AUTEX-2019, GHENT, 11-14 JUNE 2019

FUNCTIONALIZATION OF POLYOLEFINS THROUGH RADICAL GRAFTING

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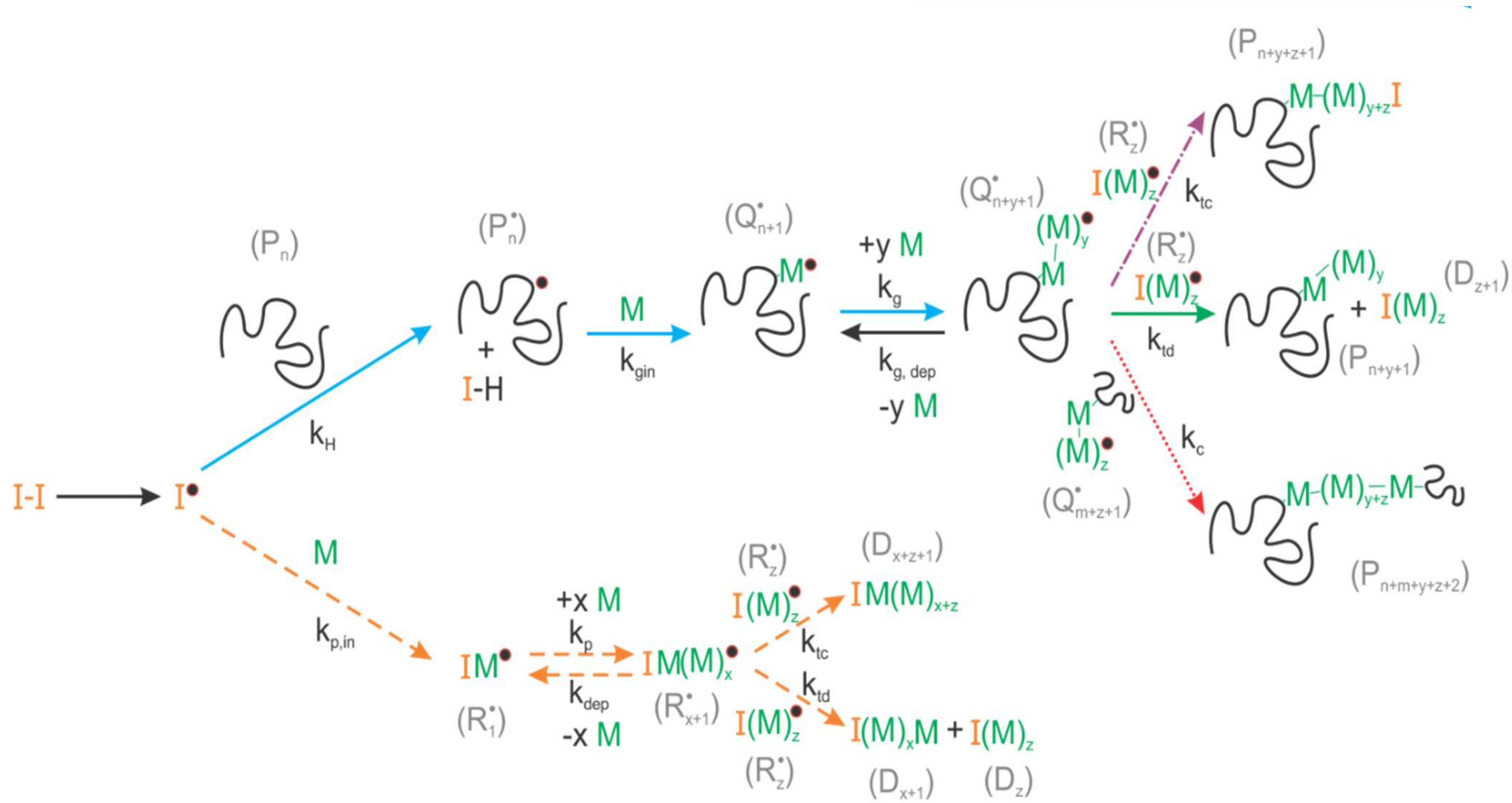
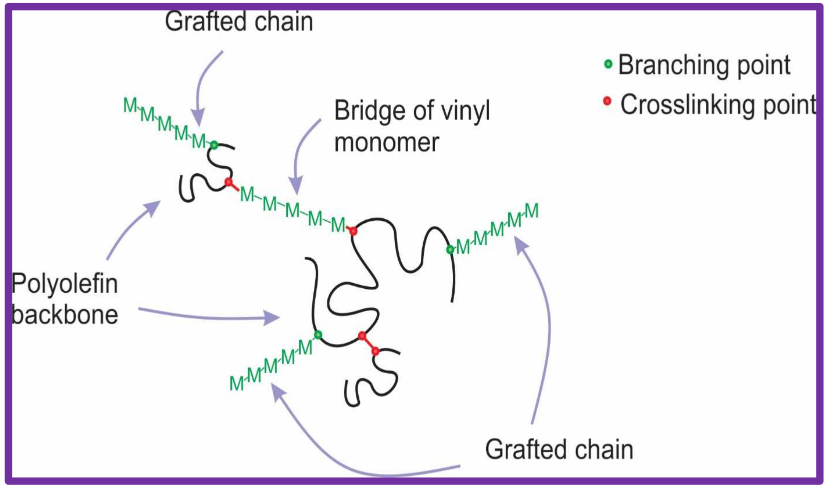
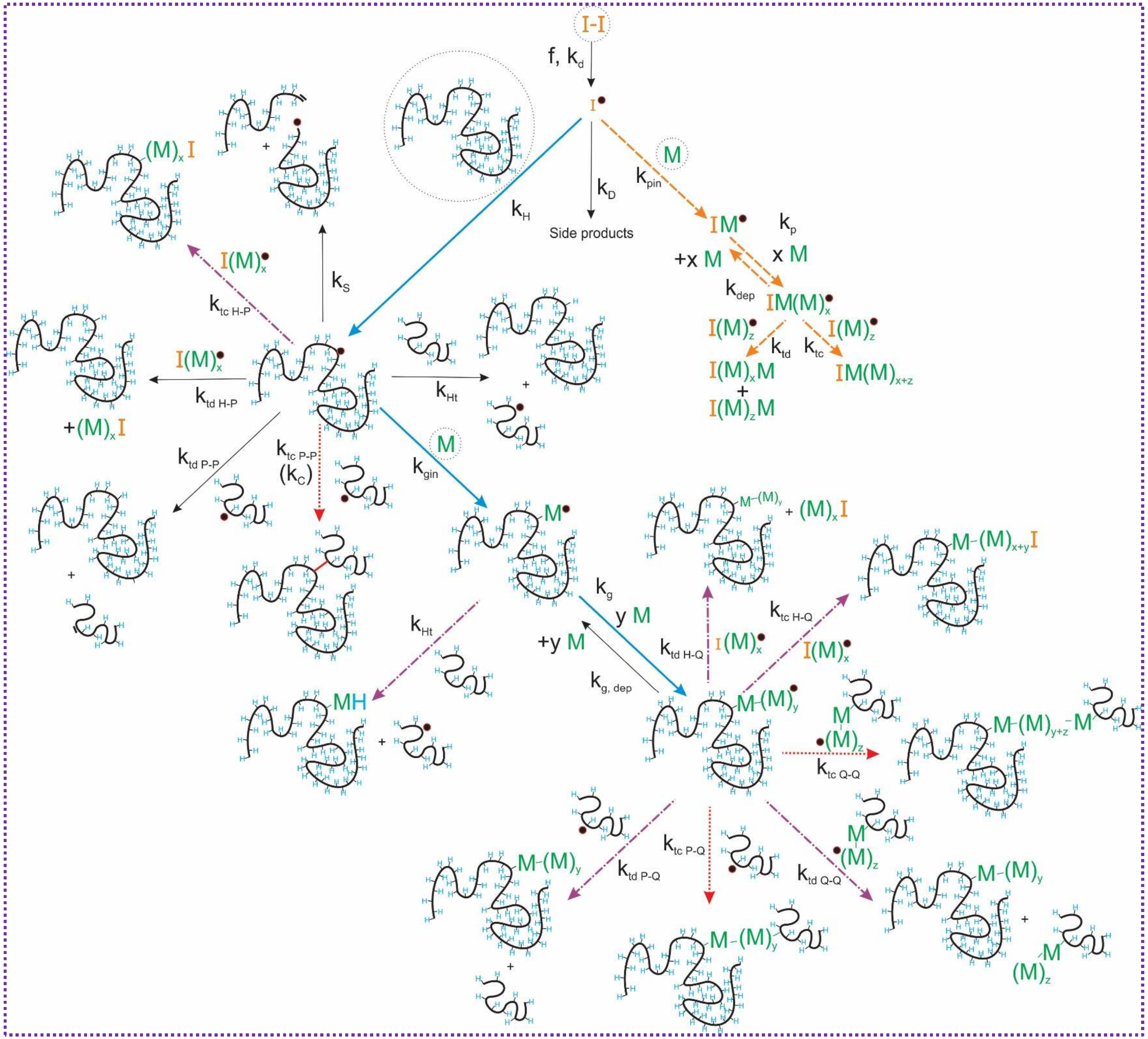
Free radical induced grafting of polyethylene: core reactions



