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Fouling in the High Pressure LDPE Process

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Experimental and Computational Investigation Approach

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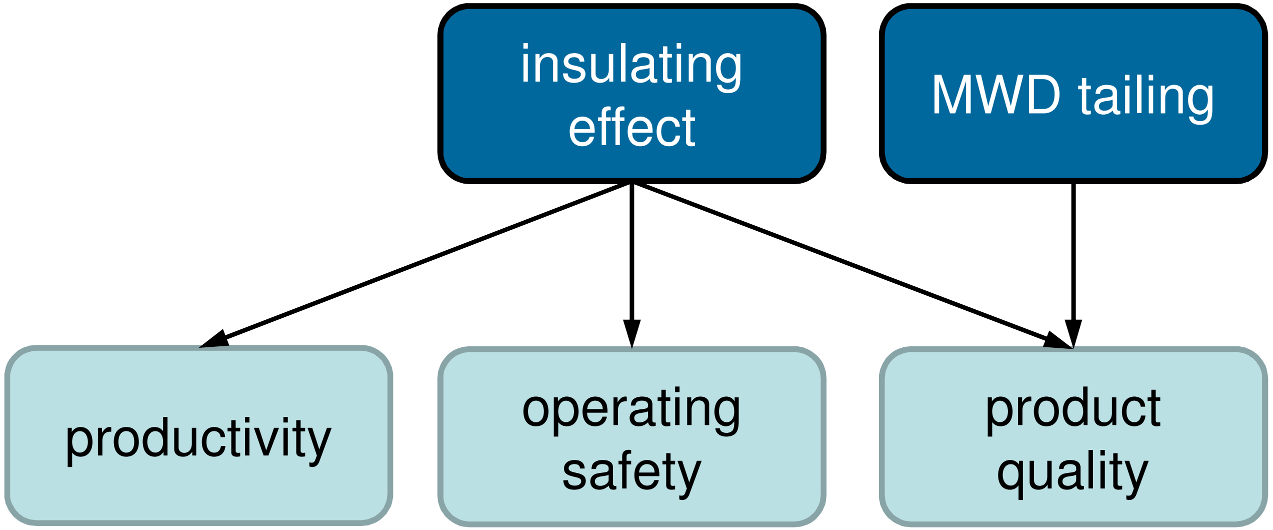
What is LDPE Fouling?

- low-density polyethylene (LDPE) is produced under high temperatures (140°C – 330°C) and pressures (1000 bar – 3500 bar)
- fouling mechanisms still not understood
- fouling impacts:



Investigation Strategy

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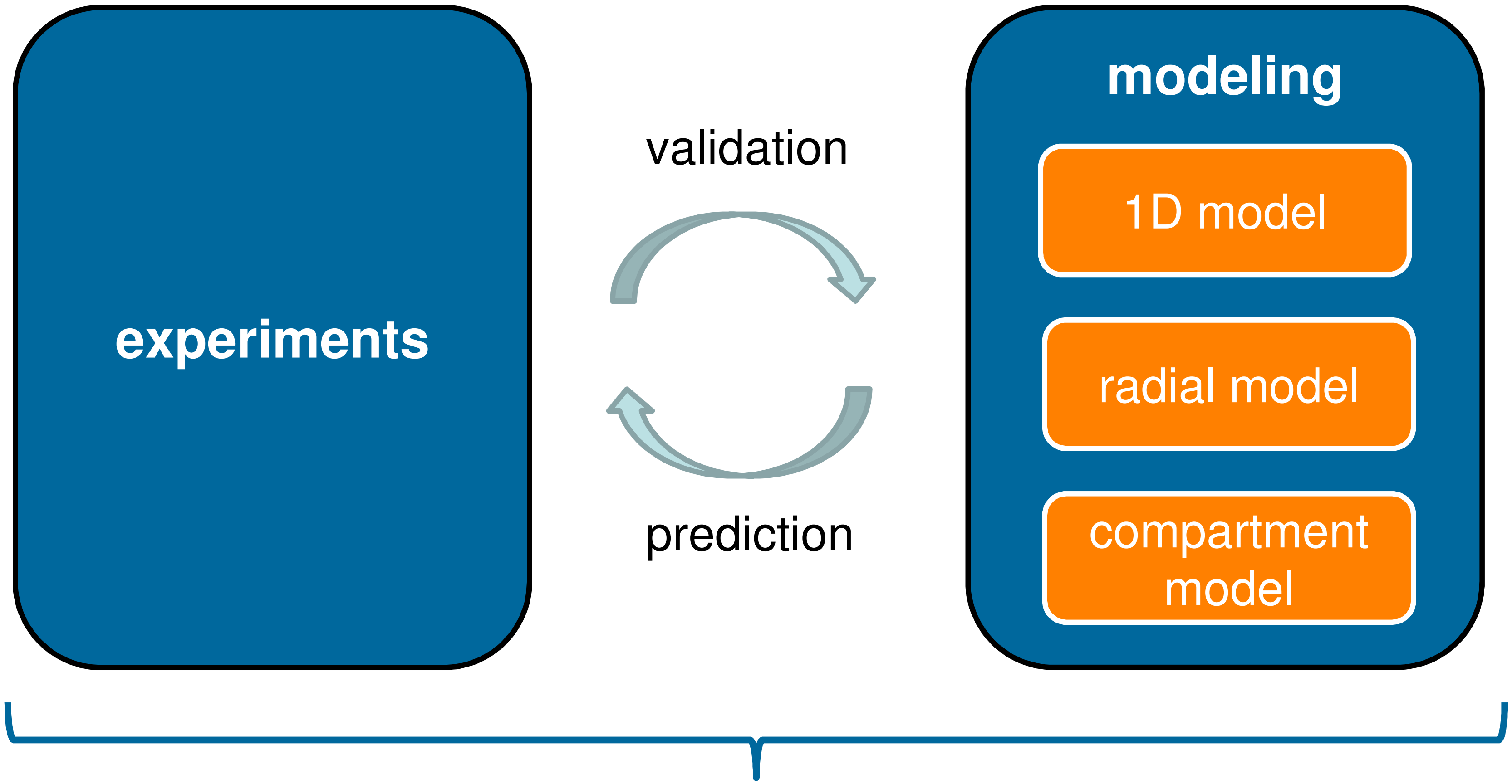


