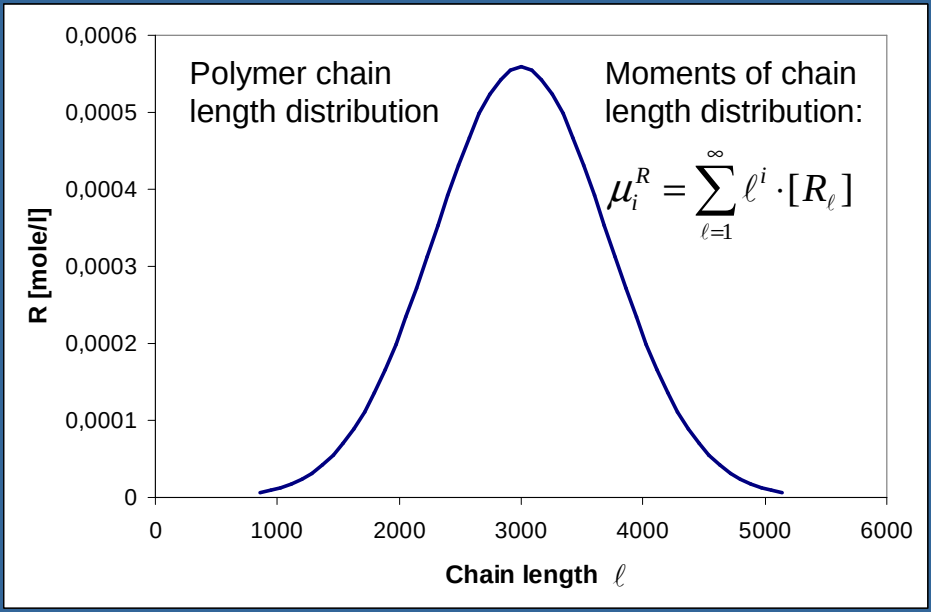
- Simplified description of weight distribution of polymer molecules by classical method of moments
- Variable material properties as a function of temperature, conversion, etc.
- Modular implementation of species- and moment source terms due to polymerization kinetics in software CFX11 via Command expression language




Method of Moment: Example Propagation Reaction

$$R_\ell + M \xrightarrow{k_P} R_{\ell+1}$$

$$\frac{\partial[R_\ell]}{\partial t} = k_P \cdot [R_{\ell-1}] \cdot [M] - k_P \cdot [R_\ell] \cdot [M] \qquad \ell = 1, N_{\max}$$

$$\frac{\partial[M]}{\partial t} = -k_P \cdot \sum_{\ell=1}^{\infty} [R_\ell] \cdot [M]$$

→ $N_{max+1}$ equations !!!!

$$\frac{\partial \rho \mu_i^R}{\partial t} = \frac{\rho^2}{M_M} \cdot k_P \cdot g_M \cdot \left[ \sum_{j=0}^{i} \binom{i}{j} \cdot \mu_j^R - \mu_i^R \right], \quad i = 0,1,2$$

$$\frac{\partial \rho g_M}{\partial t} = -\frac{\rho}{M_R} \cdot k_P \cdot \mu_0^R \cdot g_M$$

→ 4 equations only

# Kinetic Scheme

## Free Radical Homo-Polymerization

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Initiator decomposition: $I \xrightarrow{k_d} 2 \cdot R_I$

Initiation: $R_I + M \xrightarrow{k_I} R_1 + R_{I,D}$

Chain growth: $R_\ell + M \xrightarrow{k_P} R_{\ell+1}$

Termination by combination: $R_\ell + R_m \xrightarrow{k_{t,D}} P_\ell + P_m$

Termination by disproportionation: $R_\ell + R_m \xrightarrow{k_{t,C}} P_{\ell+m}$

Transfer to monomer: $R_\ell + M \xrightarrow{k_{tr,M}} P_\ell + R_1$

Transfer to modifier: $R_\ell + X \xrightarrow{k_{tr,X}} P_\ell + R_1$

# Model Validation I

## Comparison of CFD Model with PREDICI™

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- PREDICI™ is a well established and validated polymer kinetics simulation tool:
  - 1D-tubular reactor, batch- or semi-batch reactor models
  - Isothermal, adiabatic or cooled/heated systems
  - Full molecular weight distribution or moment mode calculations
  - Arbitrary polymer kinetics can be taken into account

- Comparison of CFD calculations with PREDICI™ allows for a detailed validation of the CFD model without **uncertainties due to experimental error** under the following conditions
  - 1D adiabatic plug flow reactor
  - PREDICI™ in moment mode
  - Consideration of polymer reaction only which due not result in closure problems of the moment equations

# Model Validation II

## Generic Test System

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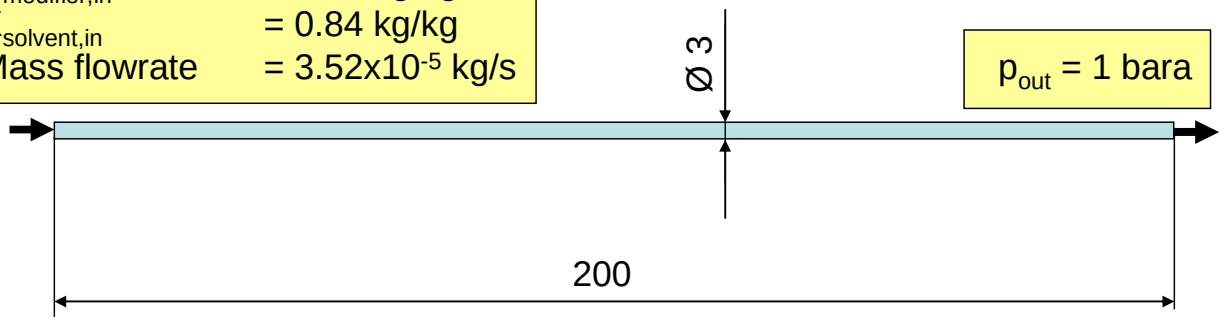
### Adiabatic plug flow reactor

| | |
|---|---|
| $T_{in}$ | = 20°C |
| $X_{monomer,in}$ | = 0.15 kg/kg |
| $X_{initiator,in}$ | = 0.01 kg/kg |
| $X_{modifier,in}$ | = 0.00 kg/kg |
| $X_{solvent,in}$ | = 0.84 kg/kg |
| Mass flowrate | = 3.52x10$^{-5}$ kg/s |