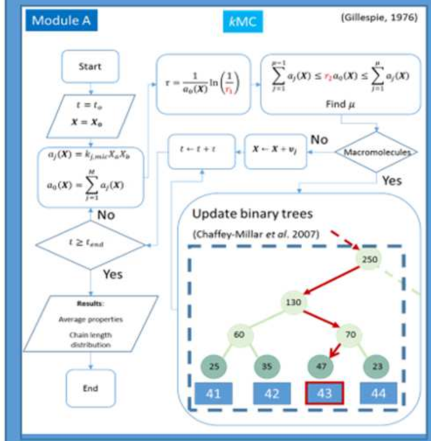
FRIG of PE: detailed reaction scheme

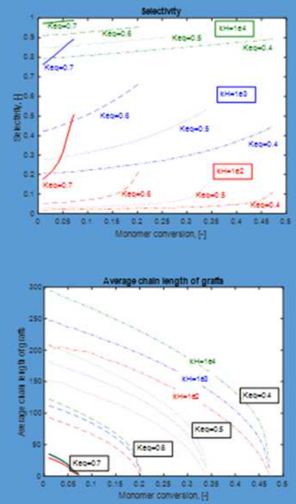




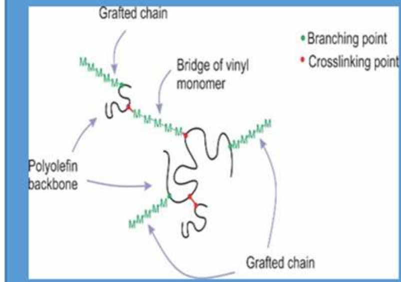
MODULAR MODELING PLATFORM

Main solver A: average FRIG properties/SEC trace

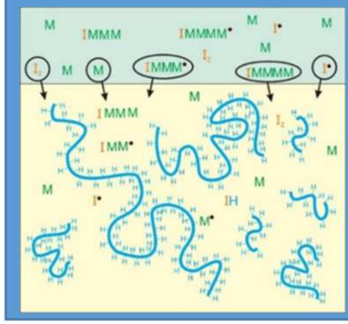




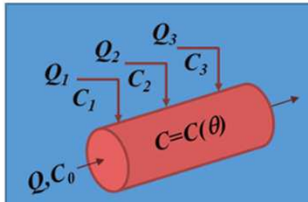
Solver B: Information per individual macrospecies



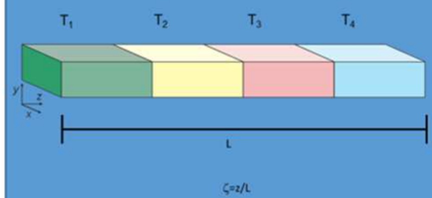
Solver C: phase segregation: mass transfer