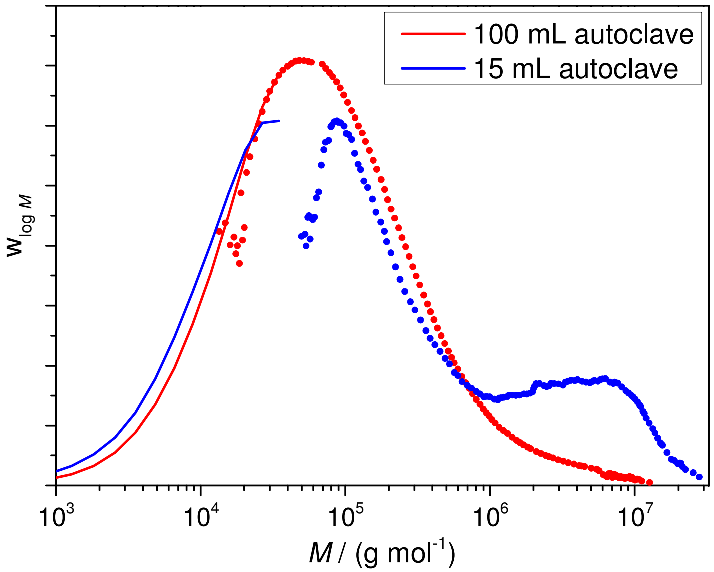
understanding fouling formation
application of countermeasures

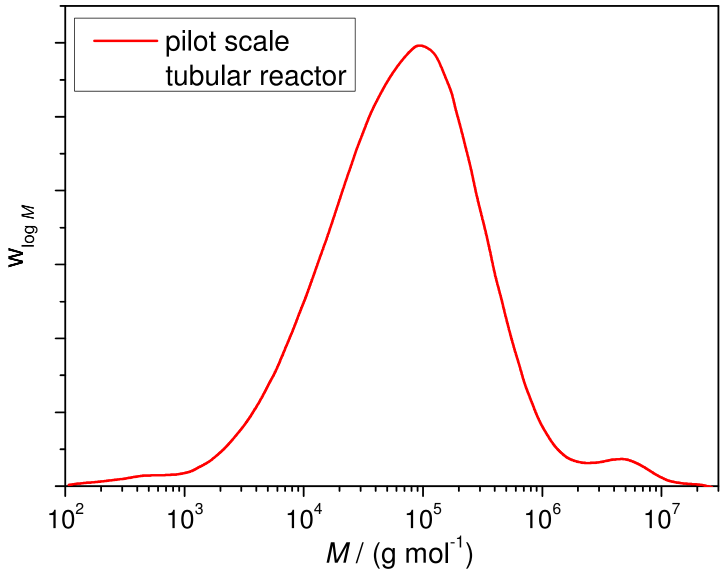
Experiments: Preliminary Considerations

- MWD tailing pronounced at higher surface-to-volume ratios and even existent at technical scales

  → fouling formation within the laminar boundary layer reasonable

  → idea: lab-scale reactor with as much laminar flow as possible





Experiments: Setup

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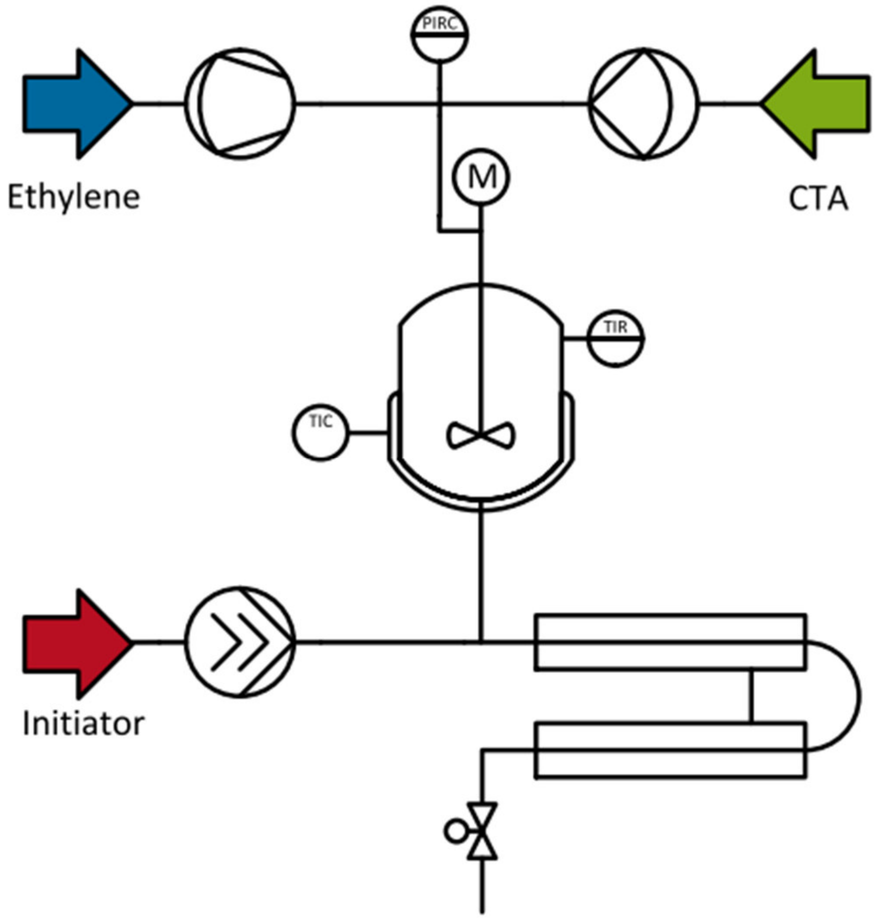

