

FUNCTIONALIZATION OF POLYOLEFINS THROUGH RADICAL GRAFTING

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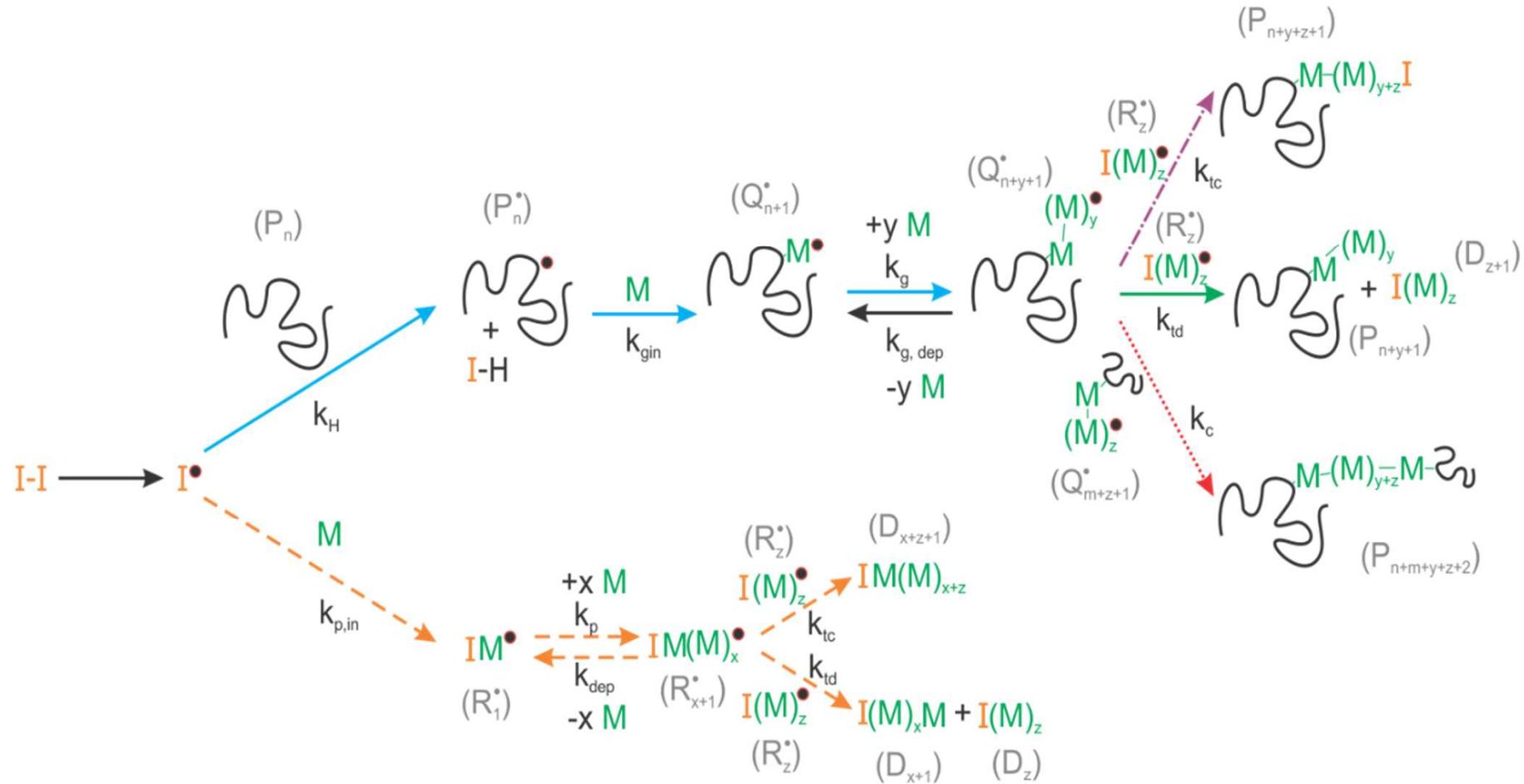
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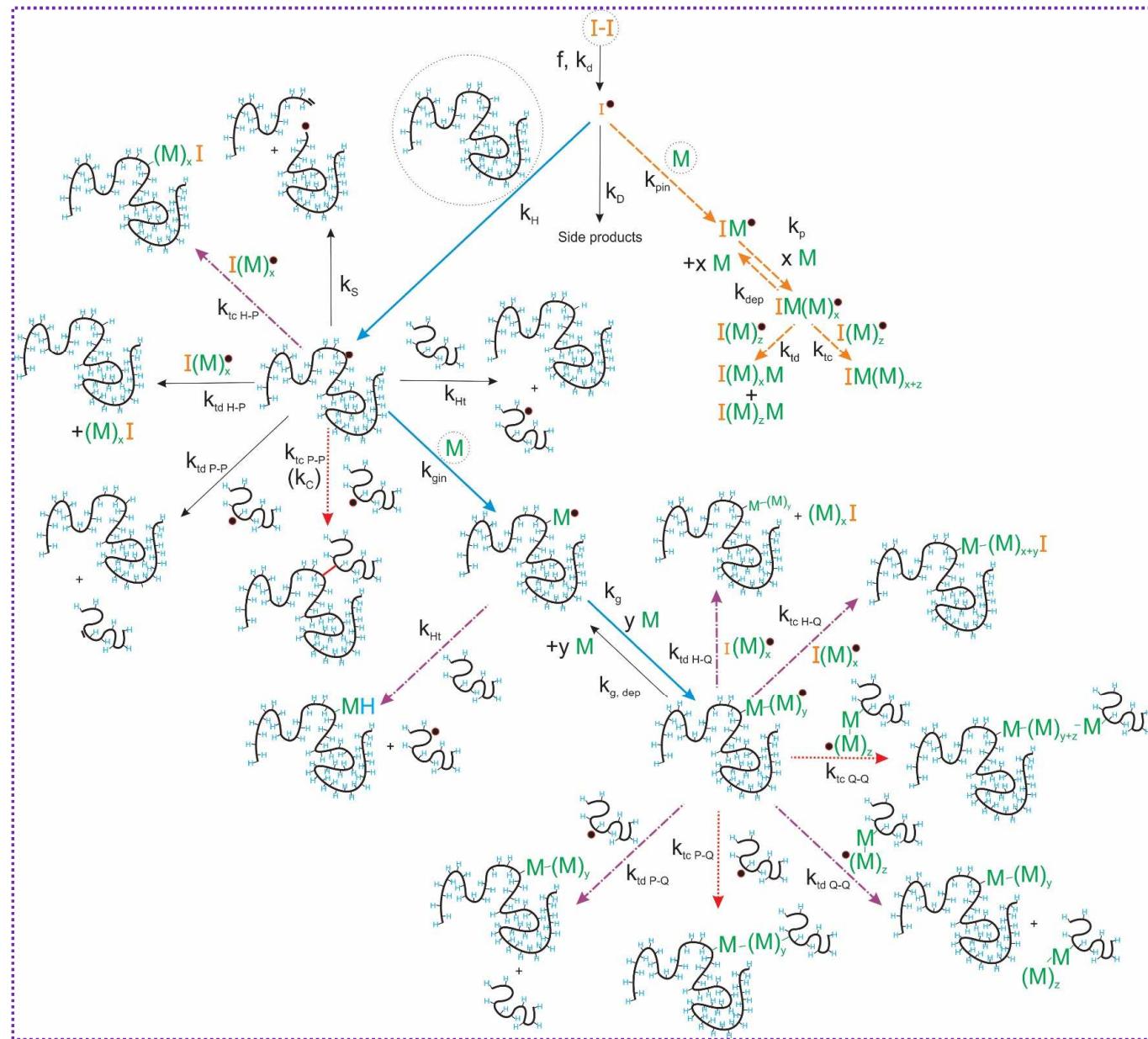
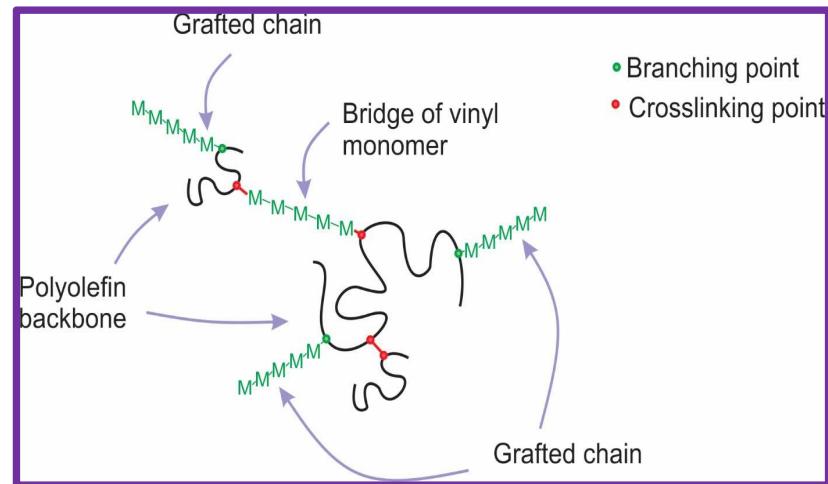
³ Centre for Textile Science and Engineering, Ghent University