Solver D: Injection points of monomer and/or initiator



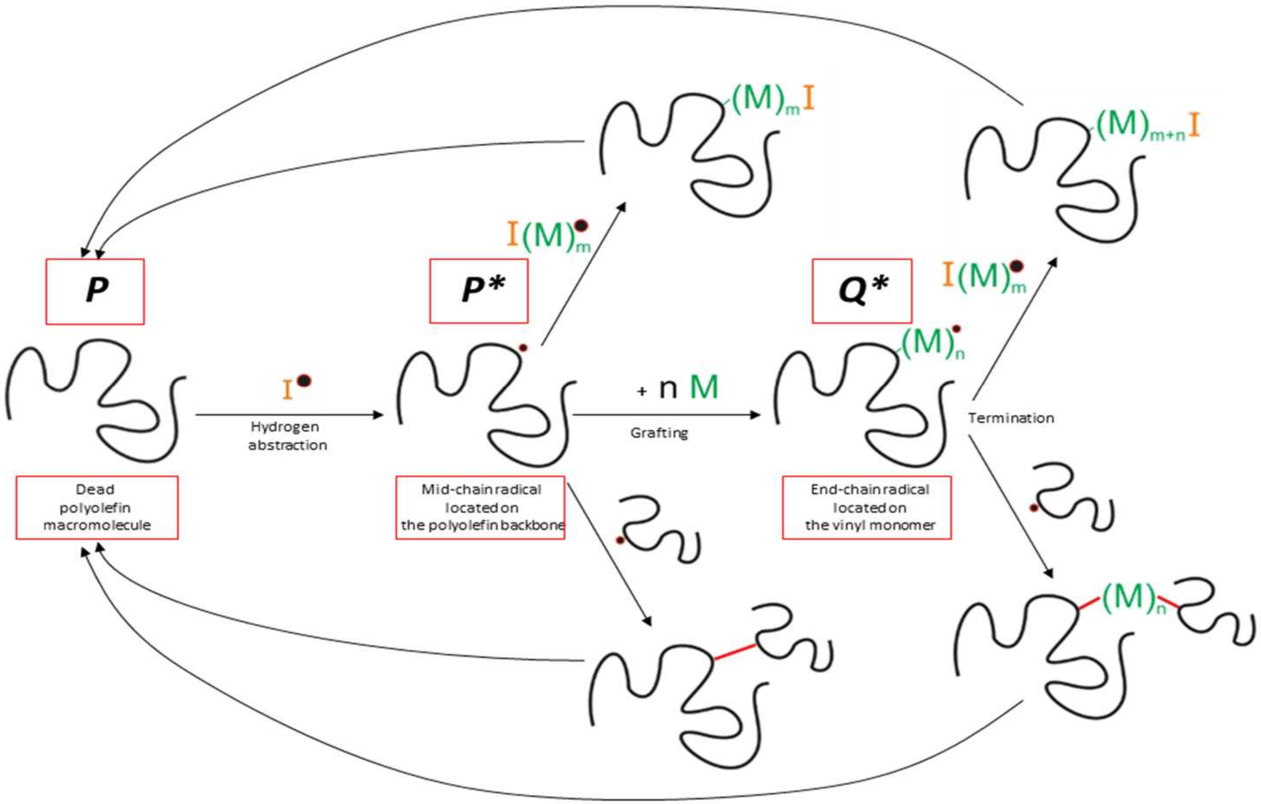
Solver D: Temperature zones

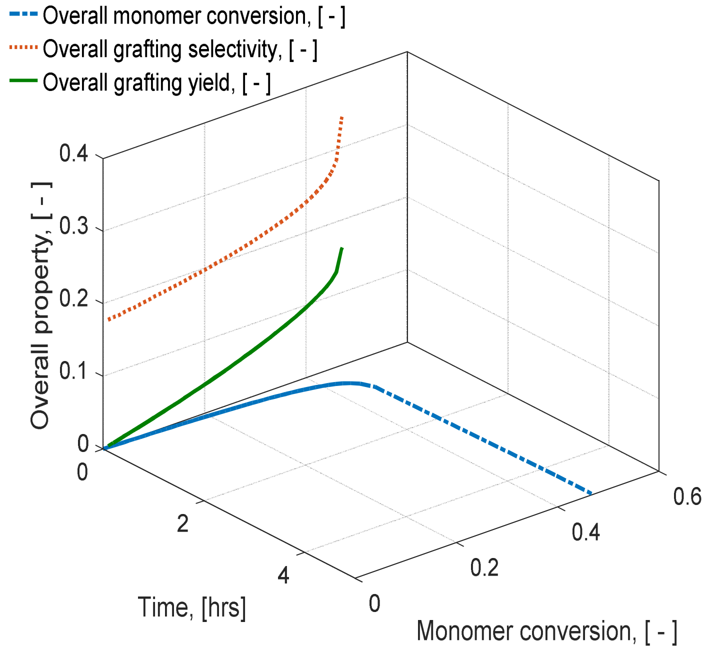


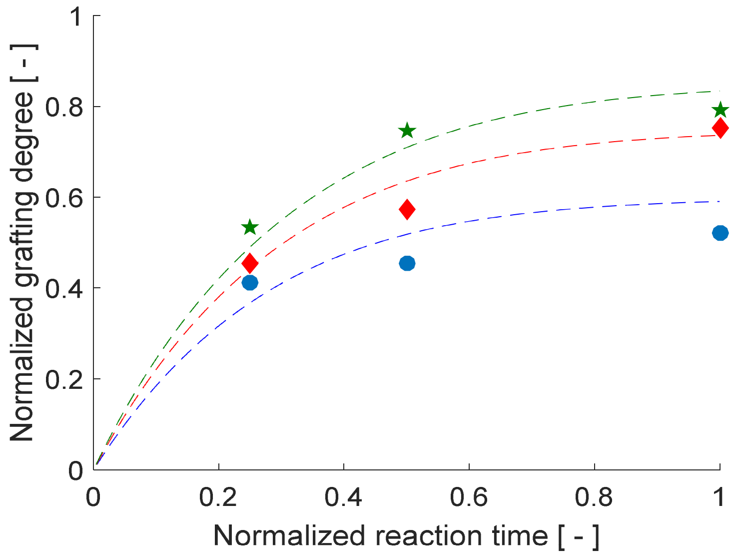
Hernandez-Ortiz, J. *et al.* *AIChE J.* 2017, 63, 4944; Hernandez-Ortiz, J. *et al.* *Macromol. Theory Simul.* 2018, 27, 1800036; Hernandez-Ortiz, J. *et al.* *Chem. Eng. J.* 2019a, in press; Hernandez-Ortiz, J. *et al.* *Chem. Eng. J.* 2019, under revision

MAIN SOLVER A:
kinetic Monte Carlo: avg. properties

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

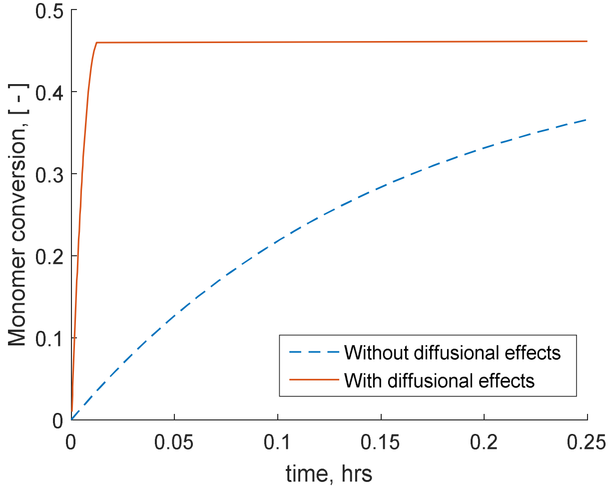


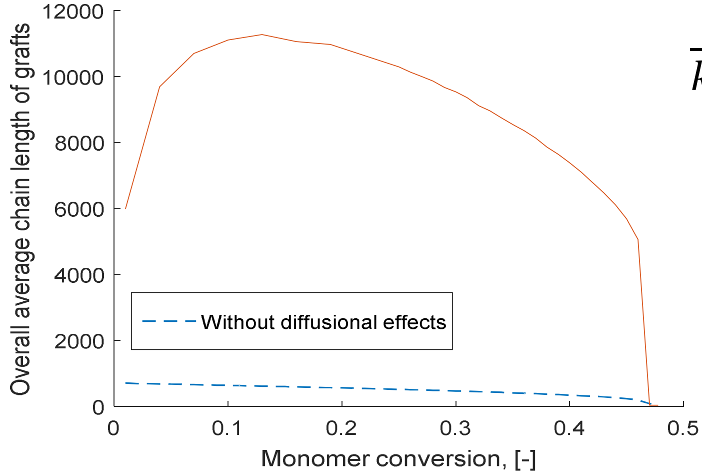




1. *Single phase lab-scale reaction system*
2. *Lumping of reaction event history*

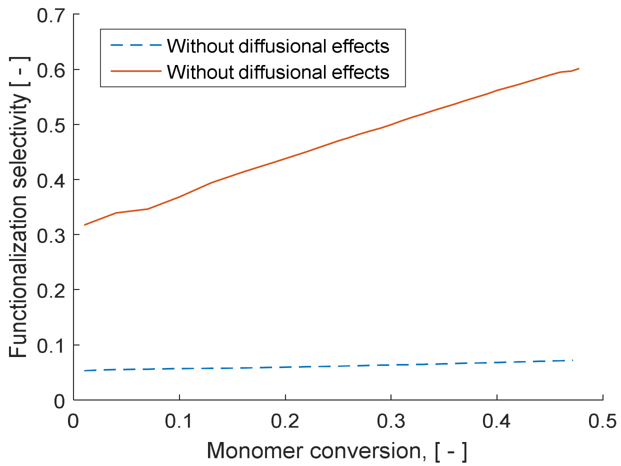
MAIN SOLVER A: relevance of diffusional limitations