- combined autoclave and tubular reactor setup
- autoclave
  - 100 mL
  - premixing, preheating
  - p = 2000 bar
- tubular reactor
  - laminar flow
  - heated
  - L = 2 m, d = 4.8 mm
  - ~ 30 sec residence time

Experiments: Results

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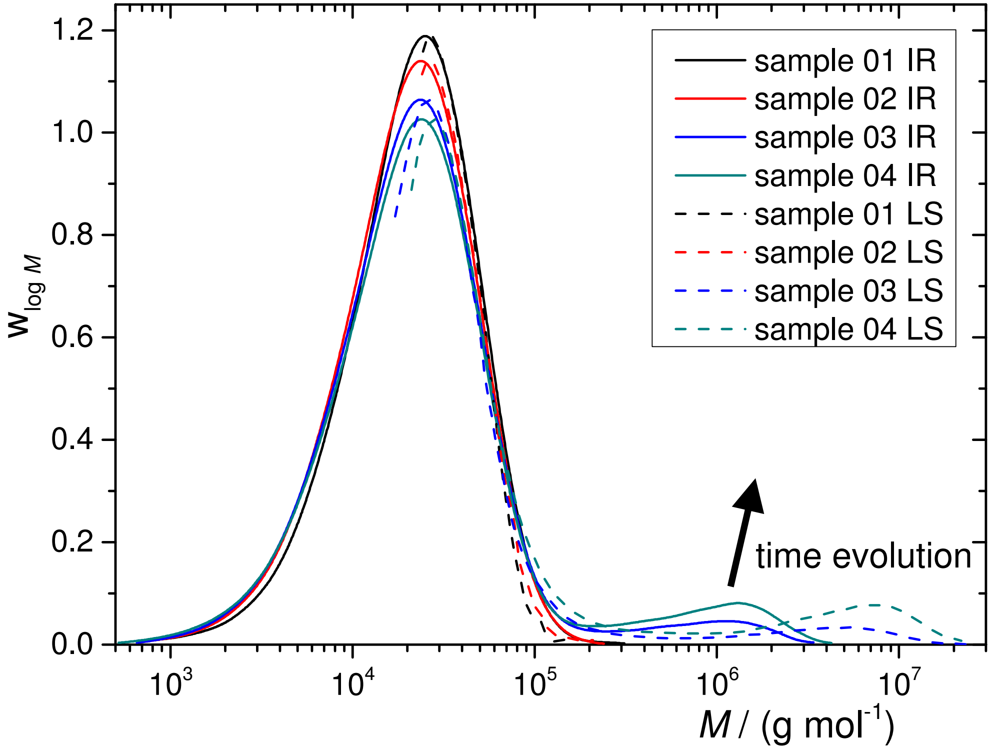
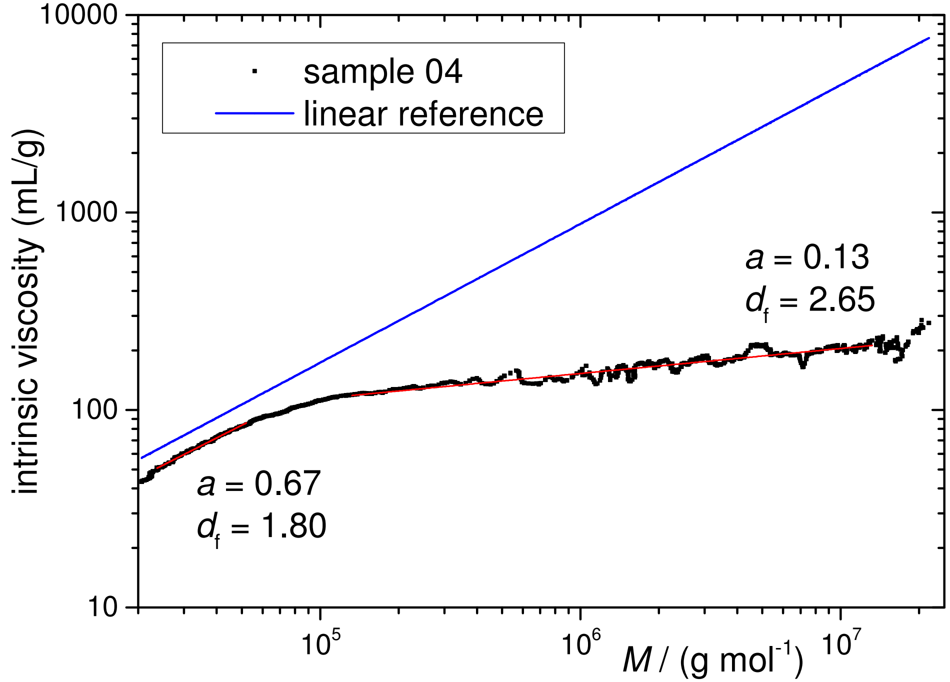


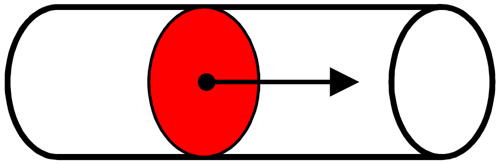
- pronounced MWD tailing with increasing running time

- fouling material strongly branched
  → indication for polymer-rich environment



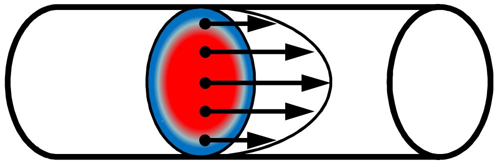
Modeling: Model Family

1D module



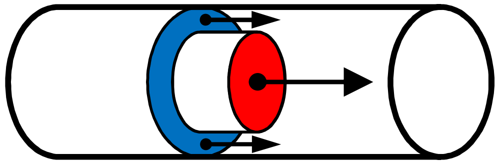
- plug flow (ODEs)
- complex reaction network with primary and secondary radicals
- rigorous MWD

radial module



- radial profiles (PDEs)
- laminar velocity profile
- wall temperature from 1D module (boundary condition)
- simplified kinetic scheme

compartment module



- two ideally mixed compartments for center and wall layer (ODEs)
- temperatures and velocities from radial module
- rigorous MWD