### Kinetic parameters

$$k_d = 2 \cdot 10^{12}\, s^{-1} \cdot \exp\left[-\frac{83900\ \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_I = 10\ \frac{\ell}{mole \cdot s}$$

$$k_P = 3 \cdot 10^{7}\ \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{25000\ \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{t,D} = 3 \cdot 10^{9}\ \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{40000\ \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{t,C} = 3 \cdot 10^{9}\ \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{40000\ \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{tr,M} = 0\ \frac{\ell}{mole \cdot s}$$

### Constant material properties

| | |
|---|---|
| • Viscosity | 10 mPas |
| • Density | 1000 kg/m³ |
| • Specific heat | 3000 J/kgK |
| • Thermal conductivity | 0.5 W/mK |

# Model Validation III

## Comparison of Temperature & Concentrations

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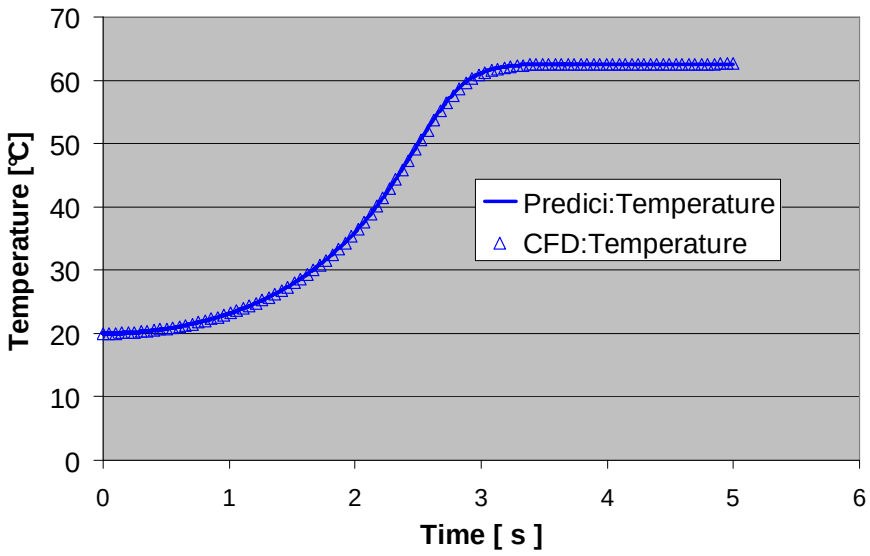
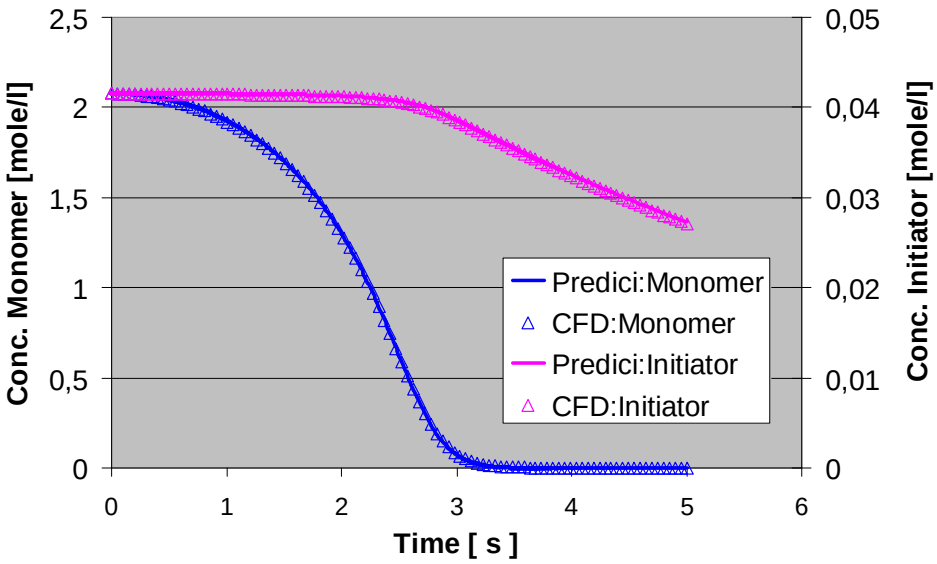
### Temperature