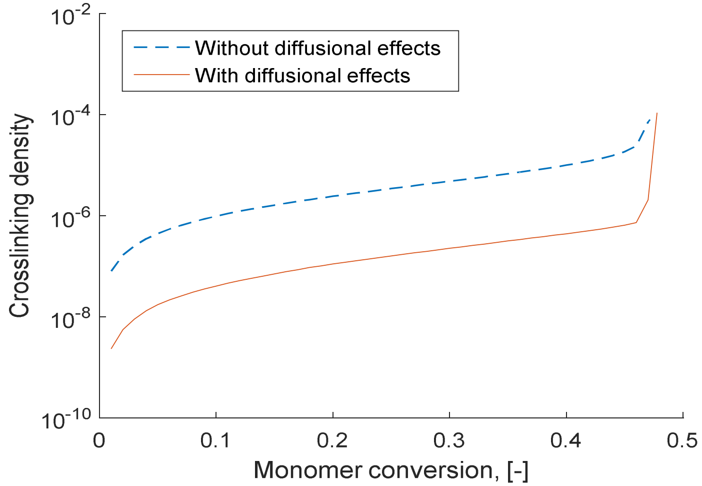




$$\frac{1}{k_{app}} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}}$$

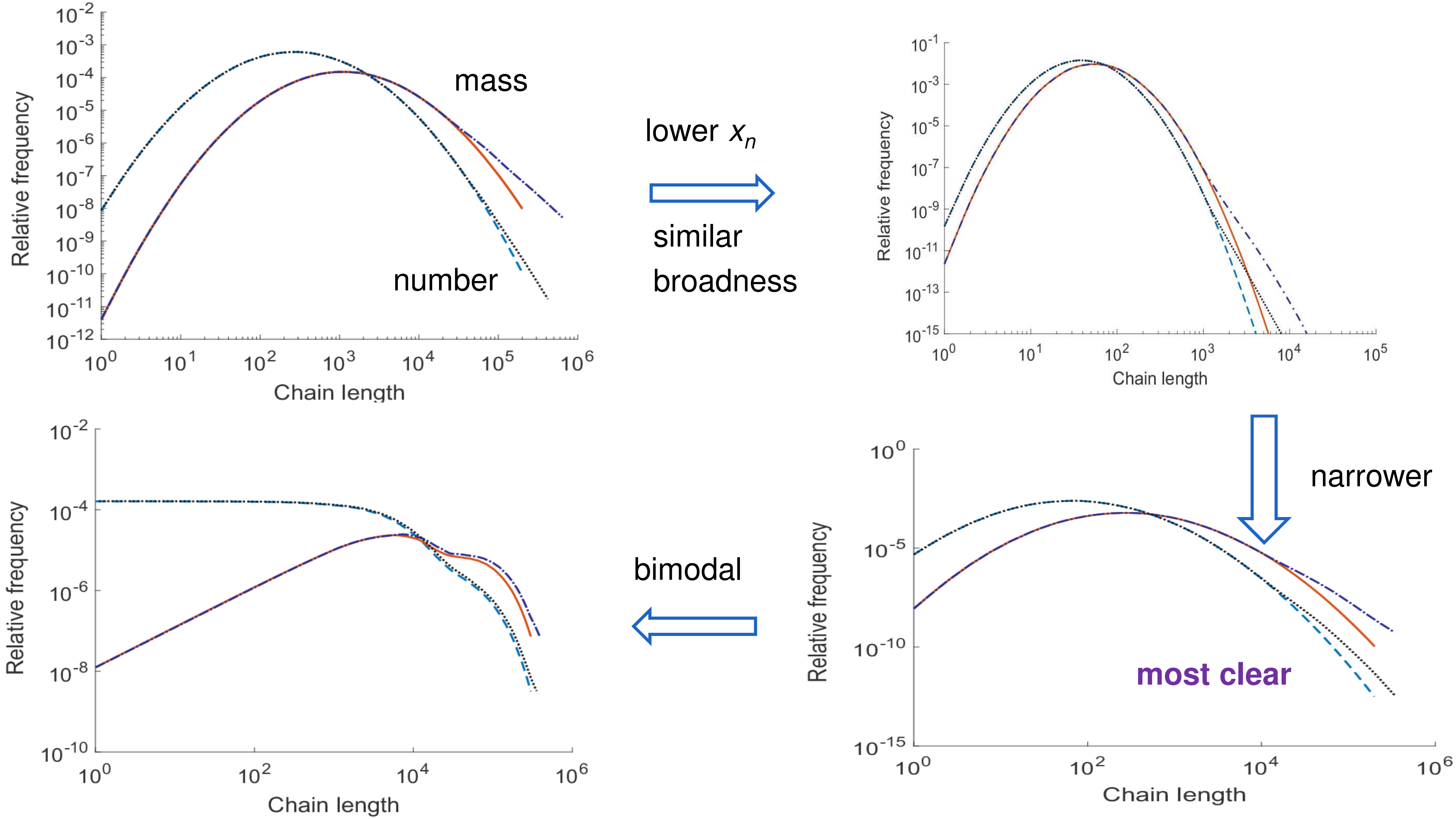
$$k_{diff} = 4\pi N_A \sigma D_{AB}$$





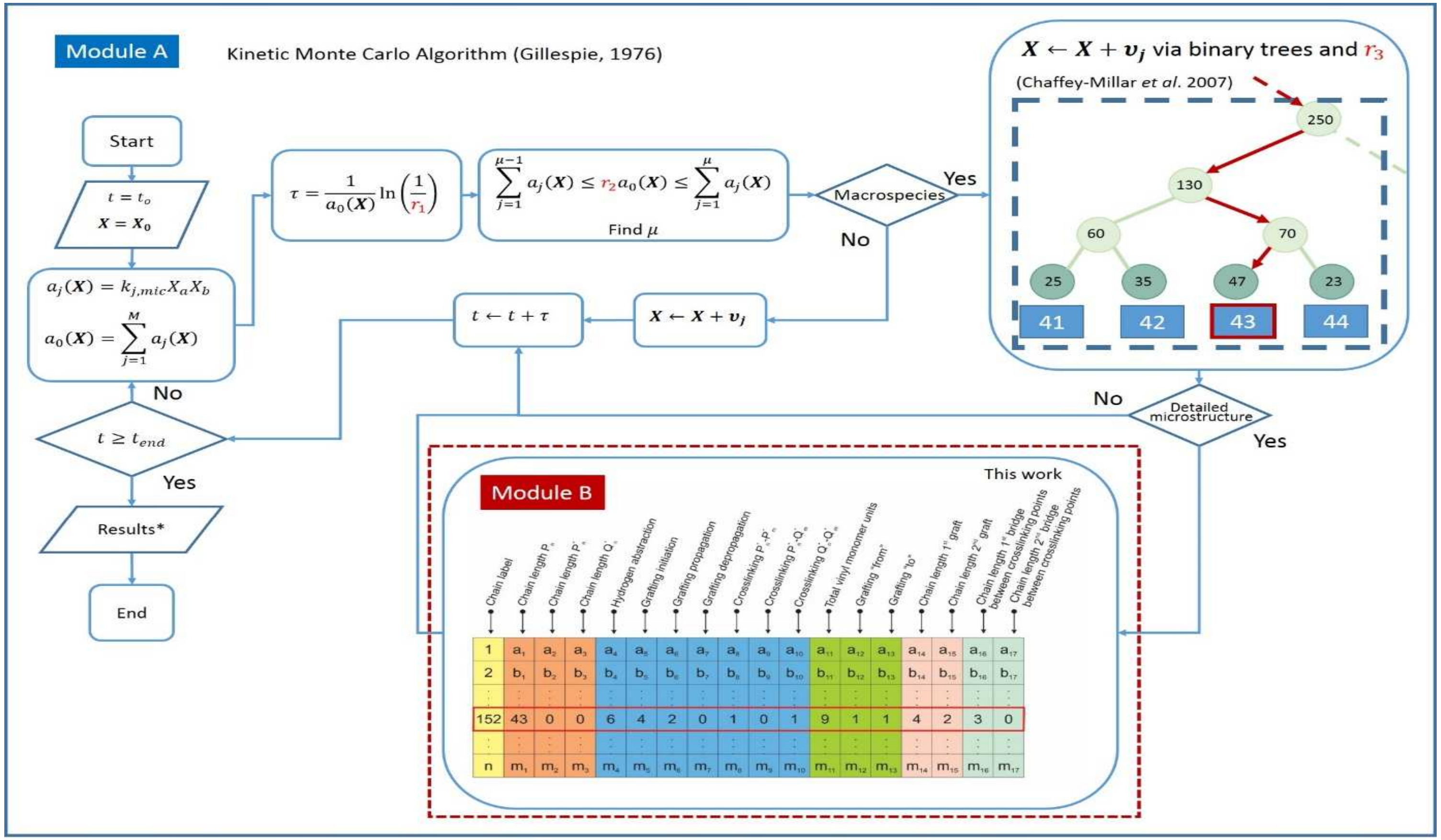
1. Single phase lab scale reaction system; 2. Lumping of reaction event history;

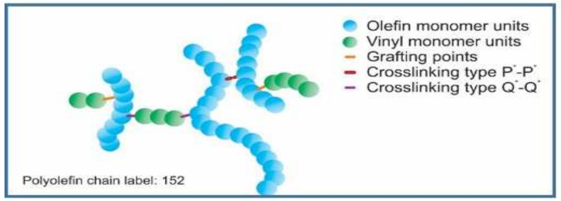
MAIN SOLVER A: relevance of initial distribution