Modeling: Model Family

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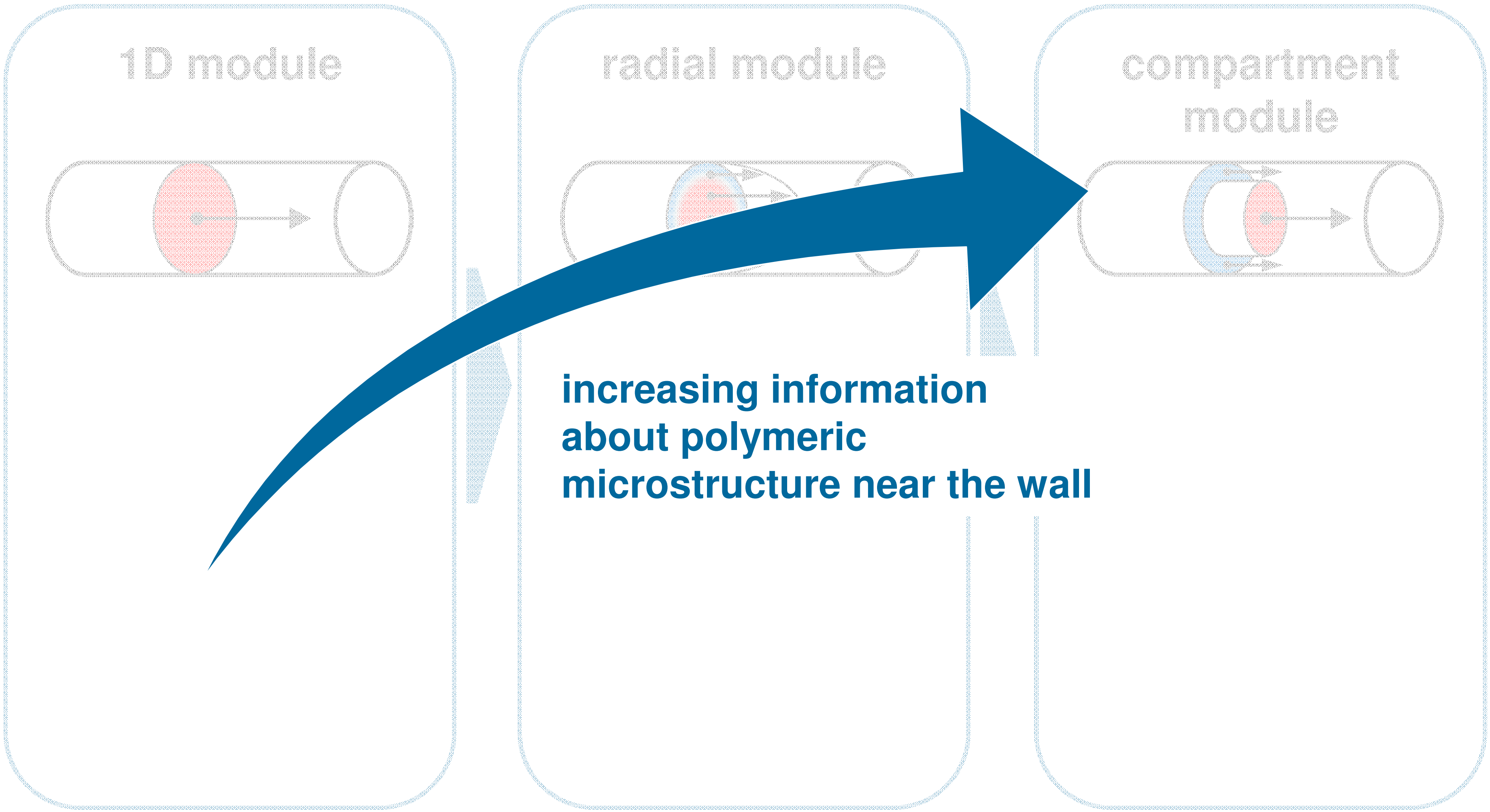
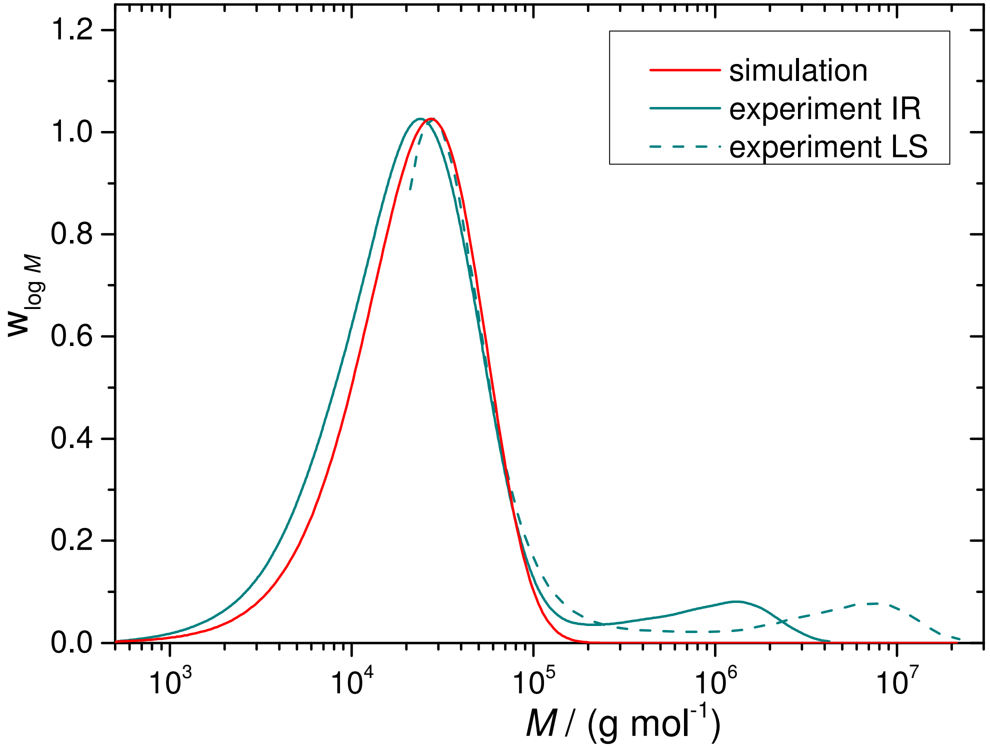
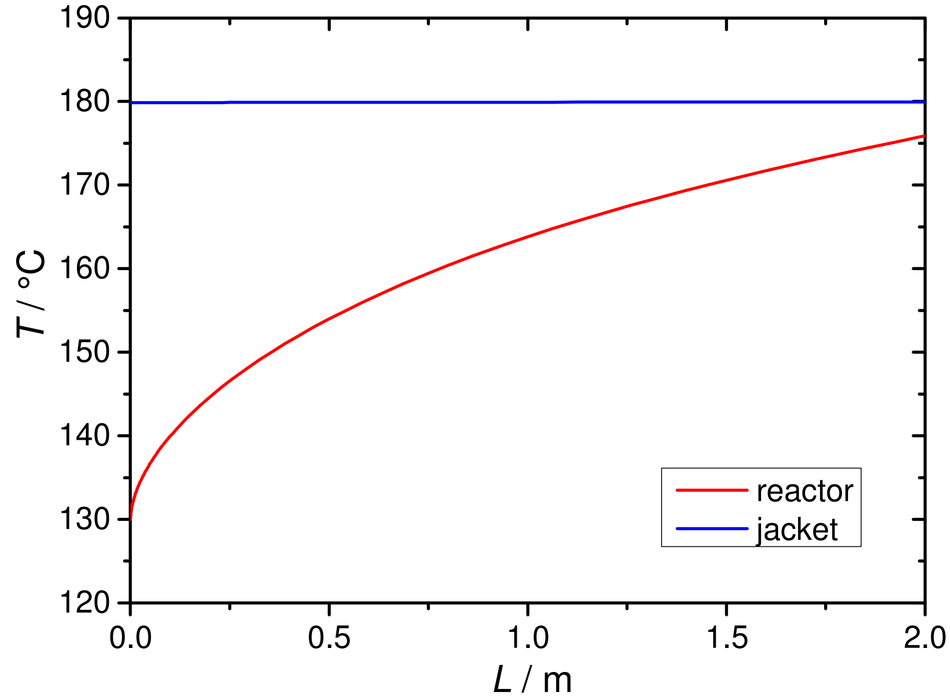