### Monomer and initiator mass fraction



# Model Validation IV

## Comparison of Molecular Properties

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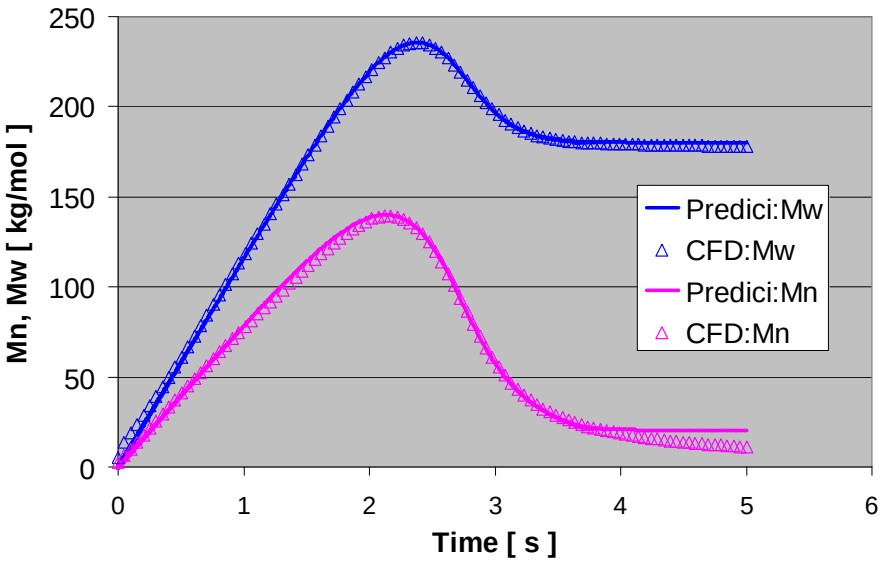
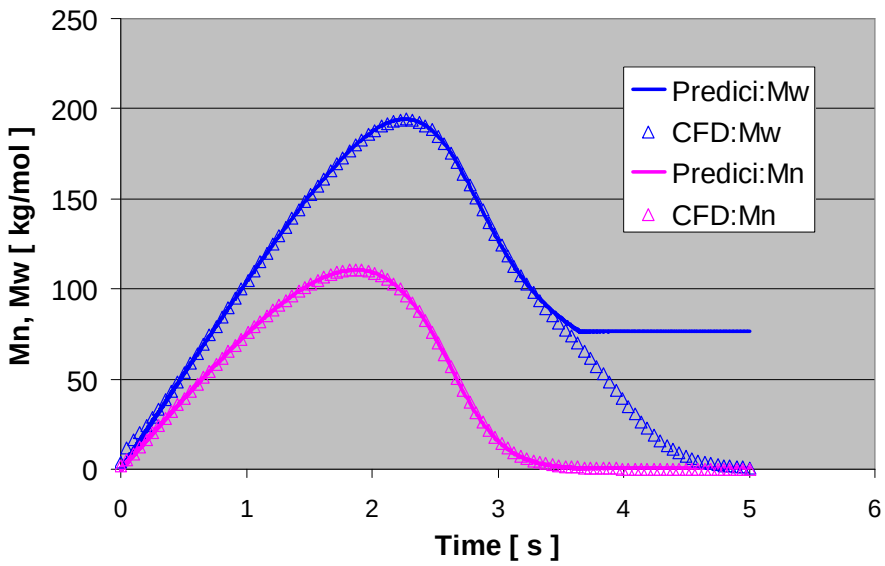
### Dead polymer




### Growing polymer



# Non-ideal tubular reactor I

## Cooled Tubular Reactor

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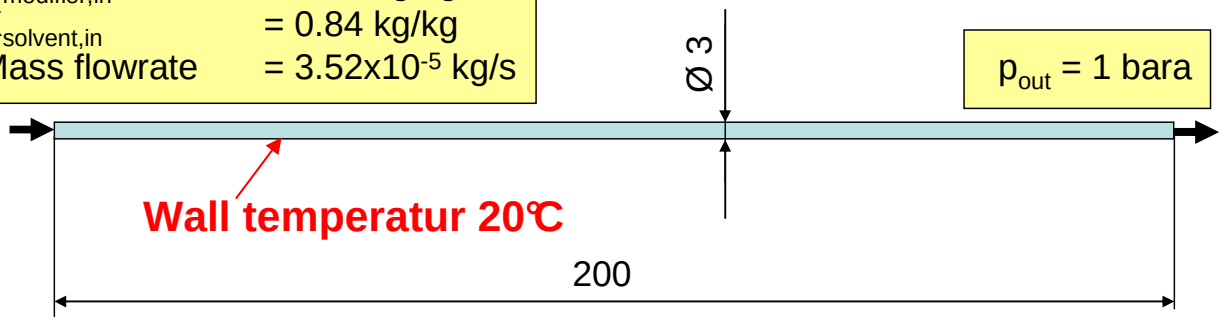
### Laminar pipe flow

| | |
|---|---|
| $T_{in}$ | = 20℃ |
| $X_{monomer,in}$ | = 0.15 kg/kg |
| $X_{initiator,in}$ | = 0.01 kg/kg |
| $X_{modifier,in}$ | = 0.00 kg/kg |
| $X_{solvent,in}$ | = 0.84 kg/kg |
| Mass flowrate | = $3.52 \times 10^{-5}$ kg/s |




### Kinetic parameters

$$k_d = 2 \cdot 10^{12}\, s^{-1} \cdot \exp\left[-\frac{83900 \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_I = 10 \frac{\ell}{mole \cdot s}$$

$$k_P = 3 \cdot 10^{7} \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{25000 \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{t,D} = 3 \cdot 10^{9} \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{40000 \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{t,C} = 3 \cdot 10^{9} \frac{\ell}{mole \cdot s} \cdot \exp\left[-\frac{40000 \frac{J}{mole}}{\Re \cdot T}\right]$$

$$k_{tr,M} = 0 \frac{\ell}{mole \cdot s}$$

### Constant material properties

| | |
|---|---|
| • Viscosity | 10 mPas |
| • Density | 1000 kg/m³ |
| • Specific heat | 3000 J/kgK |
| • Thermal conductivity | 0.5 W/mK |