Free radical induced grafting of polyethylene: core reactions



FRIG of PE: detailed reaction scheme



MODULAR MODELING PLATFORM

Main solver A:
average FRIG properties/SEC trace

Module A: kMC (Gillespie, 1976)

```

    graph TD
        Start([Start]) --> t0[t = t0]
        t0 --> X0[X = X0]
        X0 --> alpha0[alpha_0(X) = k_{j,init} X_j X_0]
        alpha0 --> sumAlpha0[alpha_0(X) = sum_{j=1}^N alpha_j(X)]
        sumAlpha0 --> r1[r = 1 / alpha_0(X) ln(1 / r_i)]
        r1 --> sumAlphaJ[sum_{j=1}^{N-1} alpha_j(X) <= r_j alpha_0(X) <= sum_{j=1}^N alpha_j(X)]
        sumAlphaJ --> FindMu[Find mu]
        FindMu --> t1[t <- t + 1]
        t1 --> X1[X <- X + v_j]
        X1 --> Macromolecules[Macromolecules]
        Macromolecules --> No{t <= t_end}
        No -- No --> Results[Average properties  
Chain length distribution]
        No -- Yes --> UpdateTrees[Update binary trees  
(Chaffey-Millar et al. 2007)]
        UpdateTrees --> End([End])
    
```

Plots: Selectivity (Y-axis 0.1 to 0.9, X-axis Monomer conversion [%] 0 to 0.5) and Average chain length of grafts (Y-axis 0 to 250, X-axis Monomer conversion [%] 0 to 0.5).

Solver B:
Information per individual macrospecies

Grafted chain structure diagram with labels: Grafted chain, Bridge of vinyl monomer, Branching point, Crosslinking point, Polyolefin backbone.

Solver C:
phase segregation:
mass transfer

Diagram illustrating phase segregation: mass transfer between different phases labeled M and I.

Solver D:
Injection points
of monomer
and/or initiator

Diagram of a cylindrical reactor showing injection points Q_1, Q_2, Q_3 and exit $C=C(\theta)$.

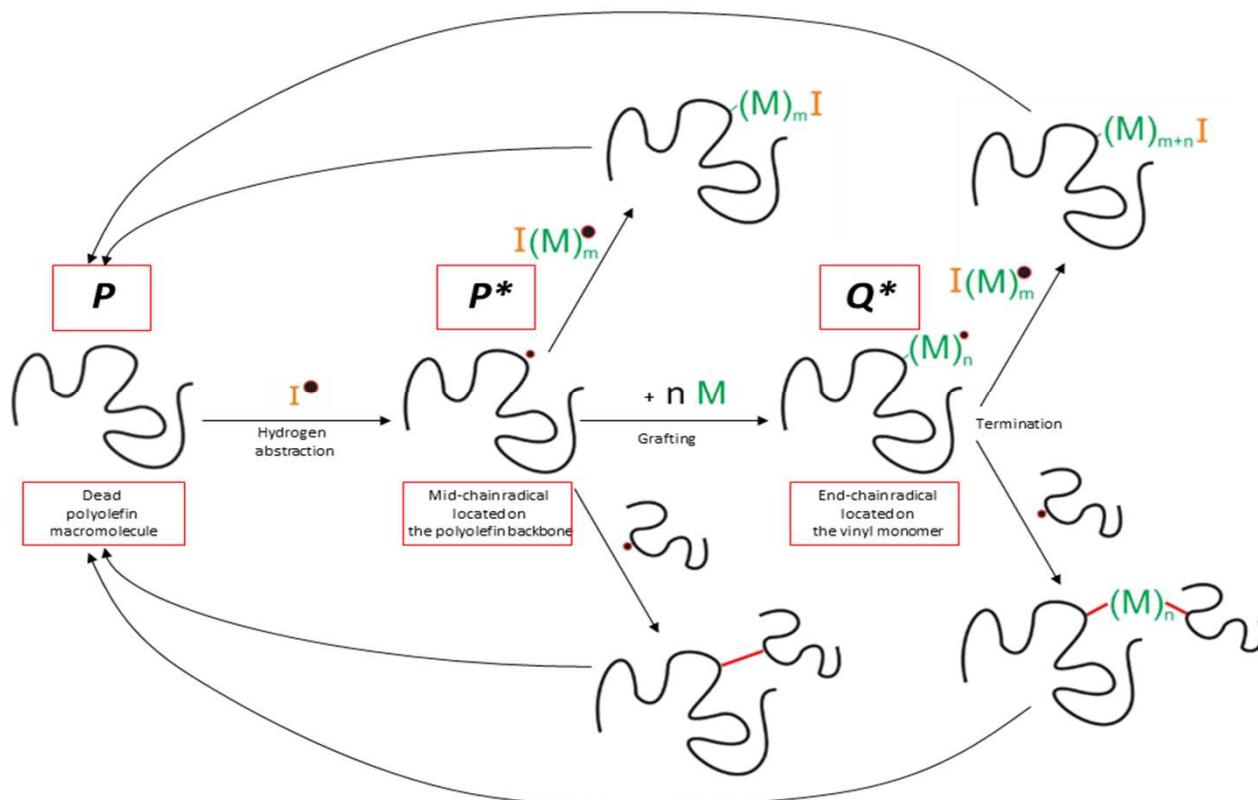
Solver D:
Temperature
zones

Diagram of a 3D block divided into four temperature zones T_1, T_2, T_3, T_4 along the $\zeta = z/L$ axis.

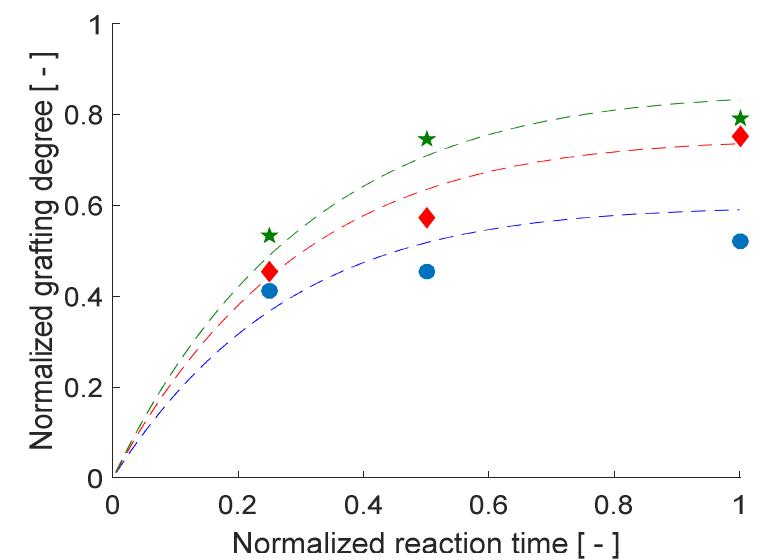
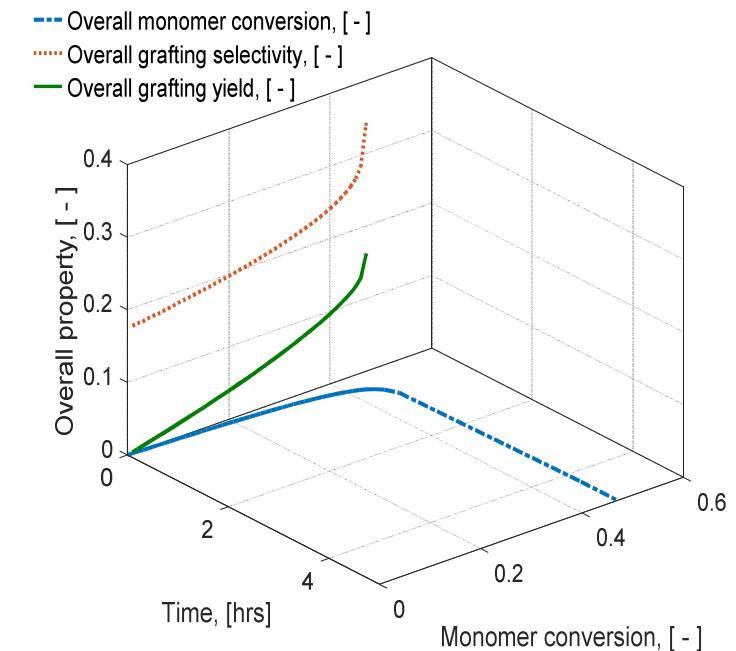
Hernandez-Ortiz, J. *et al.* *AICHE J.* 2017, 63, 4944; Hernandez-Ortiz, J. *et al.* *Macromol. Theory Simul.* 2018, 27, 1800036; Hernandez-Ortiz, J. *et al.* *Chem. Eng. J.* 2019a, *in press*; Hernandez-Ortiz, J. *et al.* *Chem. Eng. J.* 2019, *under revision*

