Digitalization of Scaled-Up Block Copolymer Syntheses via RAFT Polymerization

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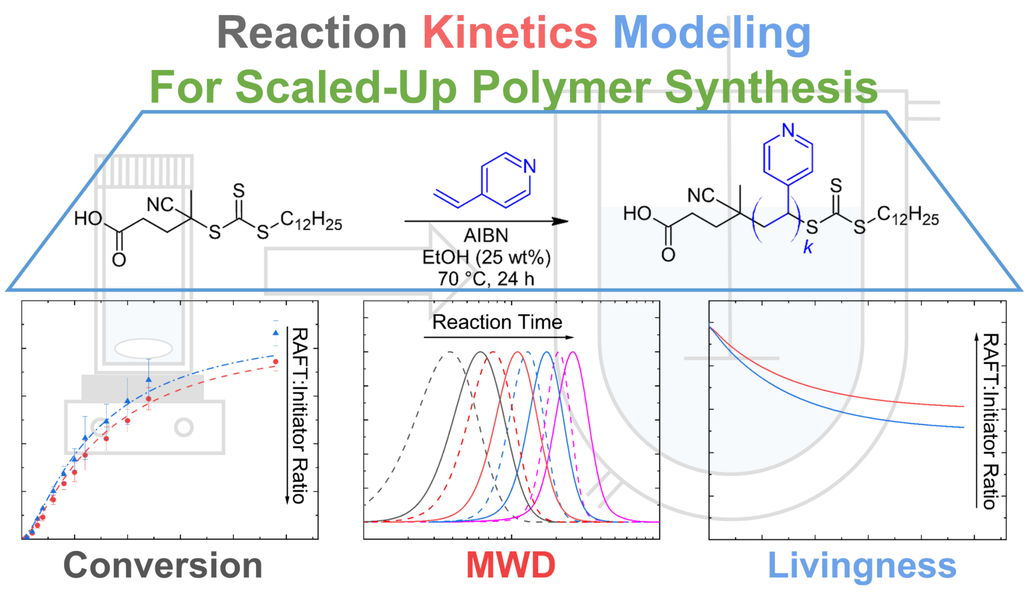
- Reversible addition-fragmentation chain transfer (RAFT) polymerization is a common techniques to prepare well-defined, rather narrow dispersed block-copolymers such as 4-vinylpyridine-*b*-styrene [1]
- Primarily utilized on small laboratory scales [1]
- Development and validation of a kinetic model as a first step to the scale-up of the 4-vinylpyridine macro-RAFT synthesis [1, 2]



Modeling of RAFT Polymerization

Kinetic Model [2, 3, 4]

1. RAFT Equlibrium

$$RAFT + P_n^* \underset{k_{frac}}{\overset{k_{add}}{\rightleftharpoons}} RAFT - P$$

2. Termination Kinetics

$$P_m^* + P_n^* \xrightarrow{k_t} P_{m+n}^d - P$$

Gel Effect + **Cross Termination** → **Parameter Estimation & Sensitivity Analysis**

Parameter Estimation [2]

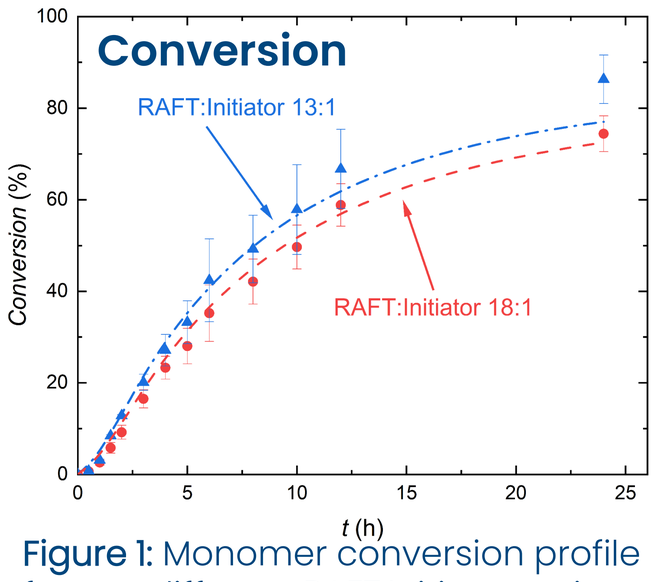


Figure 1: Monomer conversion profile for two different RAFT:Initiator ratios.

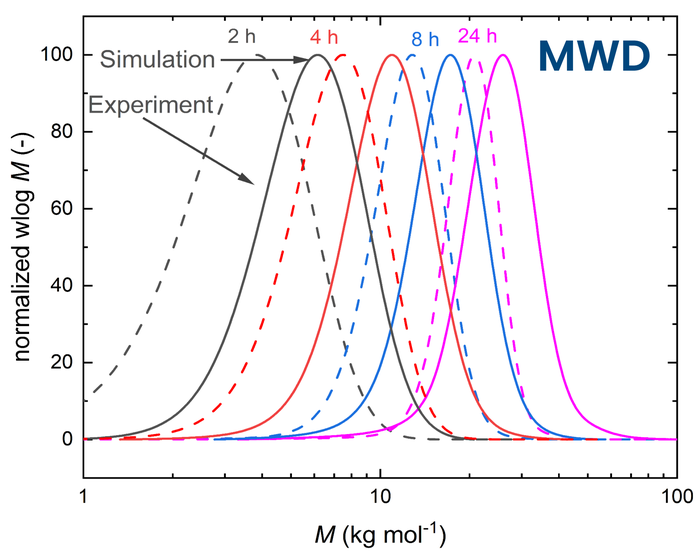


Figure 2: Simulated and experimental GPC distributions at different spots in time of the reaction.