# Non-ideal tubular reactor II

## Qualitative Results – Temperature & Concentrations

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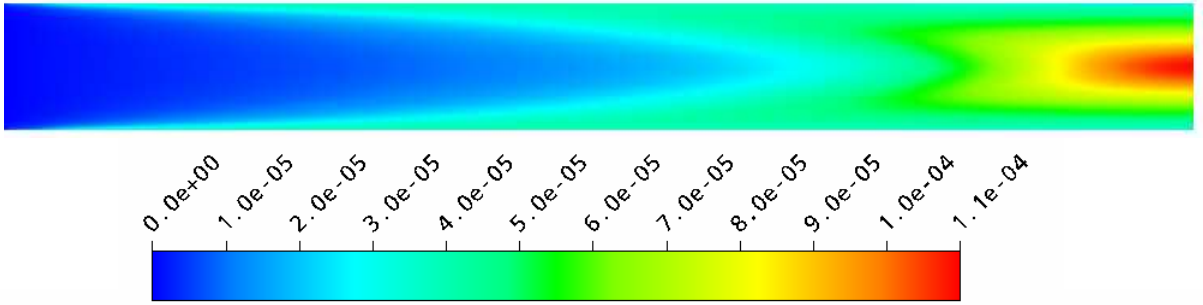
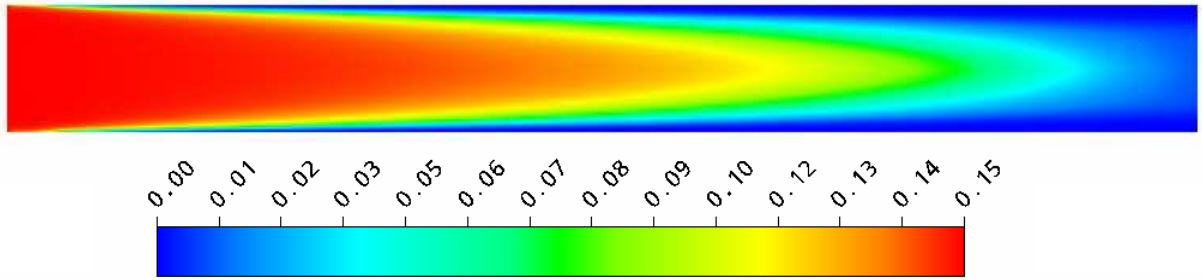
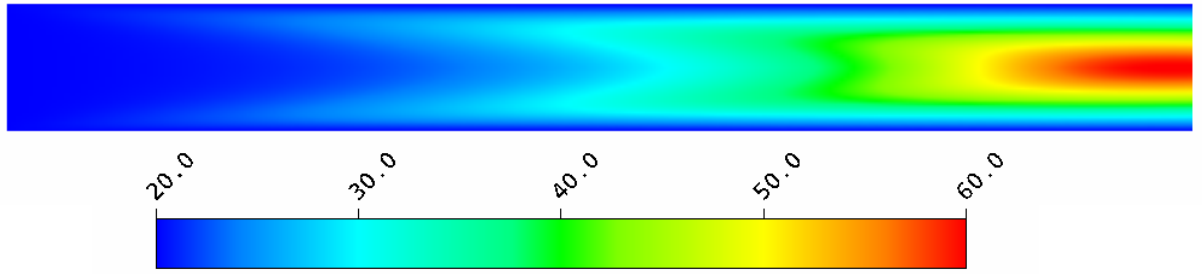
Radical mass fraction
[kg/kg]




Monomer mass fraction
[kg/kg]




Temperature
[℃]



# Non-ideal tubular reactor III

## Qualitative Results – Molecular Properties

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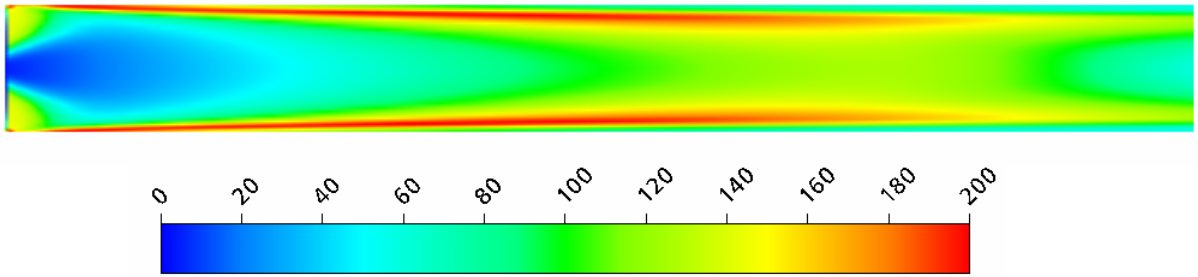
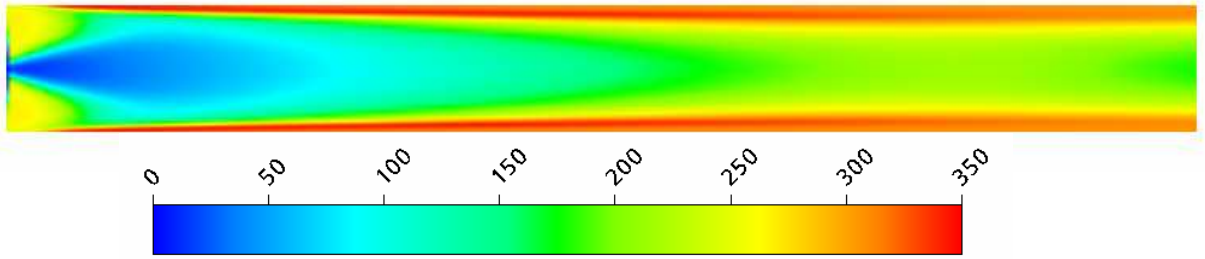
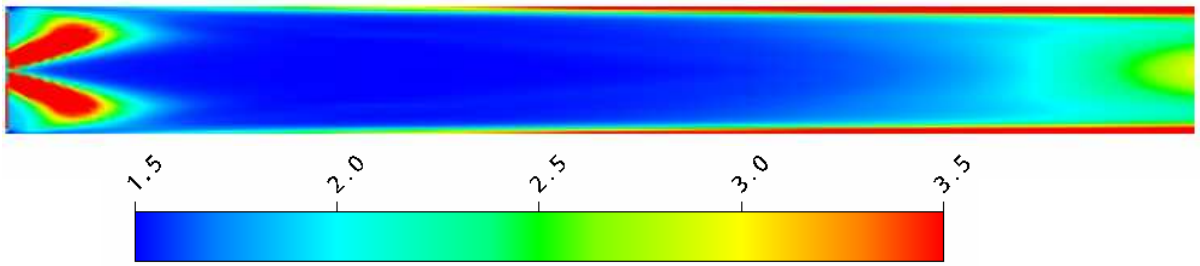
Number averaged polymer weight [kg/mole] Dead polymer




Mass averaged polymer weight [kg/mole] Dead polymer




Polydispersity = $M_W/M_N$ [-]