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

SOLVER B: beyond averages: individual chains

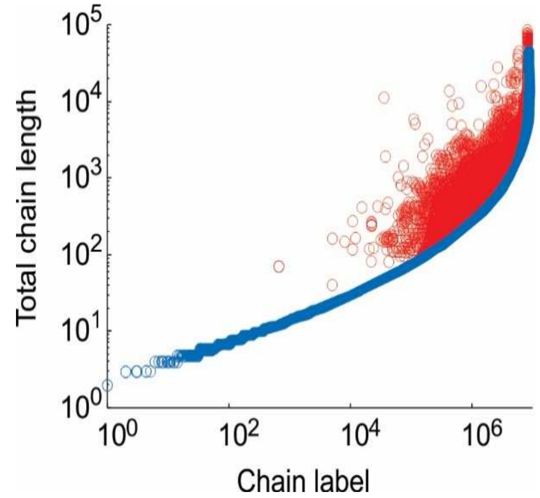


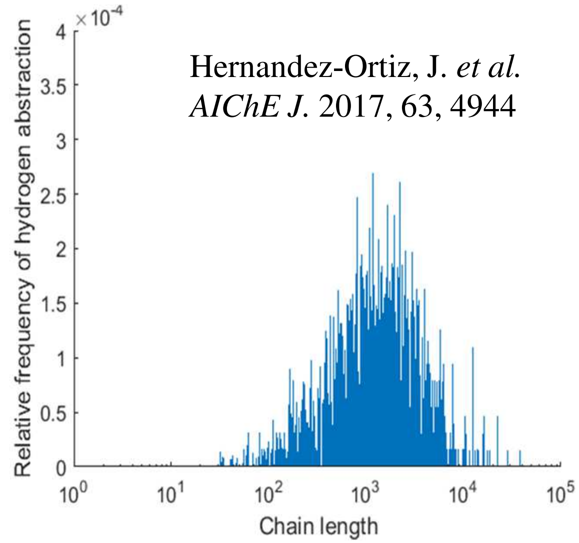


***Results:**

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

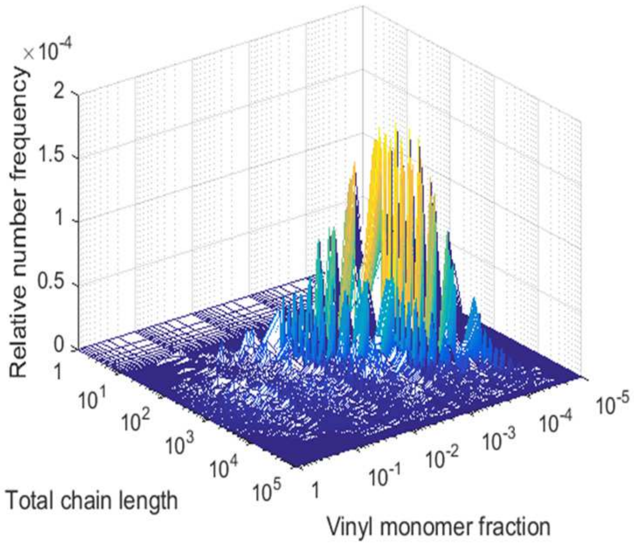


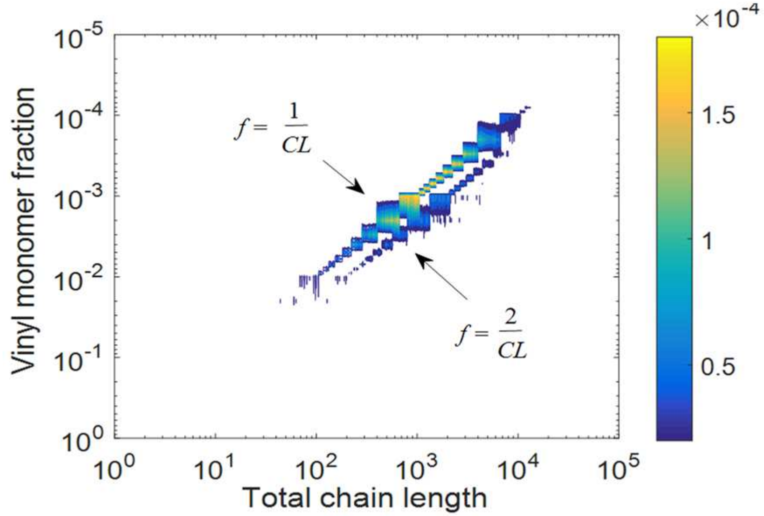


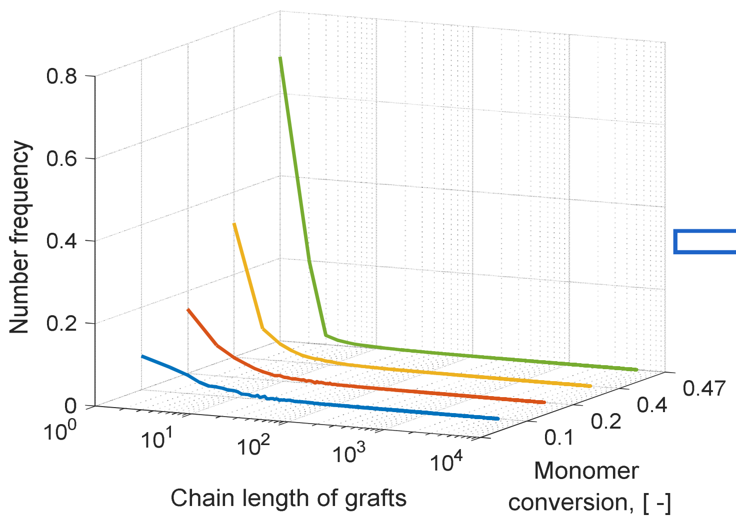
Hernandez-Ortiz, J. *et al.* *AIChE J.* 2017, 63, 4944