Modeling: 1D Module

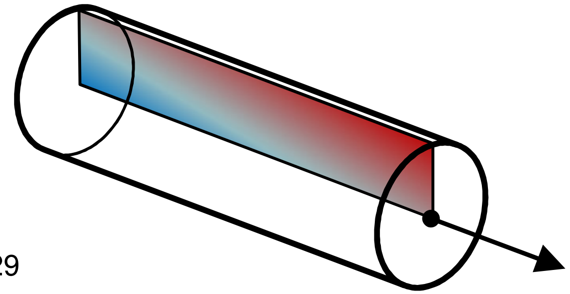


- satisfying agreement of modeled distribution with main MWD

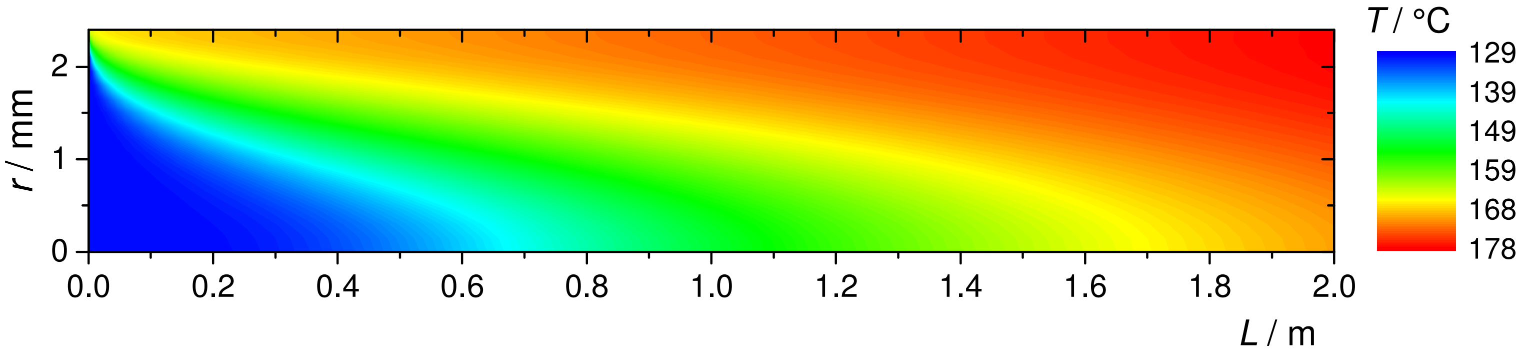
- slow heating due to laminar flow



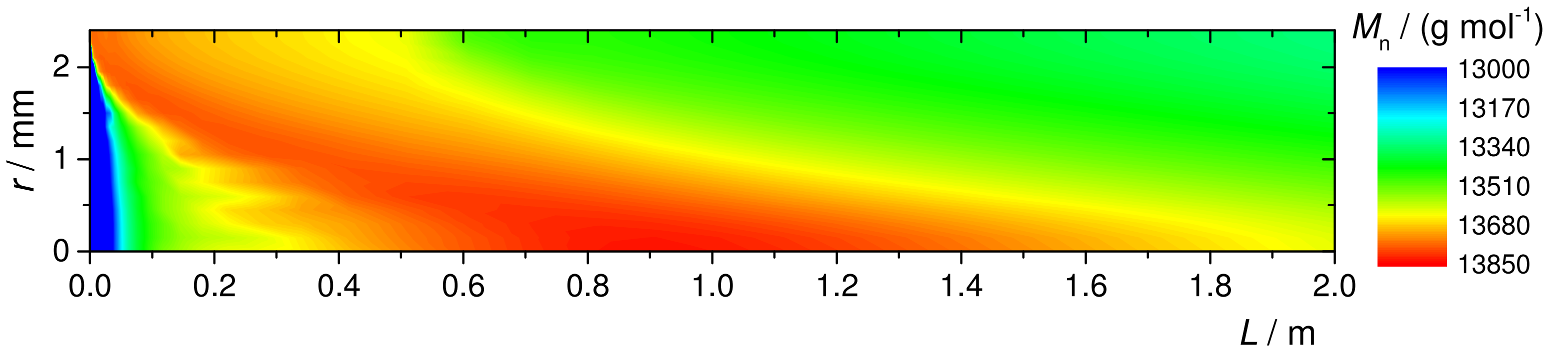
Modeling: Radial Module



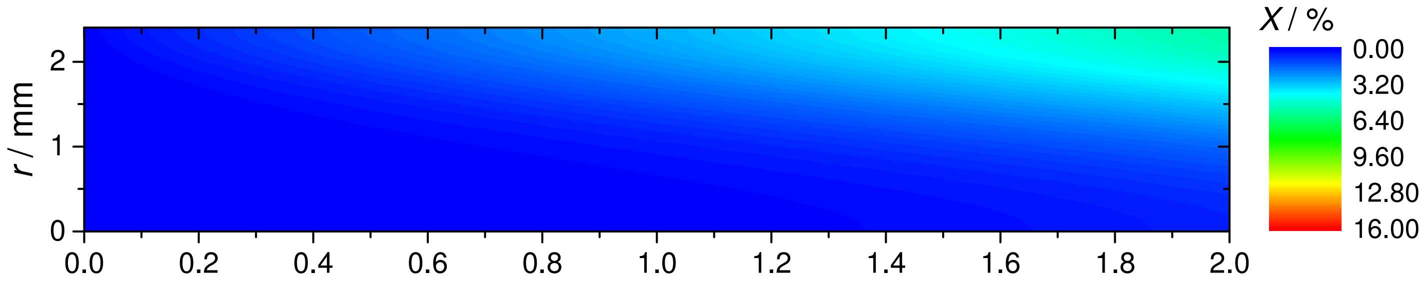
- temperature contour plot
  - faster heat transport in the outer area