# Non-ideal tubular reactor IV

## Comparison of CFD Calculation with PREDICI™

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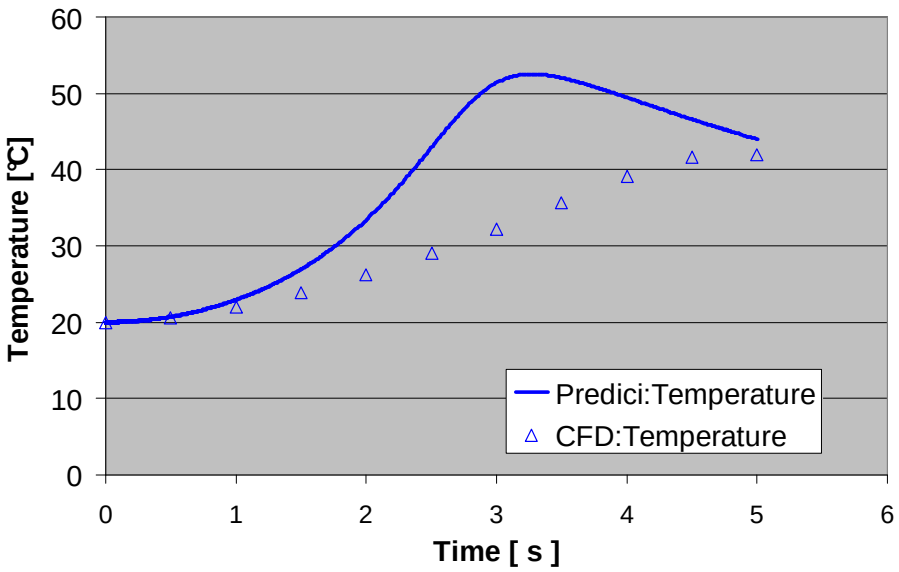
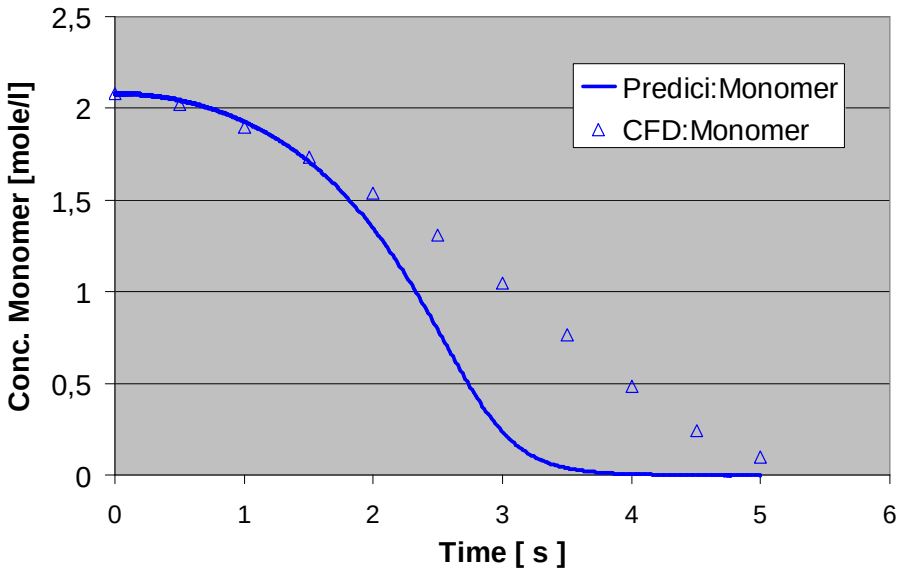
### Average temperature




### Average monomer concentration



# Non-ideal tubular reactor V

## Comparison of CFD Calculation with PREDICI™

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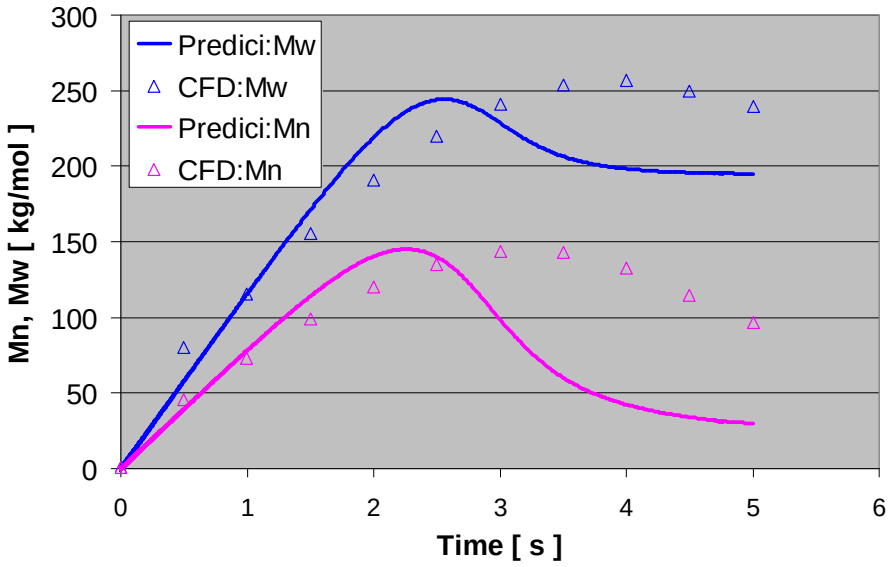
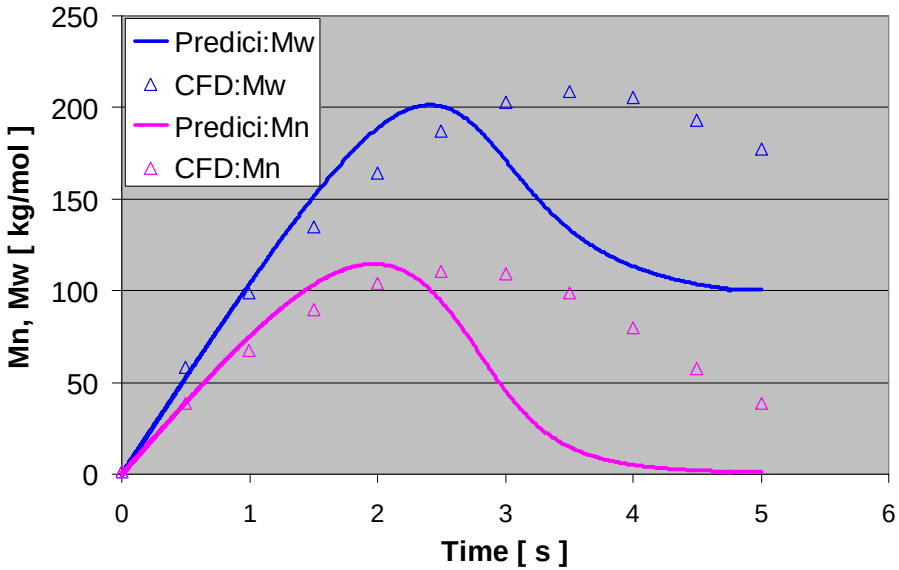
### Averaged weights (dead polymer)