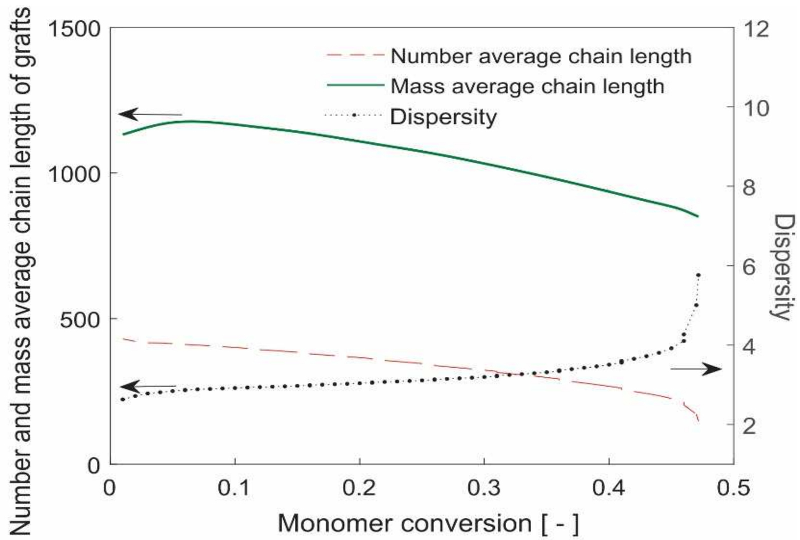
Single phase reaction system

SOLVER B: beyond averages: individual chains/grafts

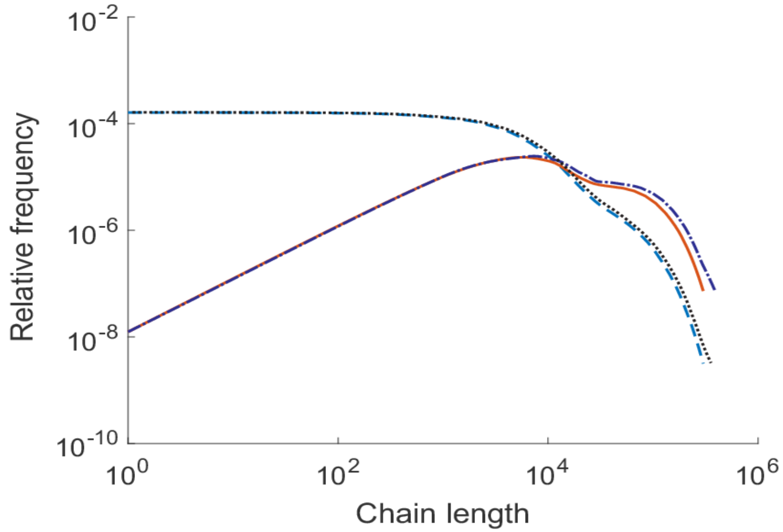




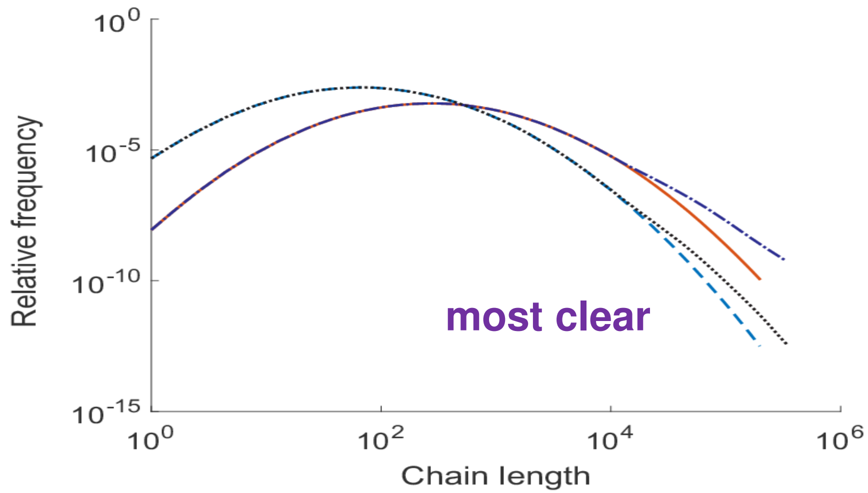


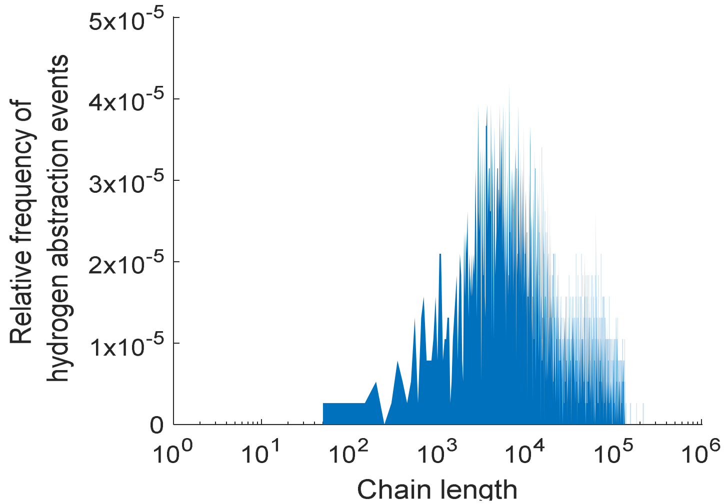


SOLVER B: beyond averages: individual chains

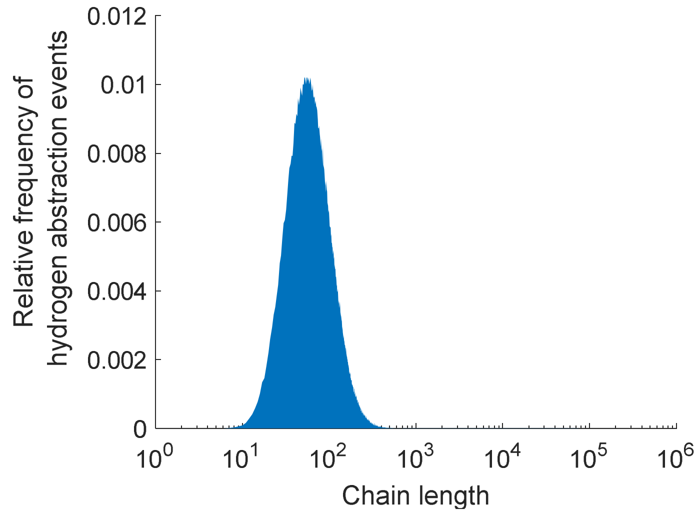


bimodal



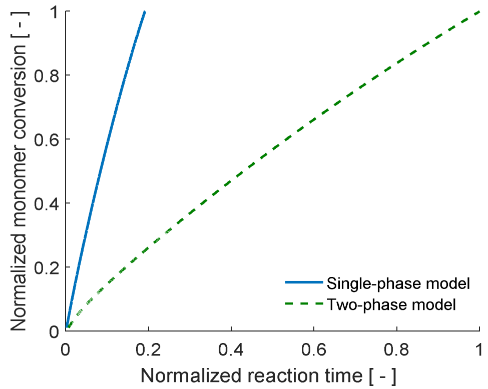


Confirmation

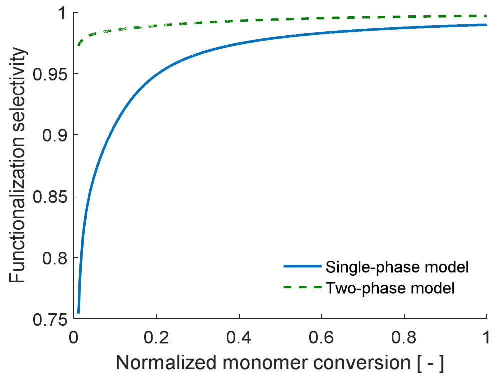


SOLVER C: 2-phase model for industrial time scales

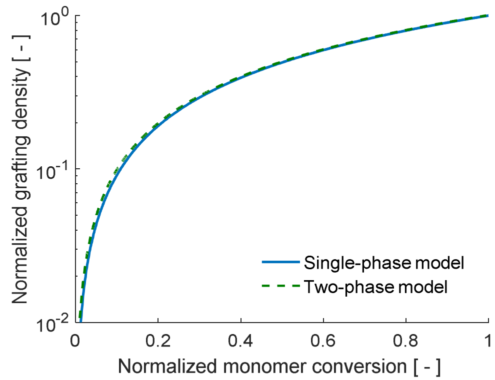
Non-homopolymerizable monomer

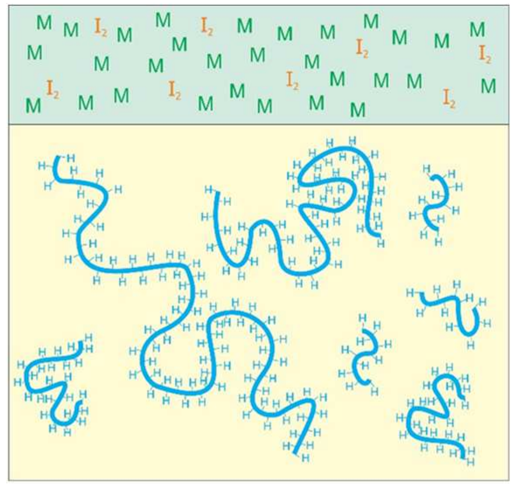


a)



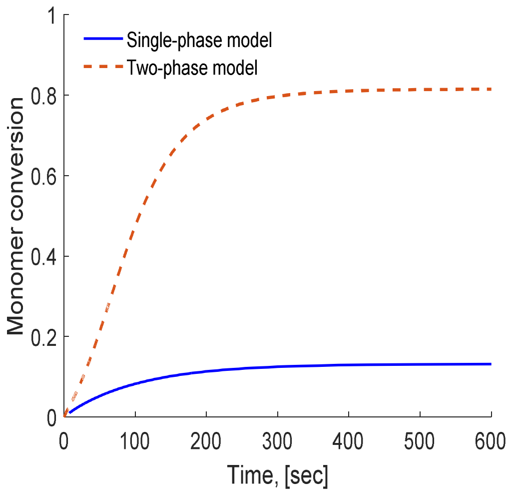
b)

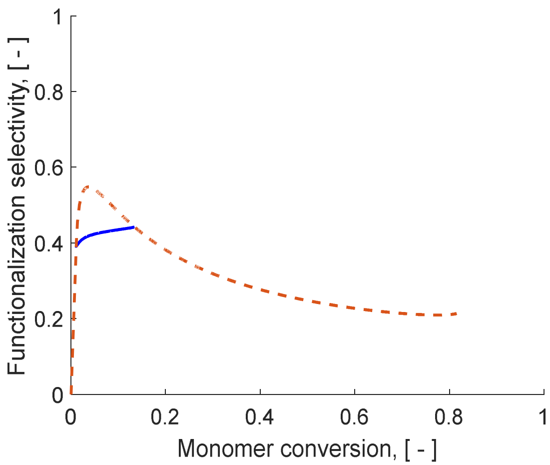


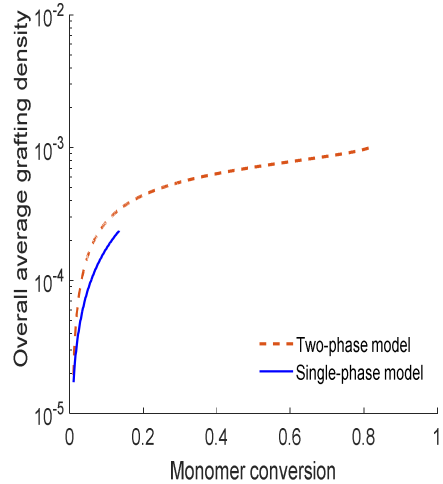


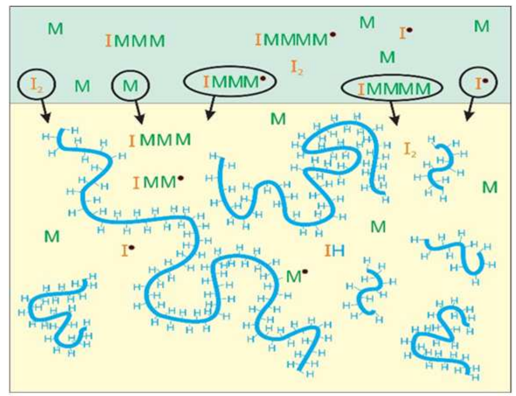
(a)