MAIN SOLVER A: kinetic Monte Carlo: avg. properties

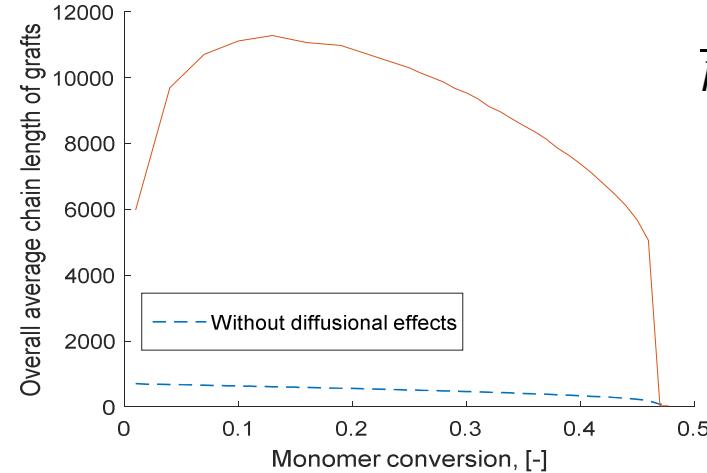
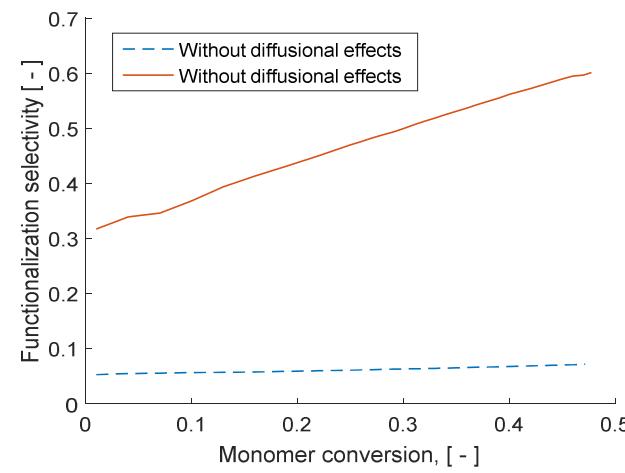
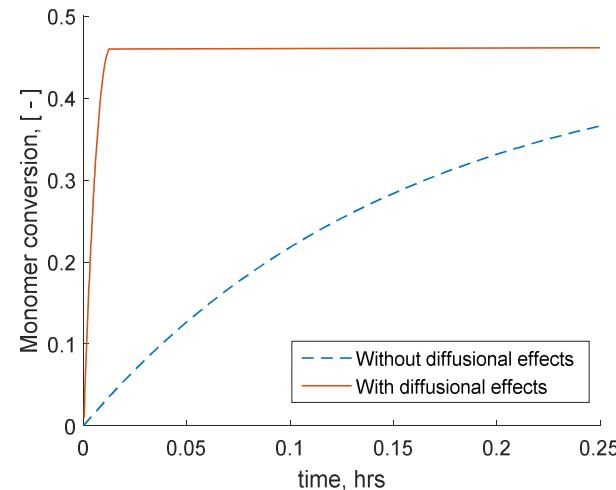
Hernandez-Ortiz, J. et al. AIChE J. 2017, 63, 4944



1. Single phase lab-scale reaction system
2. Lumping of reaction event history

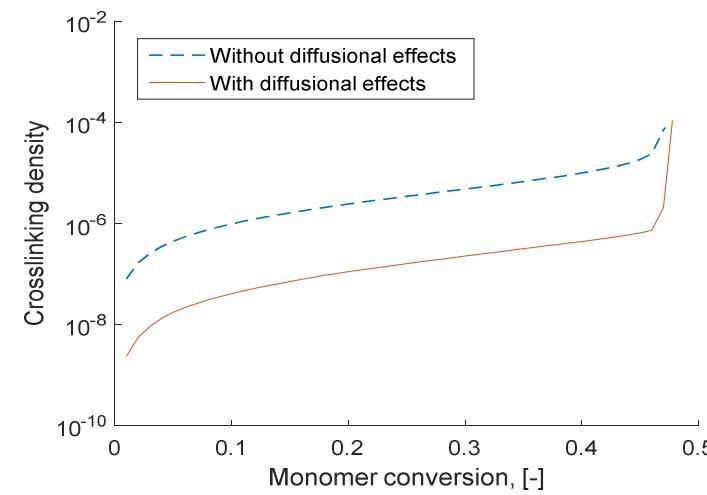


MAIN SOLVER A: relevance of diffusional limitations



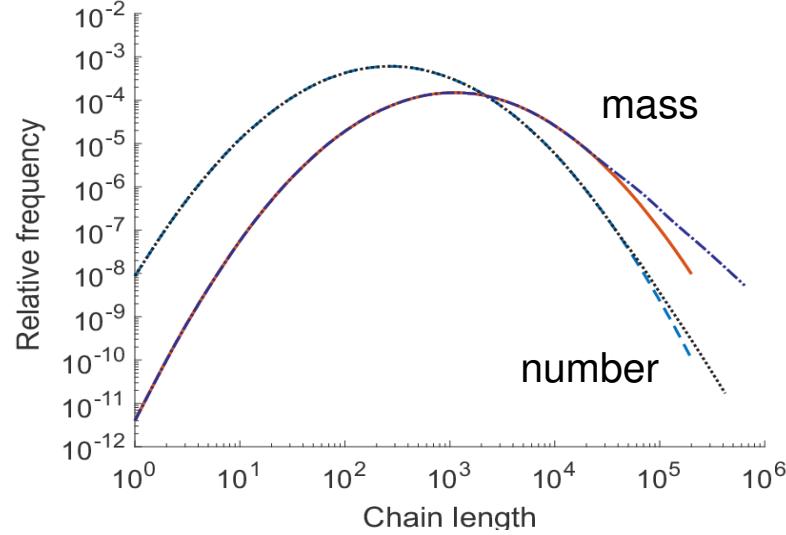
$$\frac{1}{k_{app}} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}}$$