### Averaged weights (Growing polymer)



# Pilot Plant Reactor I

## Reactor Geometry and Operating Conditions

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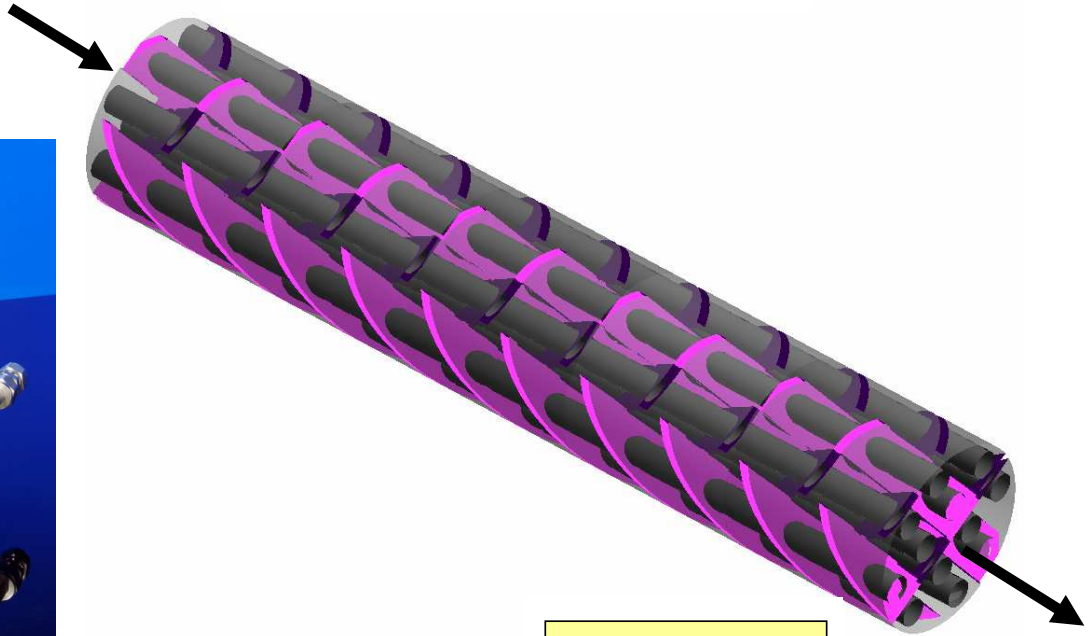
Fluitec CSE/XR™ static mixer reactor
Inner diameter 27 mm
Length 135 mm
Cooled internal pipes

| | |
|---|---|
| $T_{in}$ | = 20°C |
| $X_{monomer,in}$ | = 0.15 kg/kg |
| $X_{initiator,in}$ | = 0.01 kg/kg |
| $X_{modifier,in}$ | = 0.00 kg/kg |
| $X_{solvent,in}$ | = 0.84 kg/kg |
| Mass flowrate | = 0.01 kg/s |