Homopolymerizable monomer





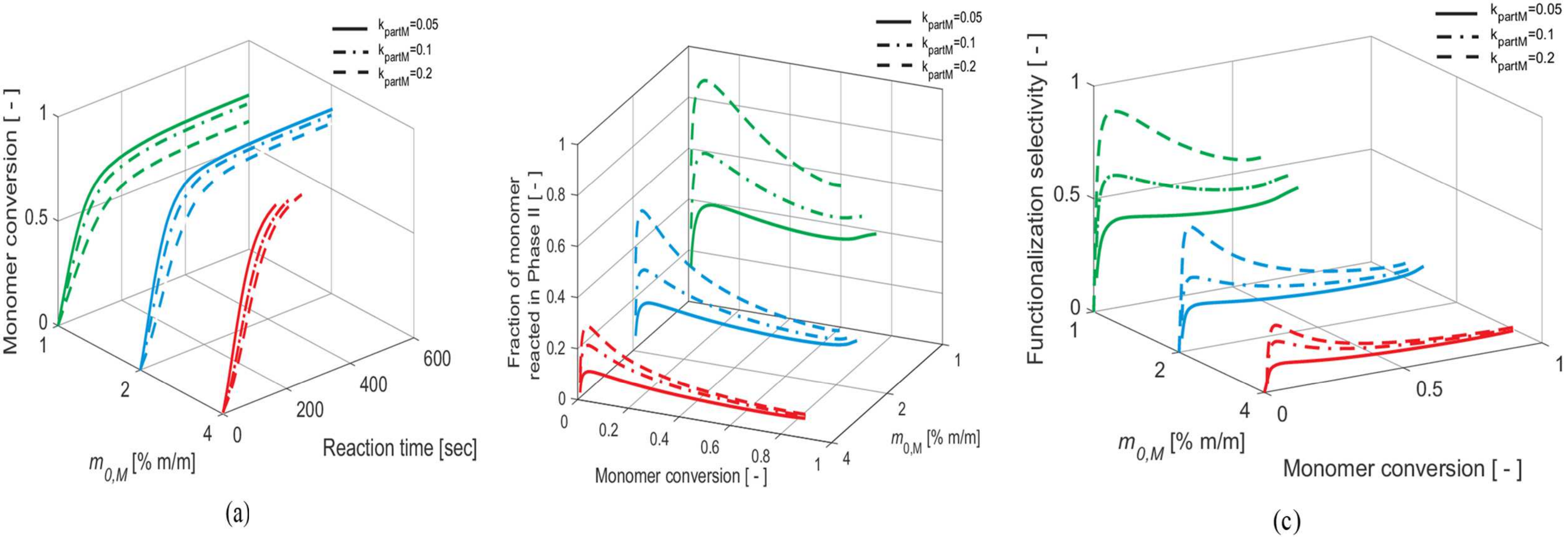




(b)

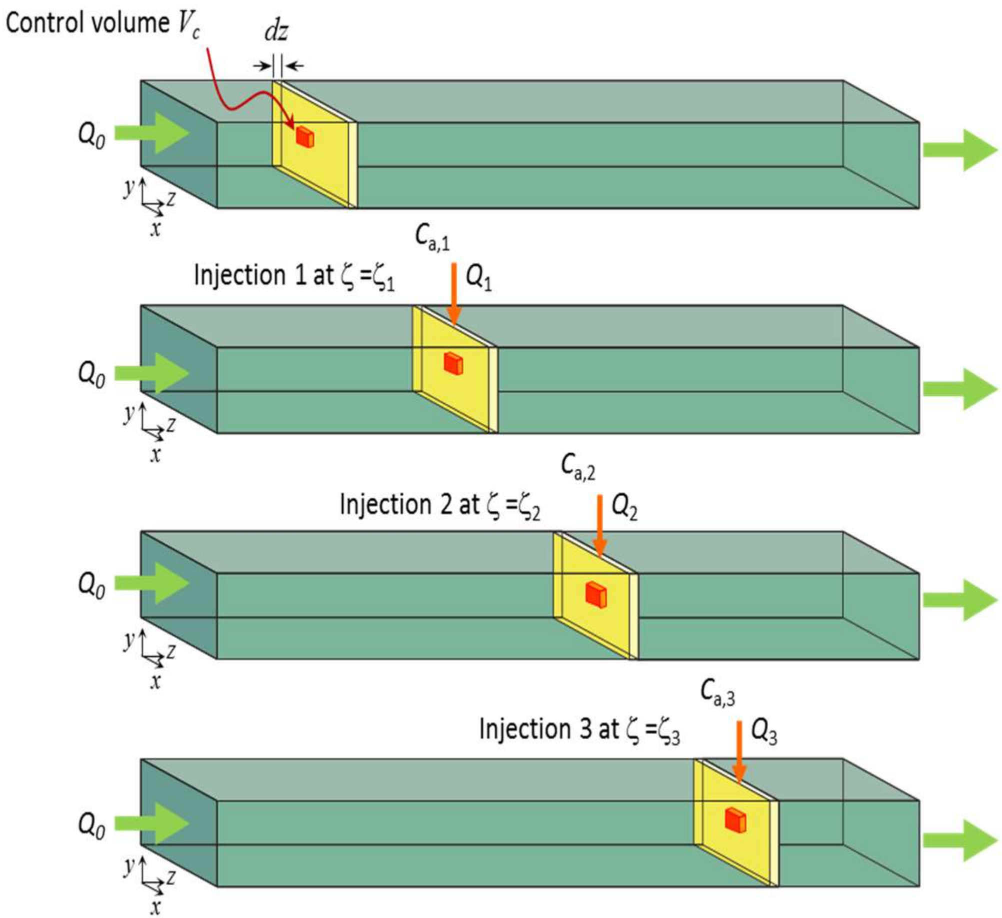
Hernandez-Ortiz, J. *et al.*
Chem. Eng. J. 2019a, in press

SOLVER C: relevance partitioning between 2 phases



Interplay of termination, depropagation and mass transfer

SOLVER D: addition profiles for monomer and/or initiator

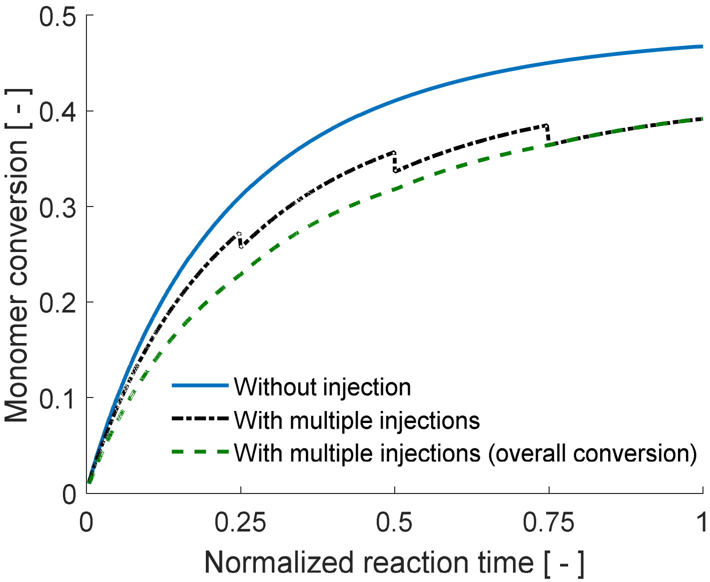


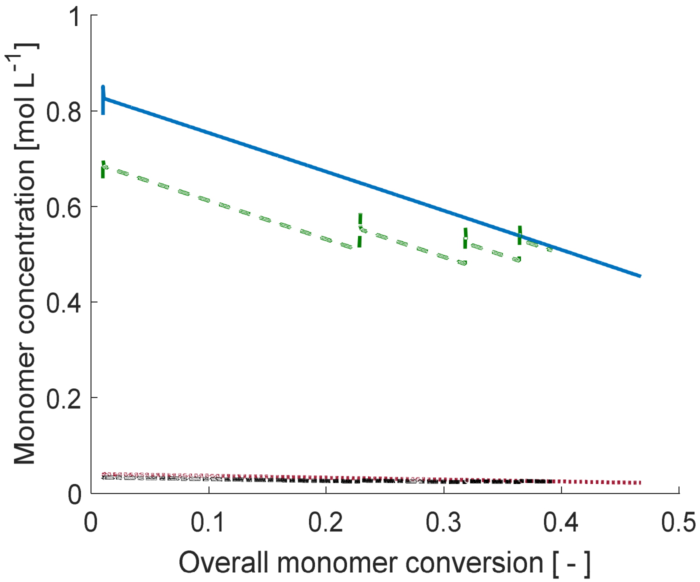
$$x_a = \frac{n_{a,MC}\big|_{\theta=0} + \sum_i^j n_{inj\ a,i,MC} - n_{a,MC}\big|_{\theta}}{n_{a,MC}\big|_{\theta=0} + \sum_i^j n_{inj\ a,i,MC}}$$