- M_n contour plot
  - slightly lower M_n at the wall → more transfer to CTA



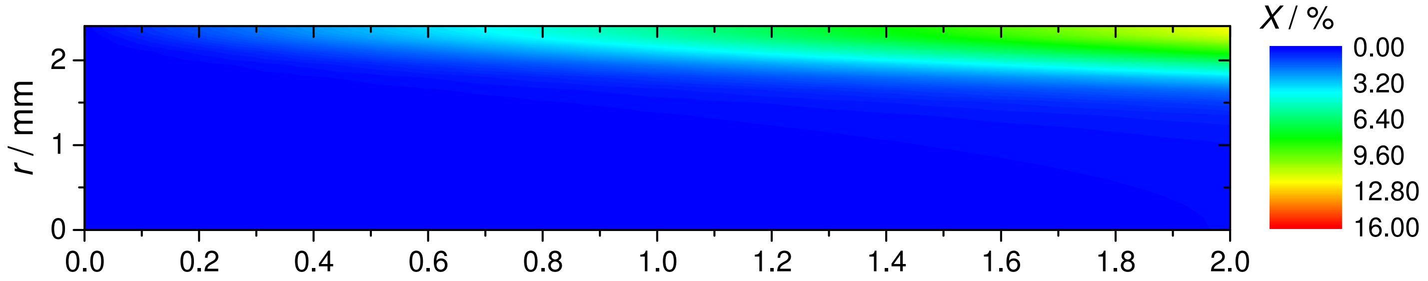
Modeling: Radial Module



$D_{polymer} = D_{monomer}$

$X_{wall} = 5.4\%$

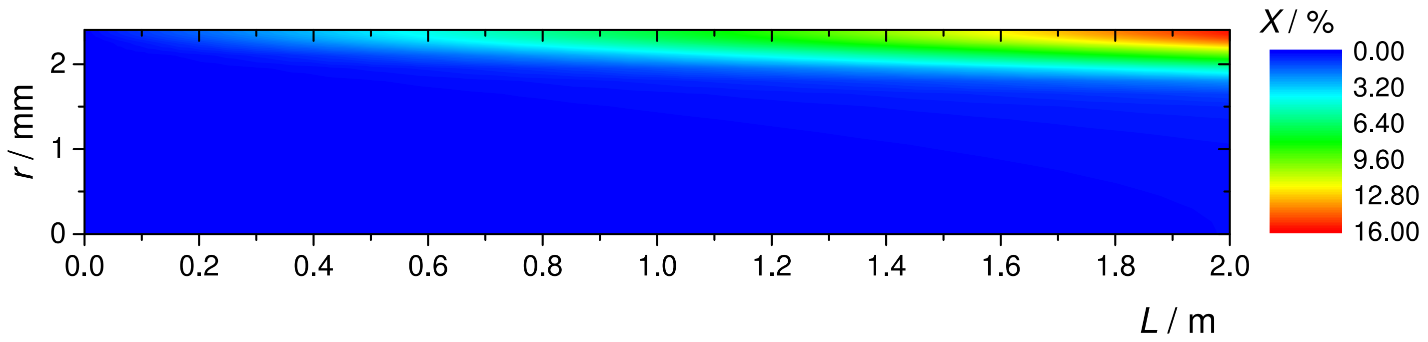
$X_{avg} = 2.7\%$



$D_{polymer} = 1/10\ D_{monomer}$

$X_{wall} = 11.9\%$

$X_{avg} = 1.9\%$

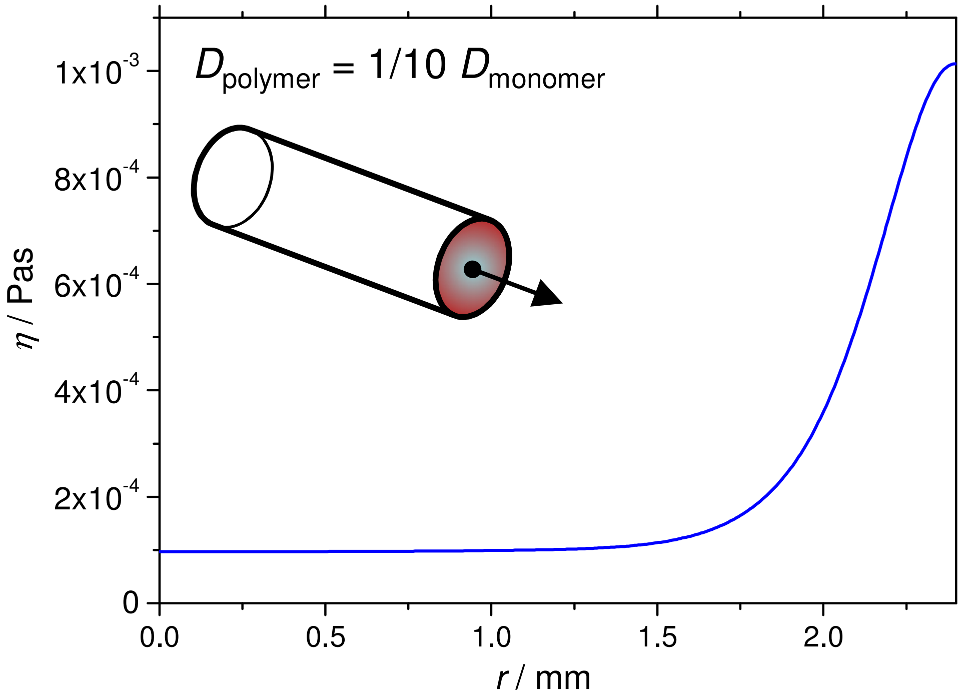


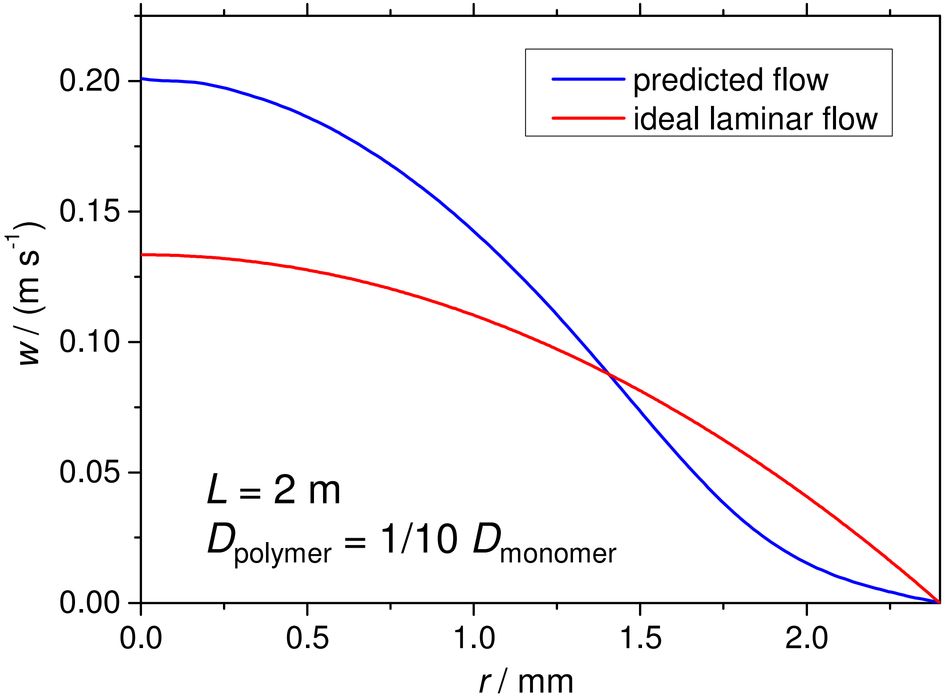
$D_{polymer} = 1/20\ D_{monomer}$

$X_{wall} = 15.7\%$

$X_{avg} = 1.8\%$

Modeling: Radial Module



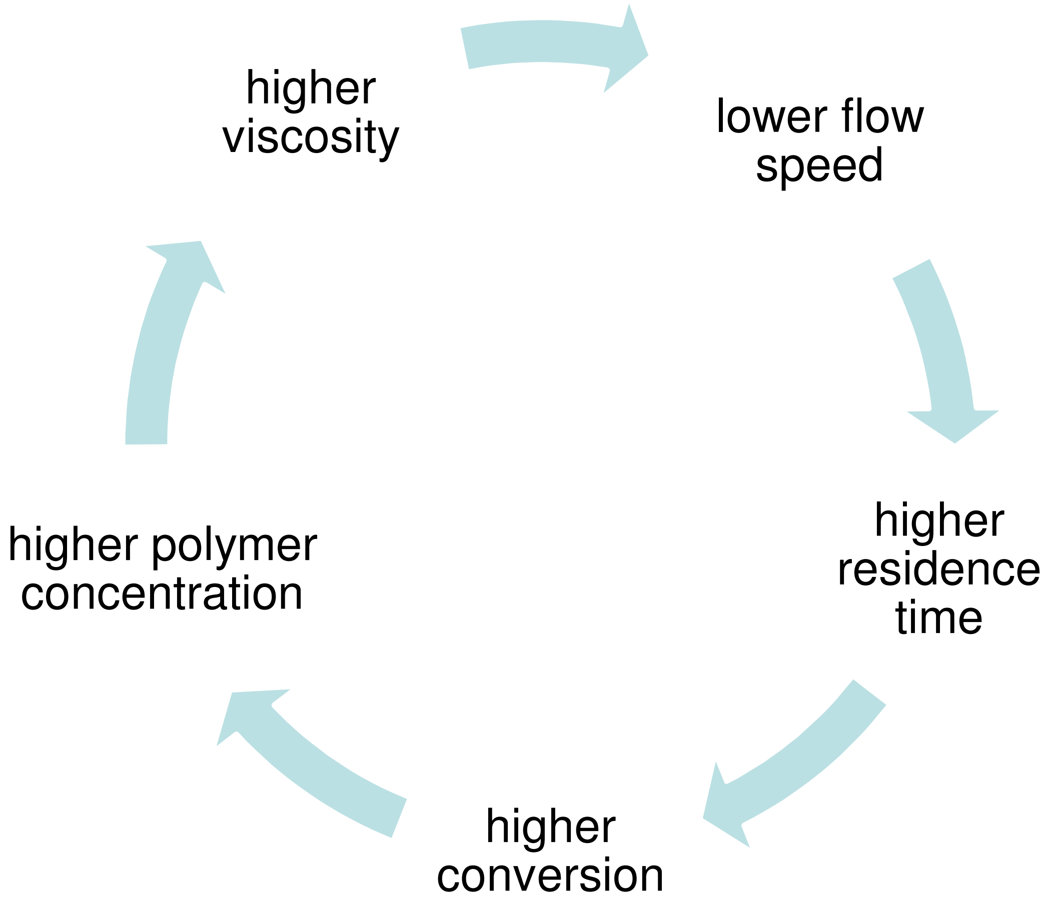


- viscosity gradient influences velocity profile