Photo by courtesy of Fluitec Georg AG, Switzerland



$p_{out}$ = 1 bara

# Pilot Plant Reactor II

## Qualitative Results – Temperature & Concentrations

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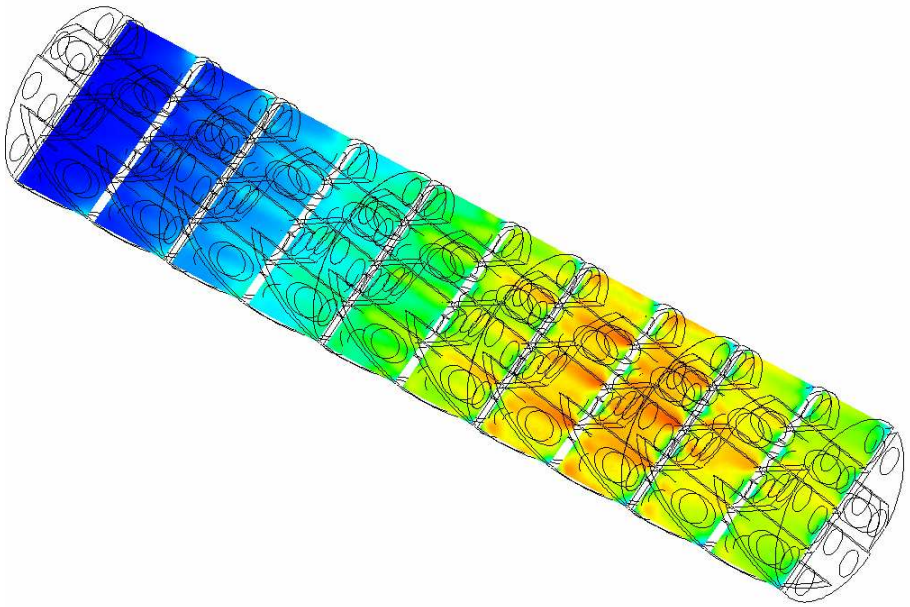
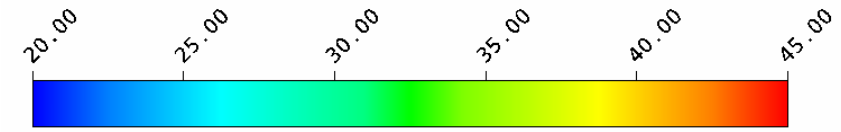
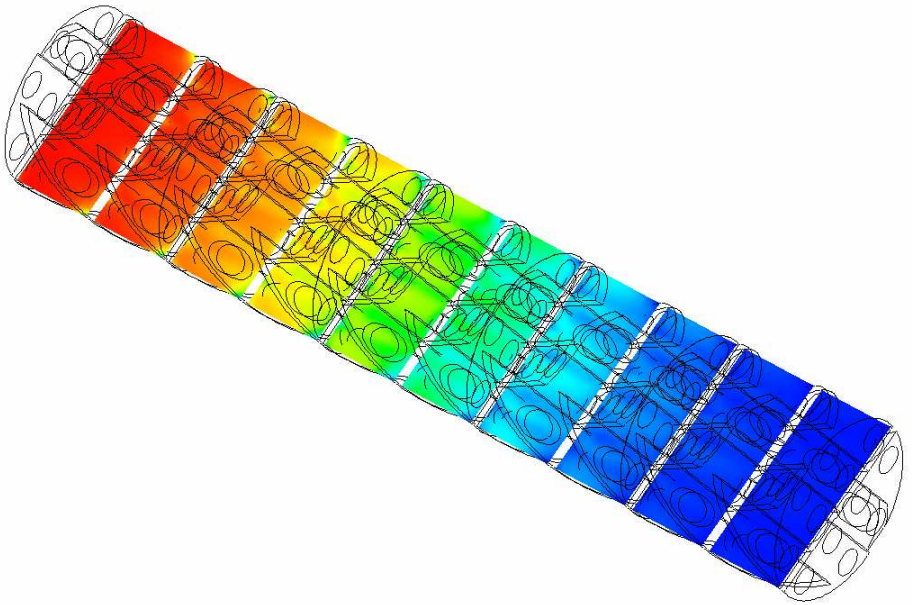
Temperature



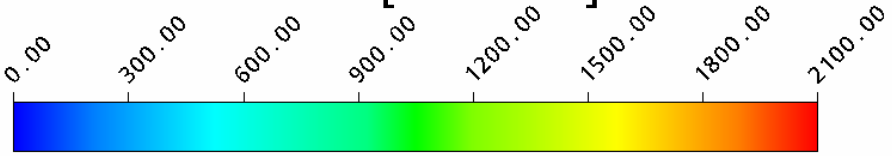
T [°C]




Monomer concentration



c [mole/m³]



# Pilot Plant Reactor III

## Qualitative Results – Temperature & Concentrations

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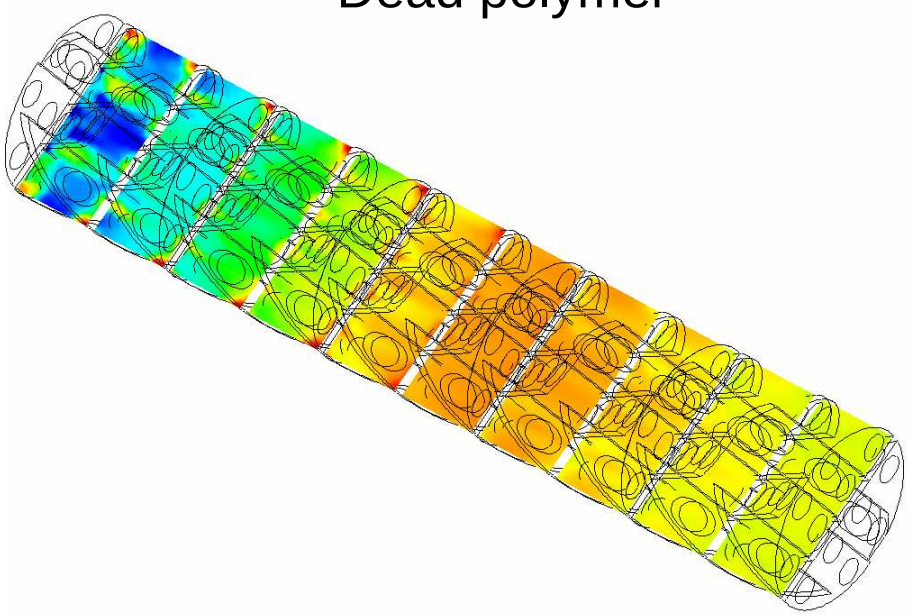
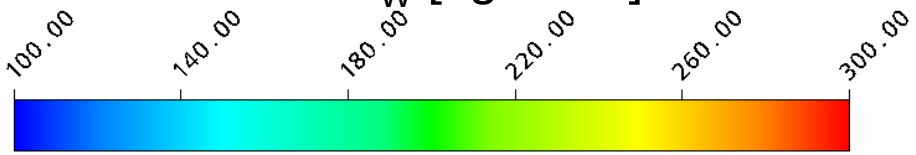
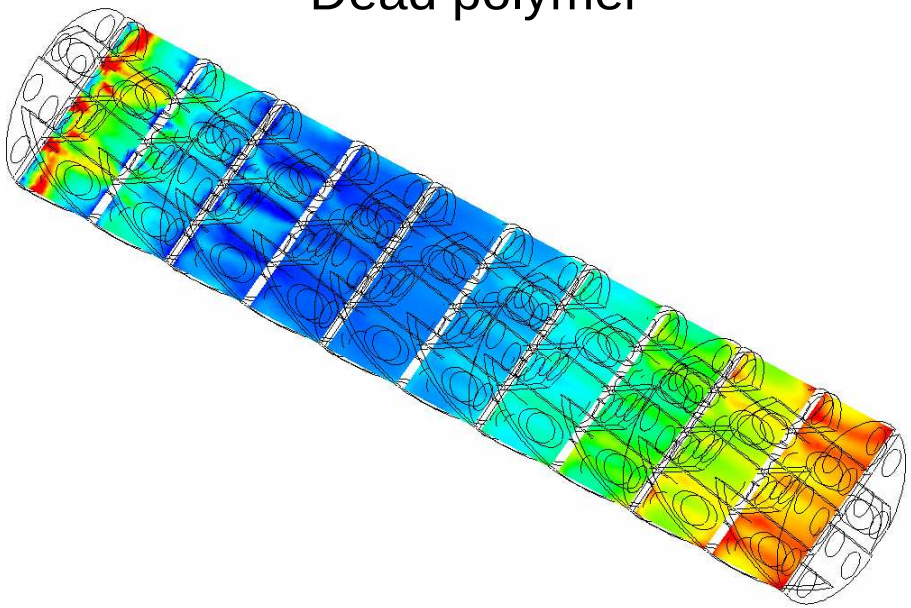
Mass averaged molecular weight
Dead polymer