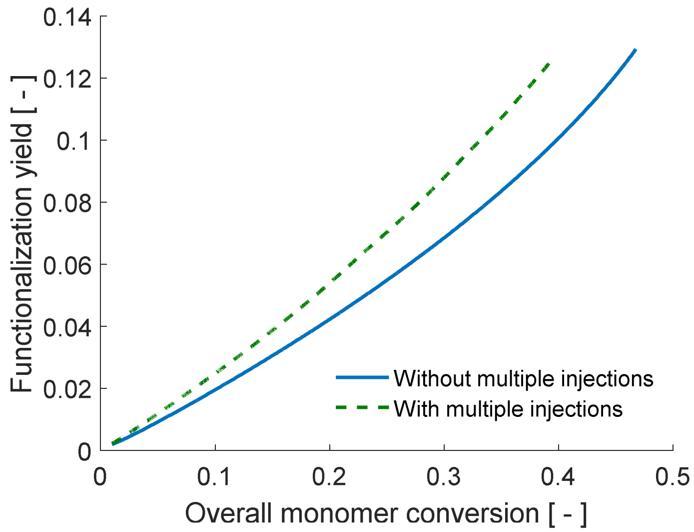
$$x_{a,overall} = \frac{n_a|_{\theta=0} + \sum_i^j n_{inj\ a,i} - n_a|_{\theta}}{n_a|_{\theta=0} + \sum_i^N n_{inj\ a,i}}$$

Hernandez-Ortiz, J. *et al. Chem. Eng. J.*. 2019b, under revision

SOLVER D: addition profiles for monomer



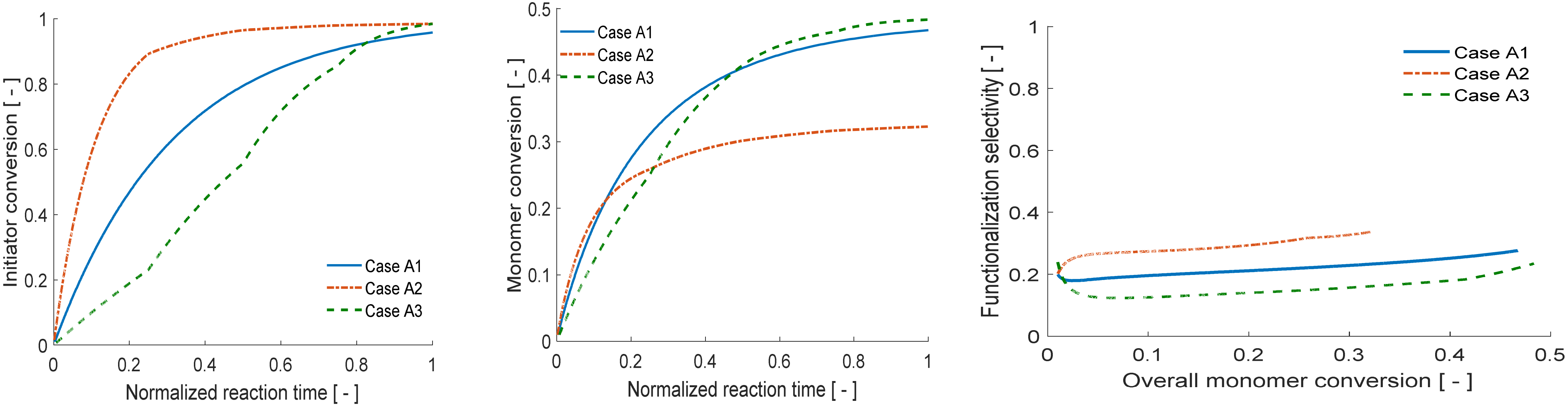




Control of relevance of homopropagation and depropagation

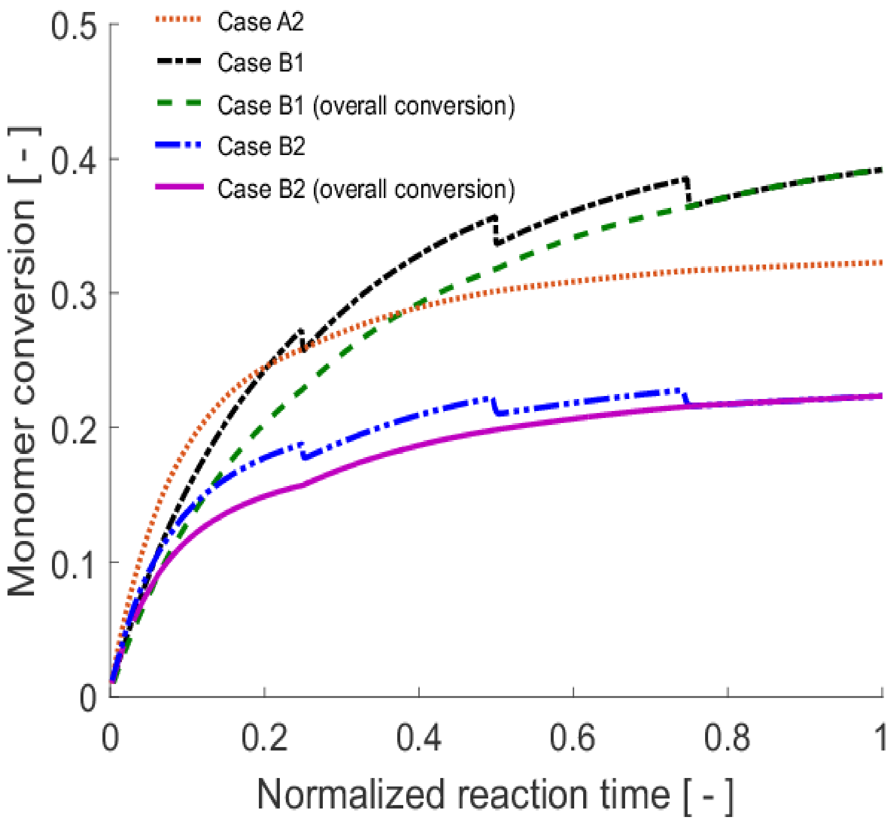
SOLVER D: temperature profile

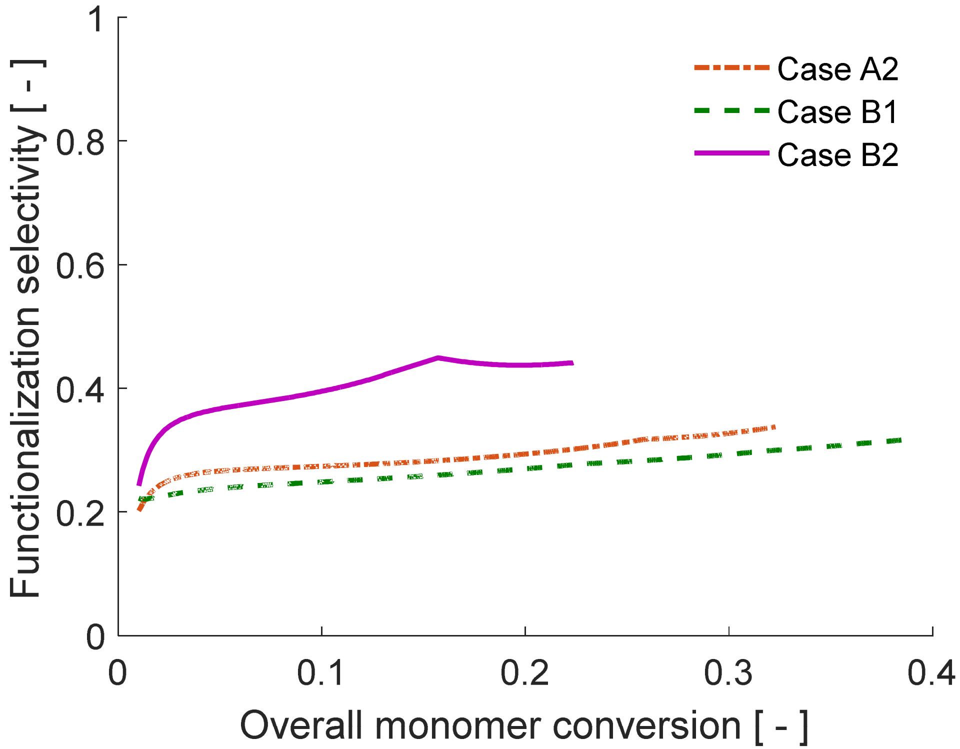
Control of hydrogen abstraction rate



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

Acknowledgments

- Long Term Structural Methusalem Funding by the Flemish Government
- Fund for Scientific Research Flanders (FWO)
- SABIC, Geleen, The Netherlands

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