- description via Stokes law possible

$$\frac{dw}{dr} = -\frac{1}{2\eta}\frac{dp}{dL}r$$

Modeling: Radial Module

- higher friction leads to lower wall speeds
- fouling as a self-acclerating process as proposed by Krasnyk *et al.*
- implementation in radial module follows

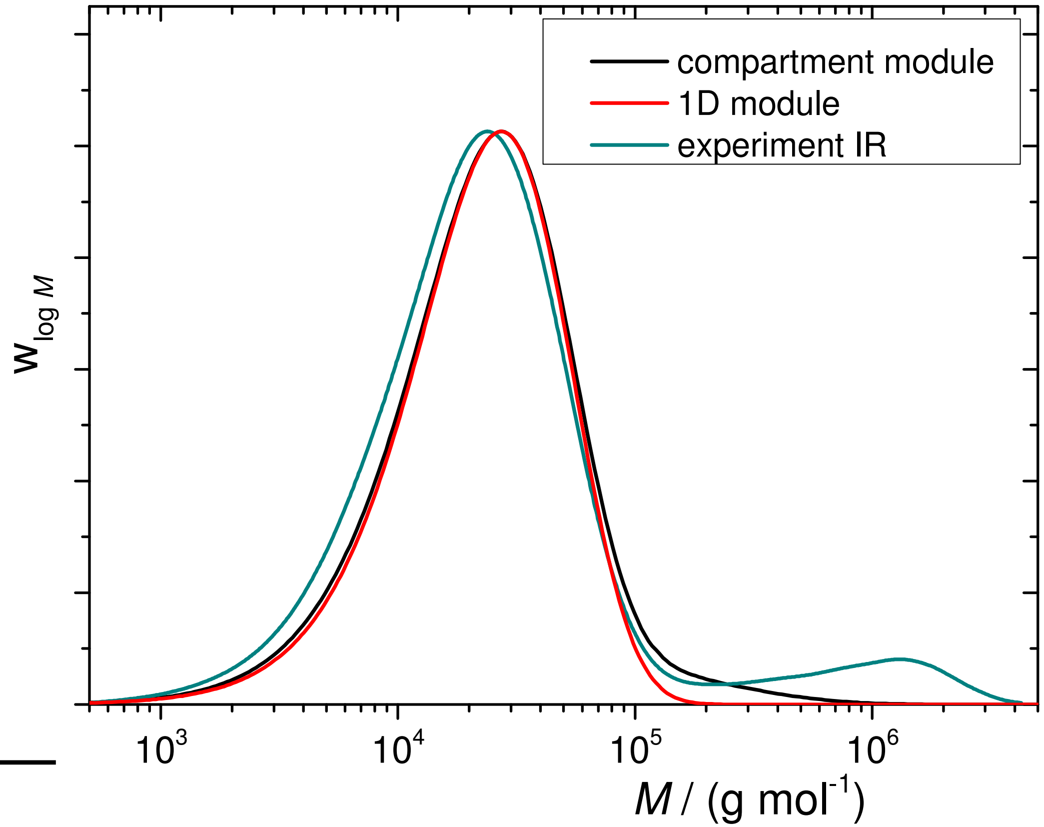


M. Krasnyk et al. *Proceedings of the 22nd ESCAPE* **2012**.

Modeling: Compartment Module

- $D_{\text{polymer}} = D_{\text{monomer}}$
  $\dot{m}_{\text{shell}} = 1/100\ \dot{m}_{\text{total}}$

- significant broadening even for fast diffusing polymer
- same prediction as radial module regarding M_n



core		shell	
M_n (kg/mol)	M_w (kg/mol)	M_n (kg/mol)	M_w (kg/mol)
13.6	31.4	13.4	81.0

Summary

- generating of tailed distributions with the chosen experimental setup possible
- fouling material highly branched

- model family delivers coherent results
- polymer diffusion speed crucial for buildup of higher polymer concentrations close to the wall
- indication that fouling is the result of a self-accelerating process; effects are to be investigated

Acknowledgements

- Computing in Technology GmbH, Rastede, Germany

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