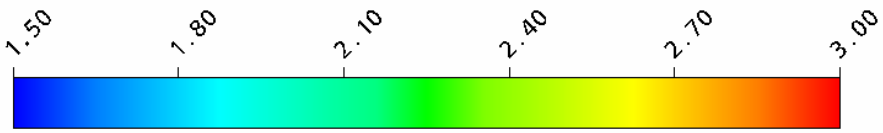
$M_W$ [kg/mole]




Polydispersity
Dead polymer



PDI = $M_W/M_N$



# Pilot Plant Reactor IV

## Comparison of Static Mixer Reactor vs Pipe Flow

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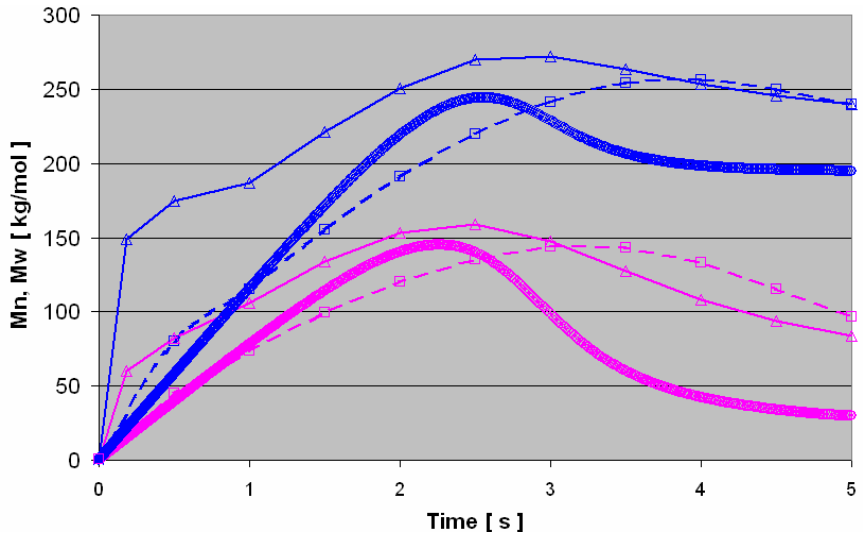
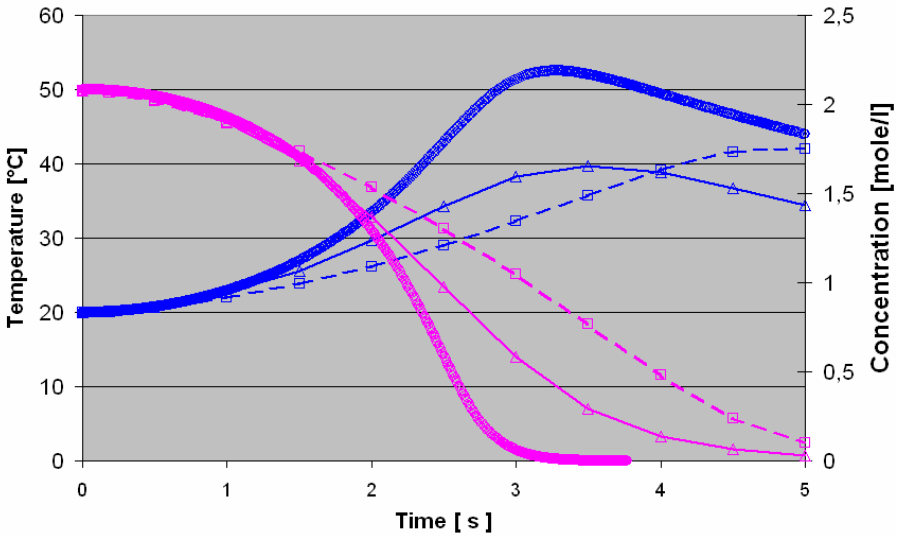
### Molecular weights - dead polymer




- Mn: Capillary reactor, 1D calculation
- Mn: Capillary reactor 3mm, CFD
- Mn: Static mixer reactor, CFD
- Mw: Capillary reactor, 1D calculation
- Mw: Capillary reactor 3mm, CFD
- Mw: Static mixer reactor, CFD

### Temperature & Concentration




- T: Capillary reactor, 1D calculation
- T: Capillary reactor 3mm, CFD
- T: Static mixer reactor, CFD
- C: Capillary reactor, 1D calculation
- C: Capillary reactor 3mm, CFD
- C: Static mixer reactor, CFD

# Conclusions & Future

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- Polymerization reactors may show significant 2D/3D effects under non-isothermal operating conditions
  - 1-D calculations for laminar capillary reactors may be misleading
  - Polymer properties are affected by 2D/3D effects
  - Conversion may change for a given residence time due to 2D/3D effects

→ **CFD is a useful tool for the scale-up of polymerization reactors**

- Future work
  - Incorporation of copolymerization based on pseudo-homopolymerization approach
  - Modeling of other polymerization processes (poly-addition, poly-condensation, ionic polymerization)

# CFD Engineers vision

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