$$k_{diff} = 4\pi N_A \sigma D_{AB}$$

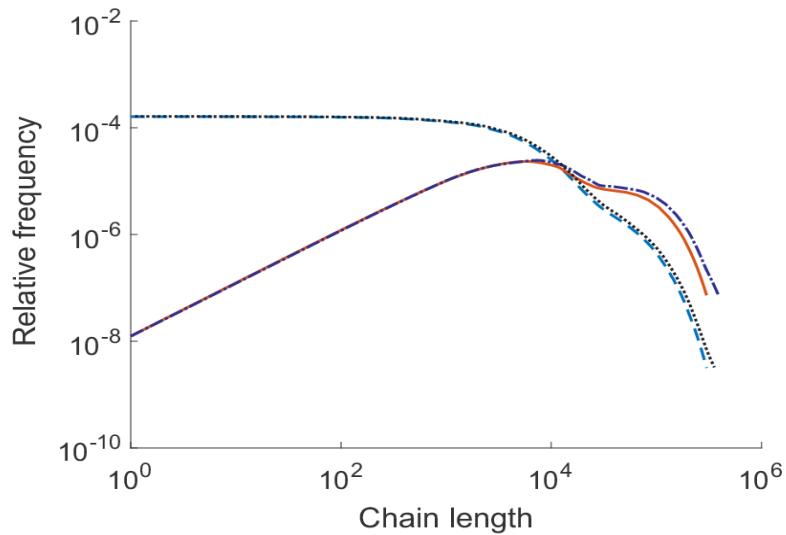


1. Single phase lab scale reaction system; 2. Lumping of reaction event history;

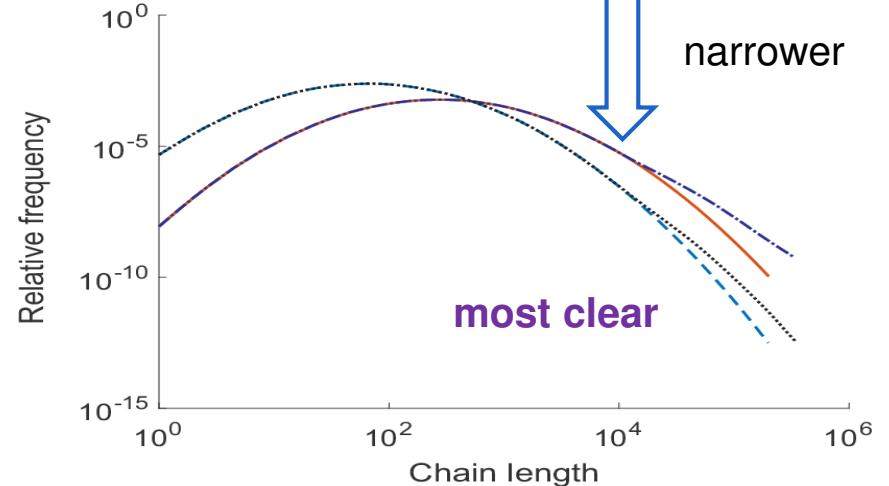
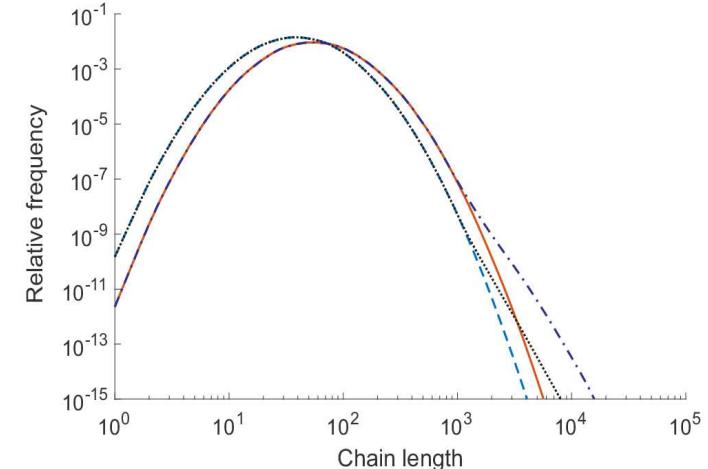
MAIN SOLVER A: relevance of initial distribution



lower x_n
↔
similar
broadness



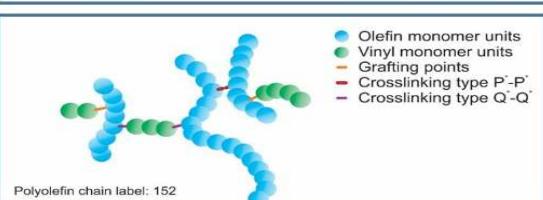
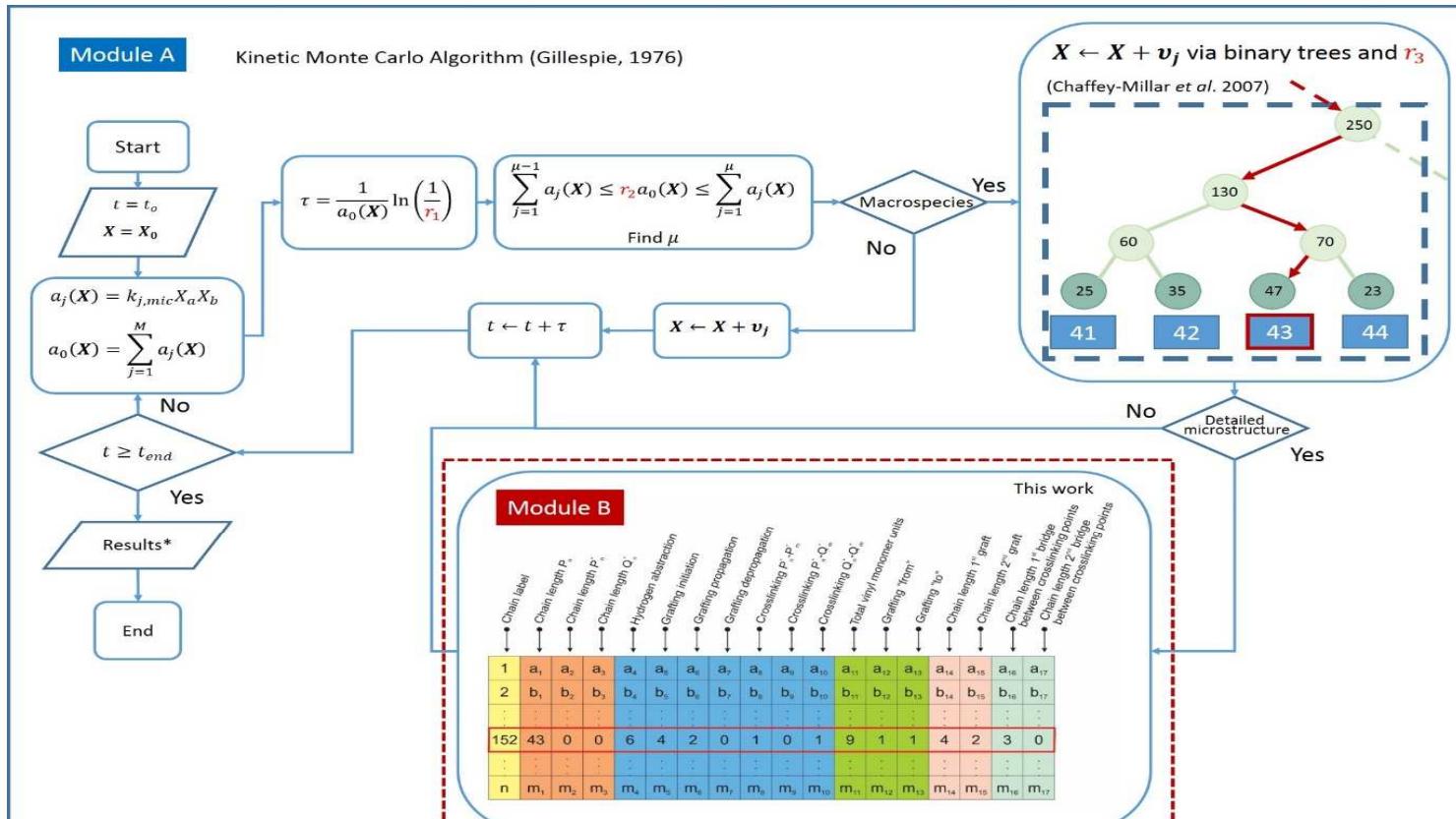
bimodal
↔



most clear

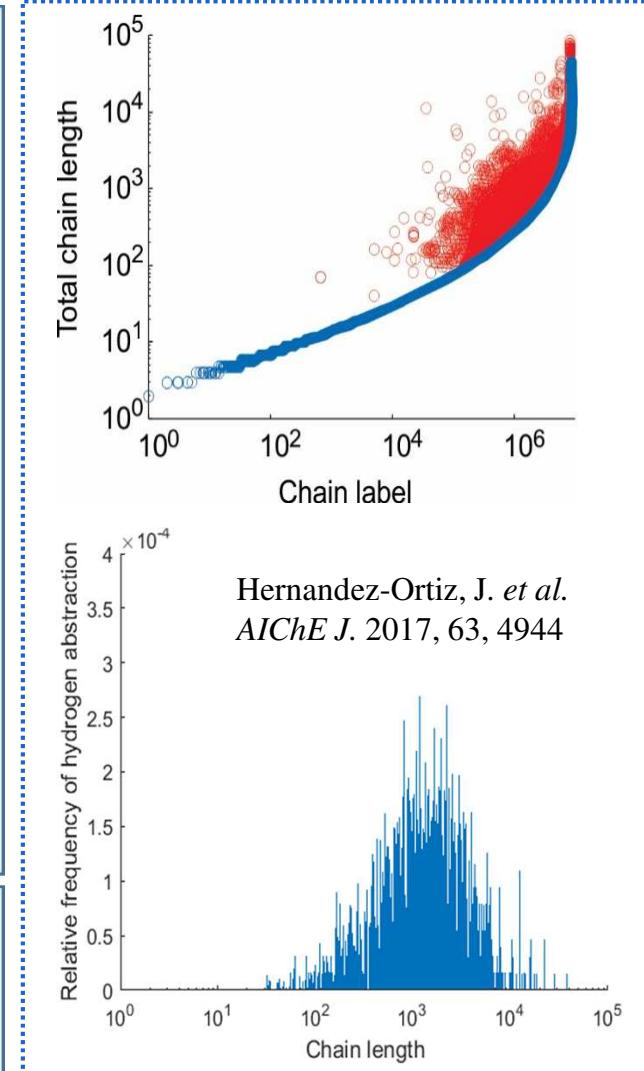
1. Single phase lab scale reaction system; 2. Lumping of reaction event history;