Parameter Estimation:

$k_{add} = 6.50 \cdot 10^4$ L mol^{-1} s^{-1}
$k_{frac} = 2.56 \cdot 10^3$ s^{-1}
$k_t^{1,1} = 3.25 \cdot 10^8$ L mol^{-1} s^{-1}

- Successful parameter estimation
- Predicted livingness fits to conversion data from second block
- Deviations at the MWDs because of the GPC data –> Multi-detector GPC necessary

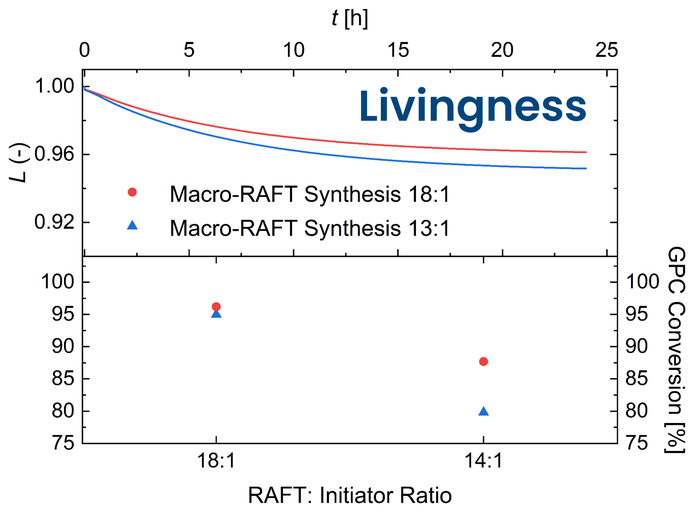


Figure 3: Living profile over the reaction time and polymer conversion (determined by GPC).

Sensitivity Analysis [2]

RAFT Equilibrium: k_{add}

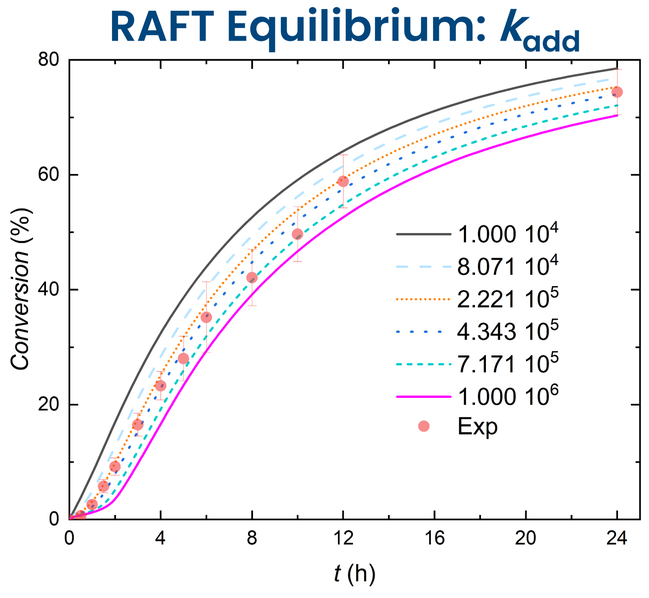


Figure 4: Sensitivity analysis of the reaction rate coefficient k_{add} compared to experimental data (RAFT:Initiator = 18:1).

Constant k_t vs. Gel Effect

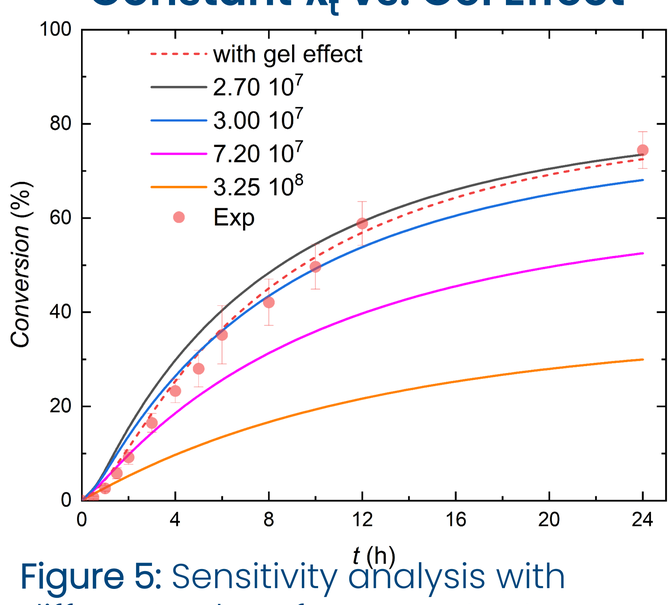


Figure 5: Sensitivity analysis with different values for a constant termination rate coefficient k_t or active gel effect model compared to experimental data (RAFT:Inititiator = 18:1).

Sensitivity Analysis

- k_{add} and k_t are highly sensitive parameters
- Explicit description of the gel effect necessary

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Literature:

[1] K. Nieswandt et al., *Polym. Chem.*, **2021**, 12, 221, DOI: 10.1039/D1PY00074H.
[2] F. Kandelhard et al., *Ind. Eng. Chem. Res.*, **2023**, DOI: 10.1021/acs.iecr.3c00607.
[3] F. Kandelhard et al., *Macromol. React. Eng.*, **2021**, 15, 4, 2000058, DOI: b10.1002/mren.202000058.
[4] E. Pashayev et al., *Macromol. React. Eng.*, **2022**, 17, 2, 2200068, DOI: 10.1002/mren.202200068.

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