SOLVER B: beyond averages: individual chains

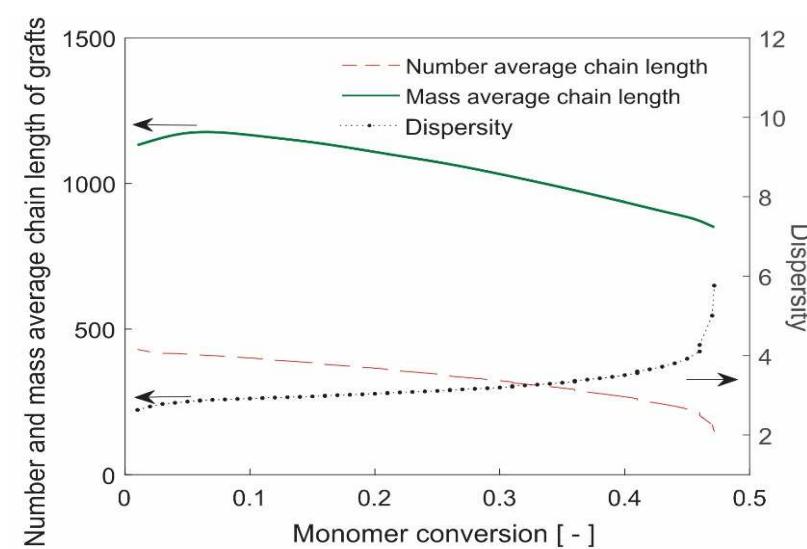
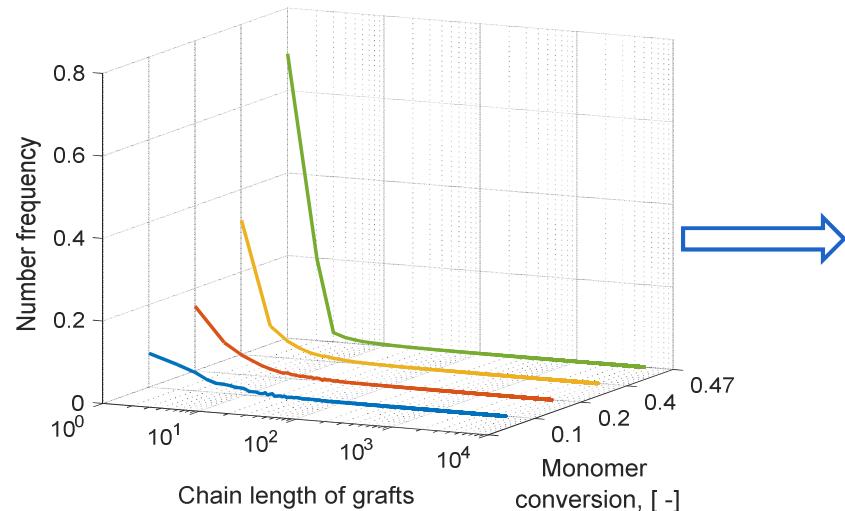
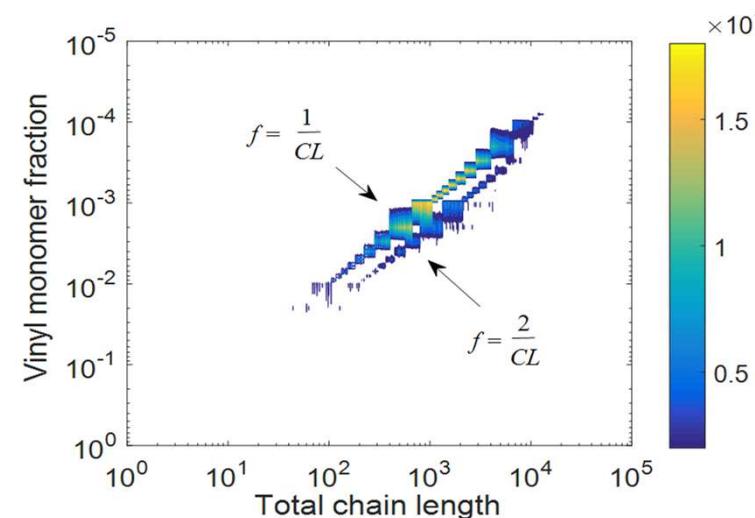
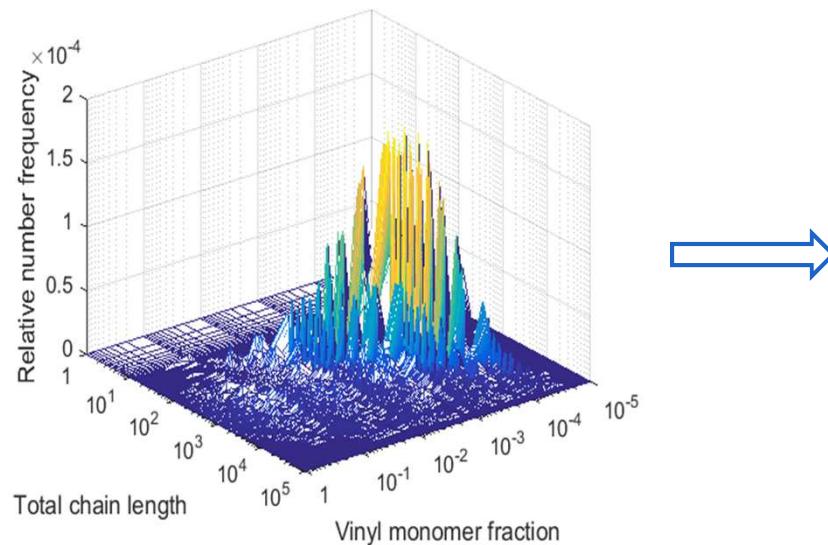


Module A: Monomer conversion, grafting selectivity and yield, chain length distribution of macrospecies, overall values of macromolecular microstructure

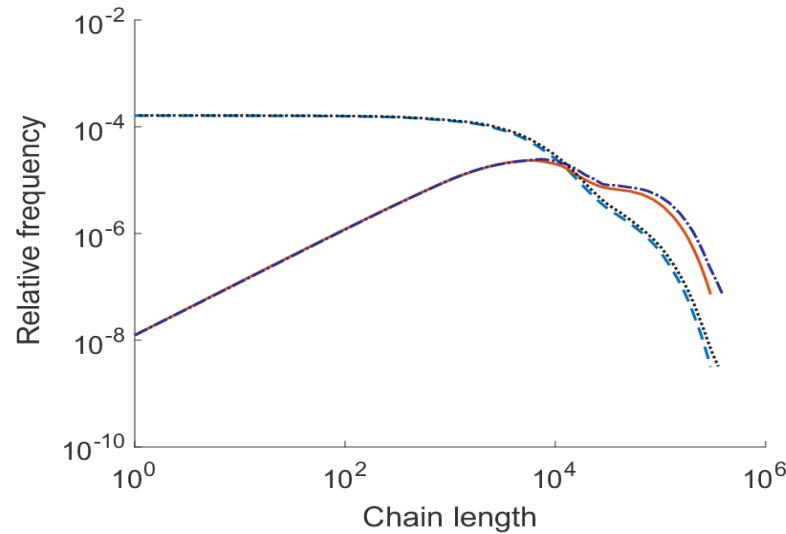
Module B: Distribution of microstructural properties, reaction event distribution



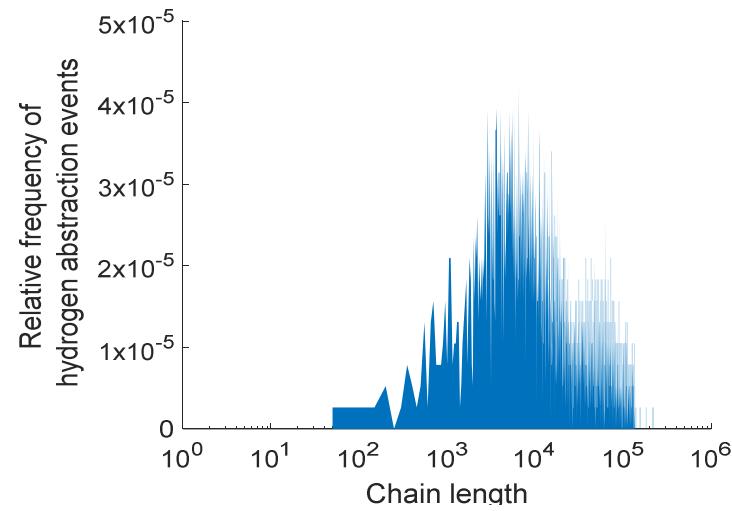
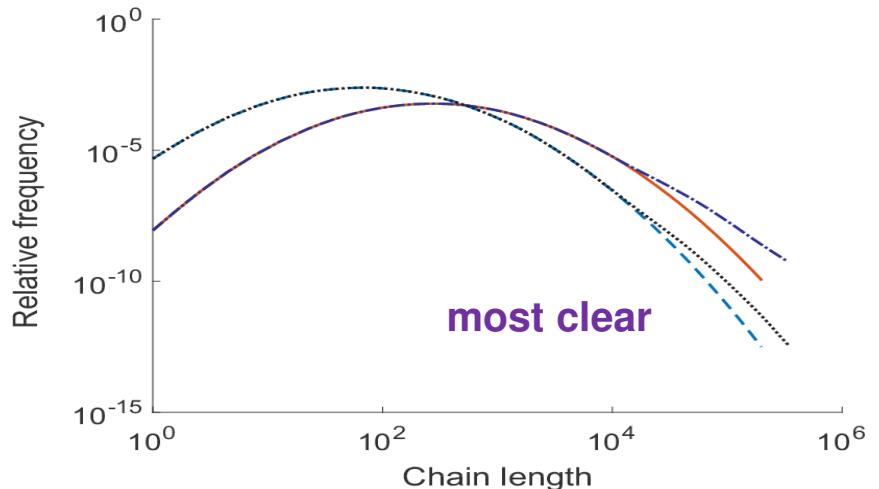
SOLVER B: beyond averages: individual chains/grafts



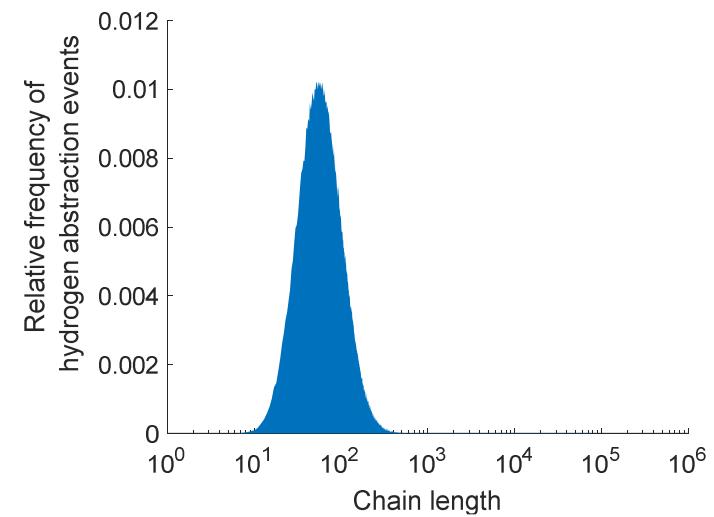
SOLVER B: beyond averages: individual chains



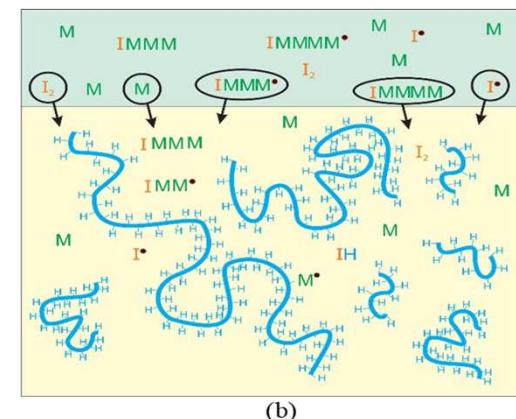
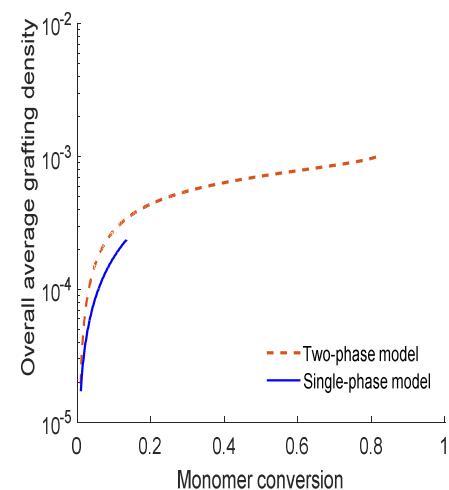
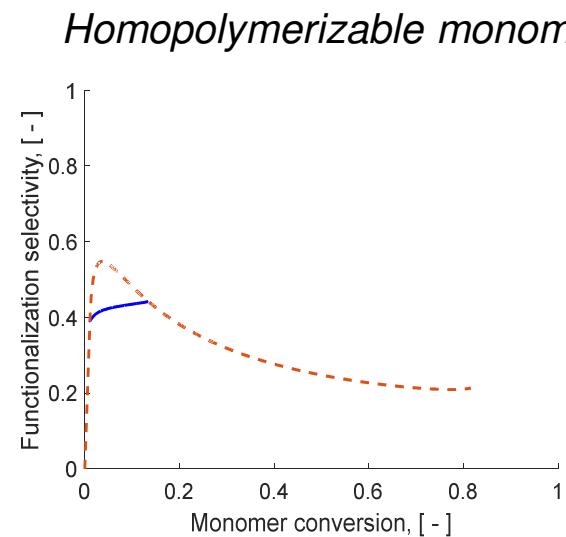
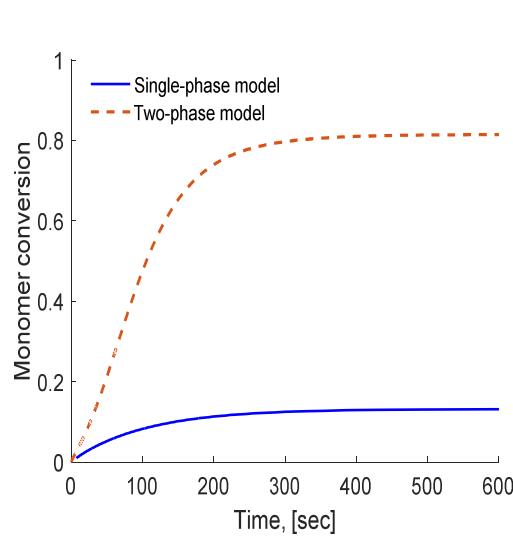
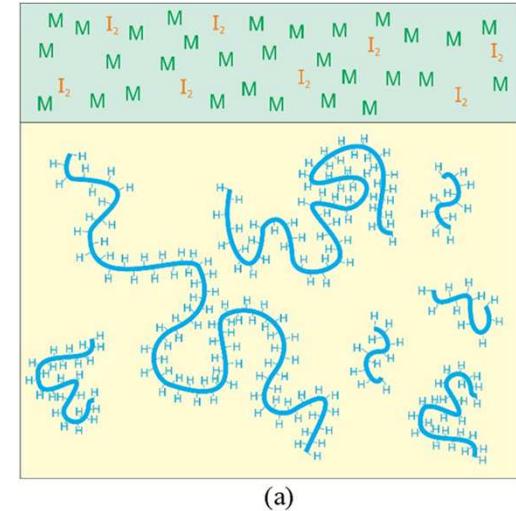
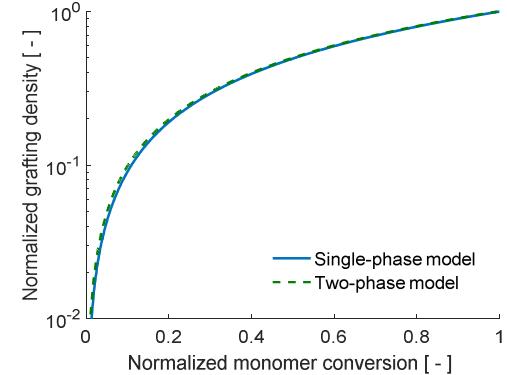
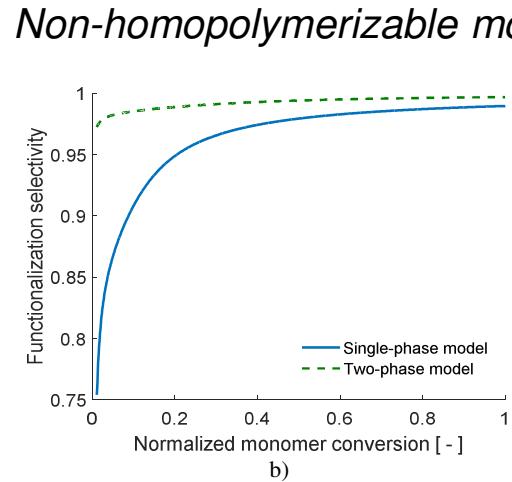
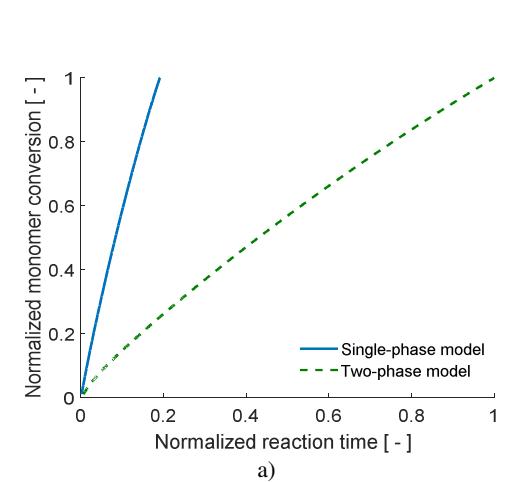
bimodal



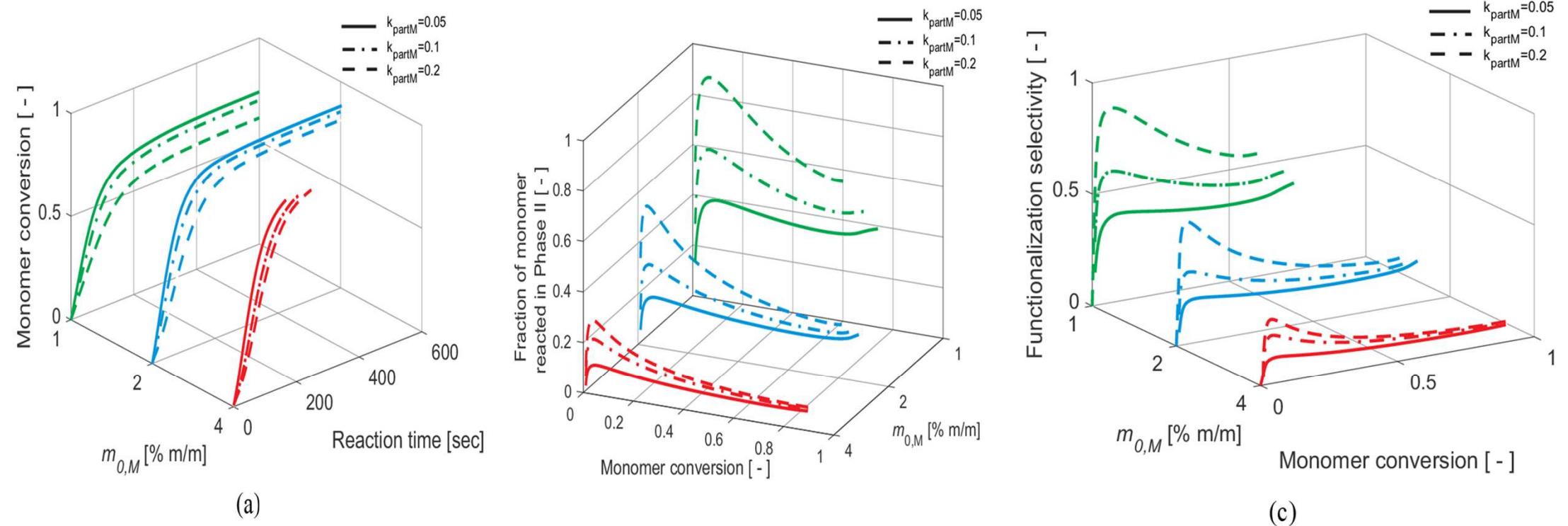
Confirmation



SOLVER C: 2-phase model for industrial time scales

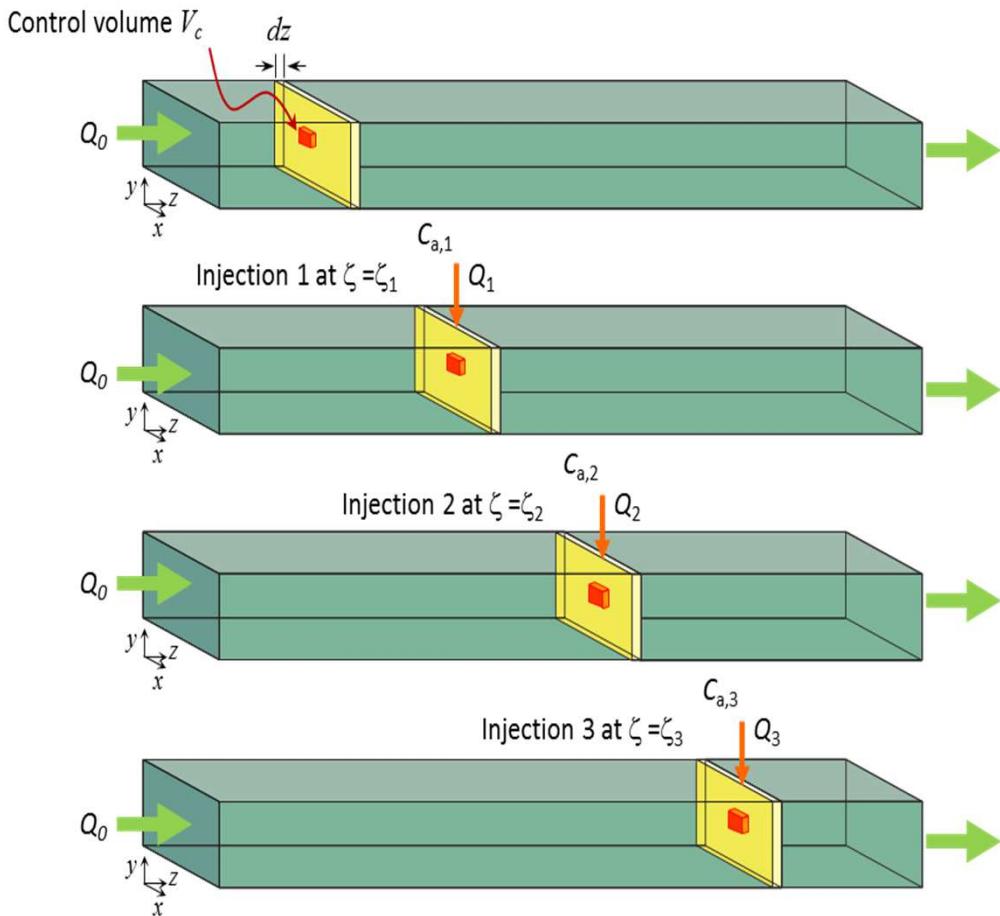


SOLVER C: relevance partitioning between 2 phases



Interplay of termination, depropagation and mass transfer

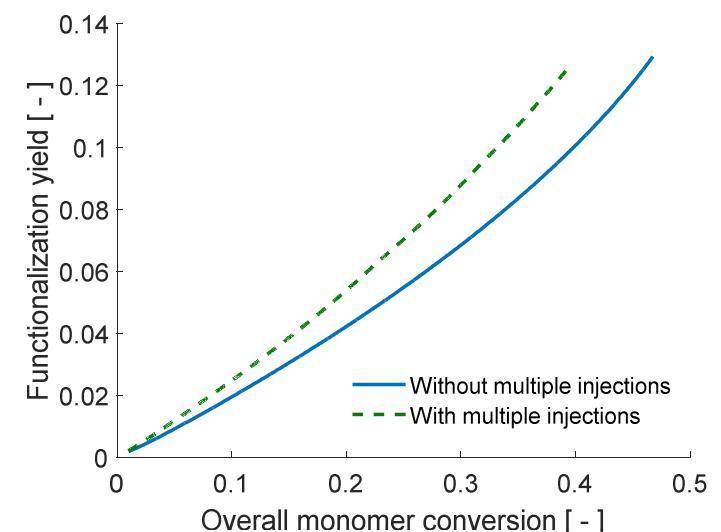
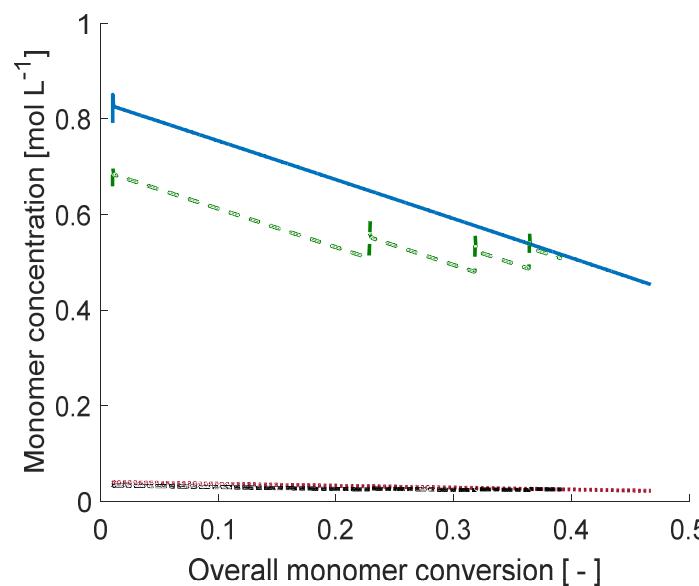
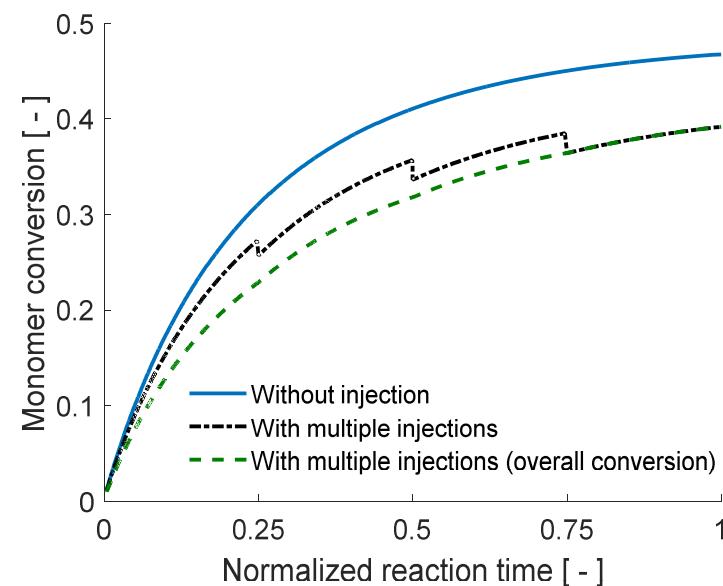
SOLVER D: addition profiles for monomer and/or initiator



$$x_a = \frac{n_{a,MC}|_{\theta=0} + \sum_i^j n_{inj\ a,i,MC} - n_{a,MC}|_{\theta}}{n_{a,MC}|_{\theta=0} + \sum_i^j n_{inj\ a,i,MC}}$$

$$x_{a,overall} = \frac{n_a|_{\theta=0} + \sum_i^j n_{inj\ a,i} - n_a|_{\theta}}{n_a|_{\theta=0} + \sum_i^N n_{inj\ a,i}}$$

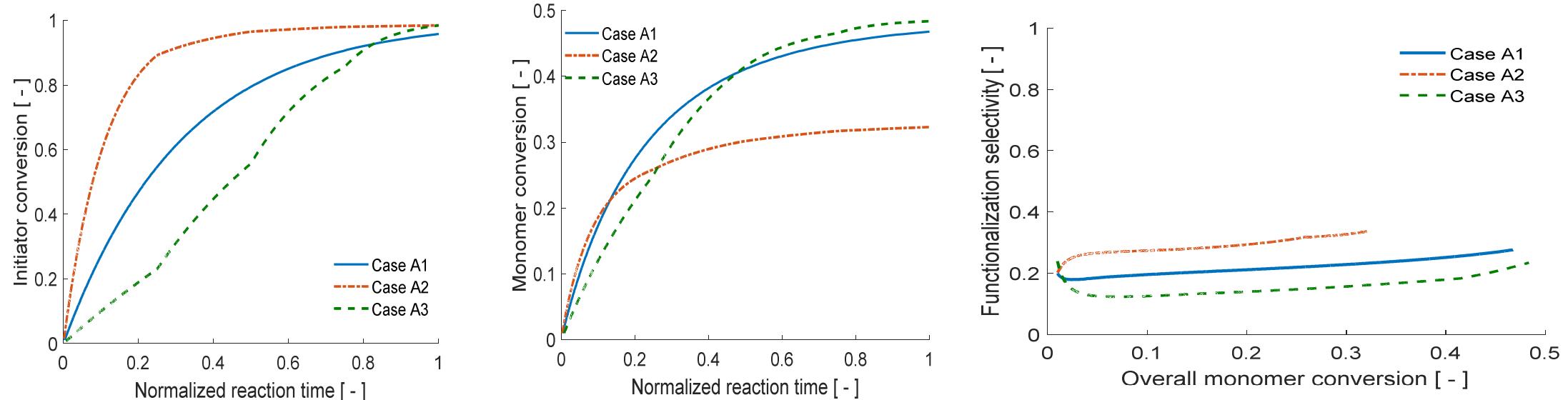
SOLVER D: addition profiles for monomer



Control of relevance of homopropagation and depropagation

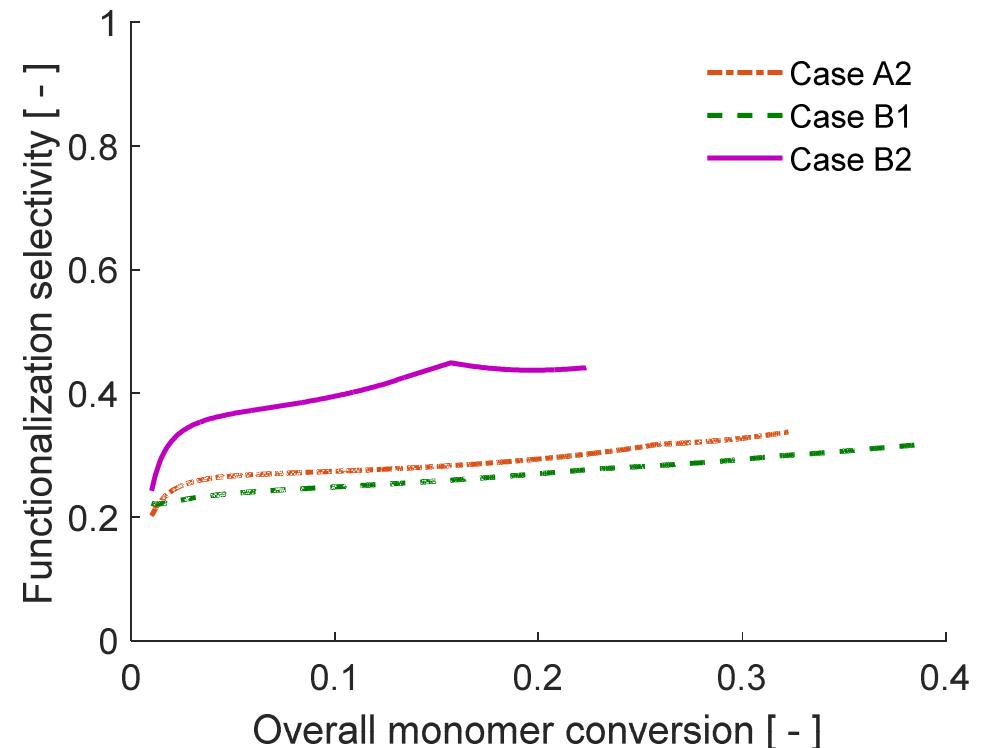
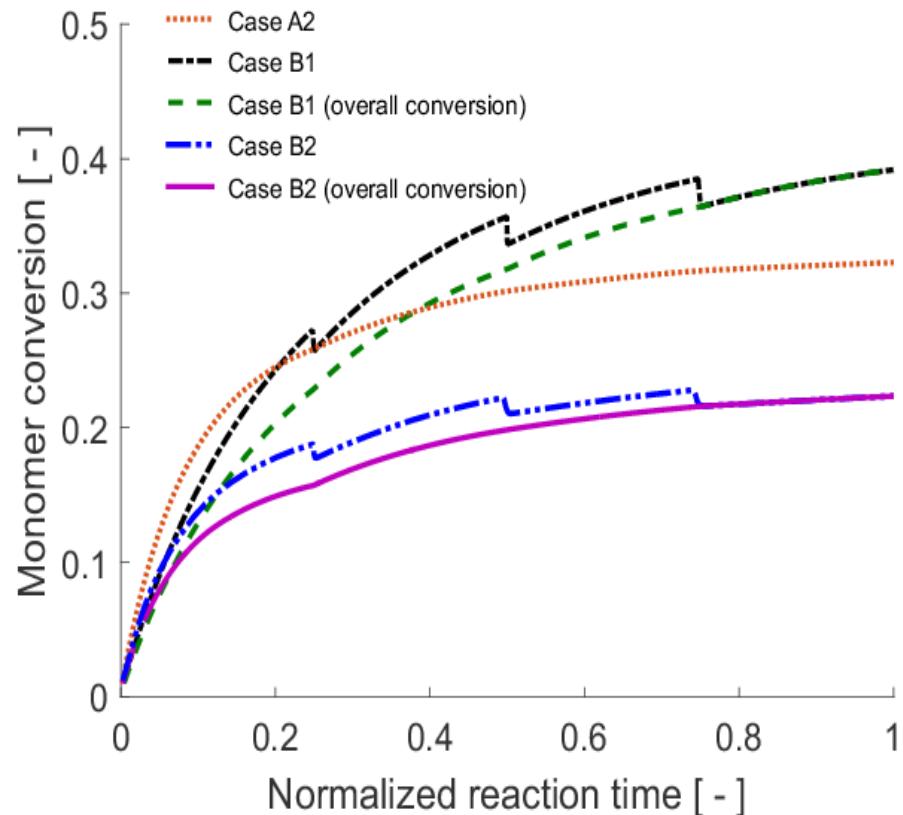
SOLVER D: temperature profile

Control of hydrogen abstraction rate



Zone	Domain	Temperature, K		
		Case A1	Case A2	Case A3
1	$0.00 \leq \zeta < 0.25$	473	488	458
2	$0.25 \leq \zeta < 0.50$	473	478	468
3	$0.50 \leq \zeta < 0.75$	473	468	478
4	$0.75 \leq \zeta < 1.00$	473	458	488

SOLVER D: monomer addition and temperature profile



Case B2: Case A2 + Case B1

Conclusions

- Solver A: all relevant average FRIG properties + diffusional limitations need to be accounted for
- Solver B: unique information on the individual chain level, including reaction event history, *e.g.* mass dependency hydrogen abstraction rate
- Solver C: absolute need of two-phase model under industrially relevant processing time scales
- Solver D: optimal functionality by consideration of multiple injection and/or temperature profiles

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