An advanced kinetic modeling for reactive polymer processing

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sabic

Outline

- Functional polymers
- Modeling by *k*MC
- Model development: Module A and Module B
- Results (Module A and Module B)
- Effect of diffusional limitations
- Conclusions

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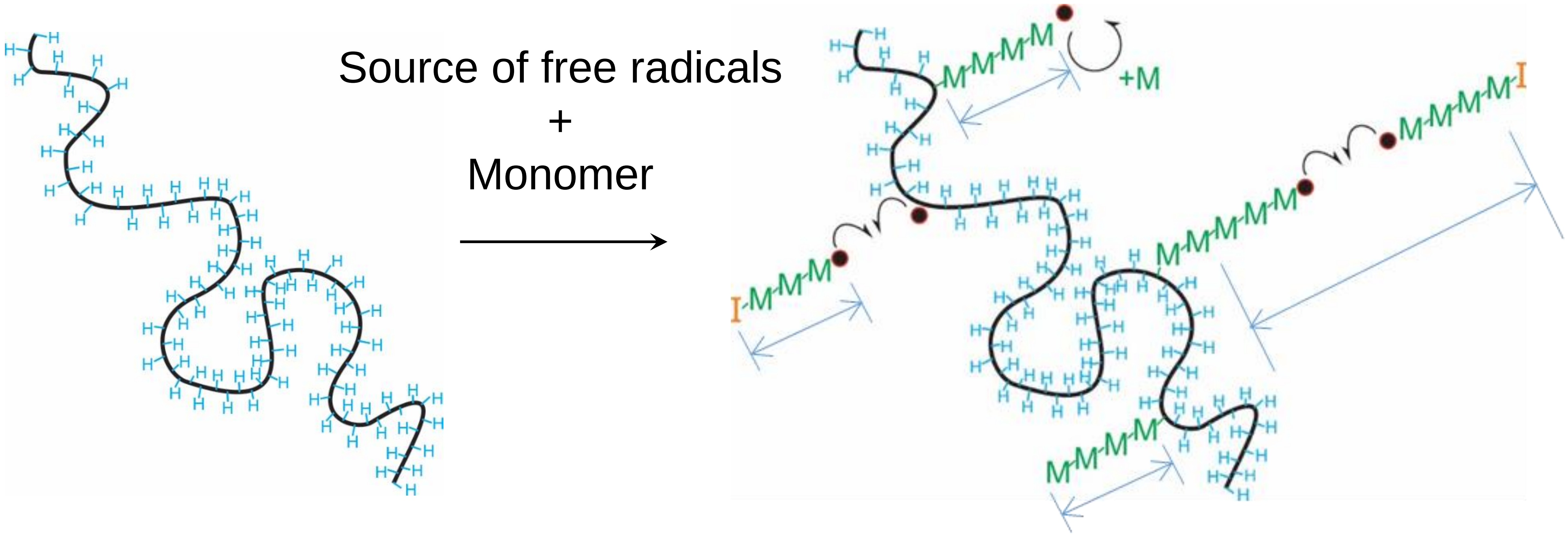
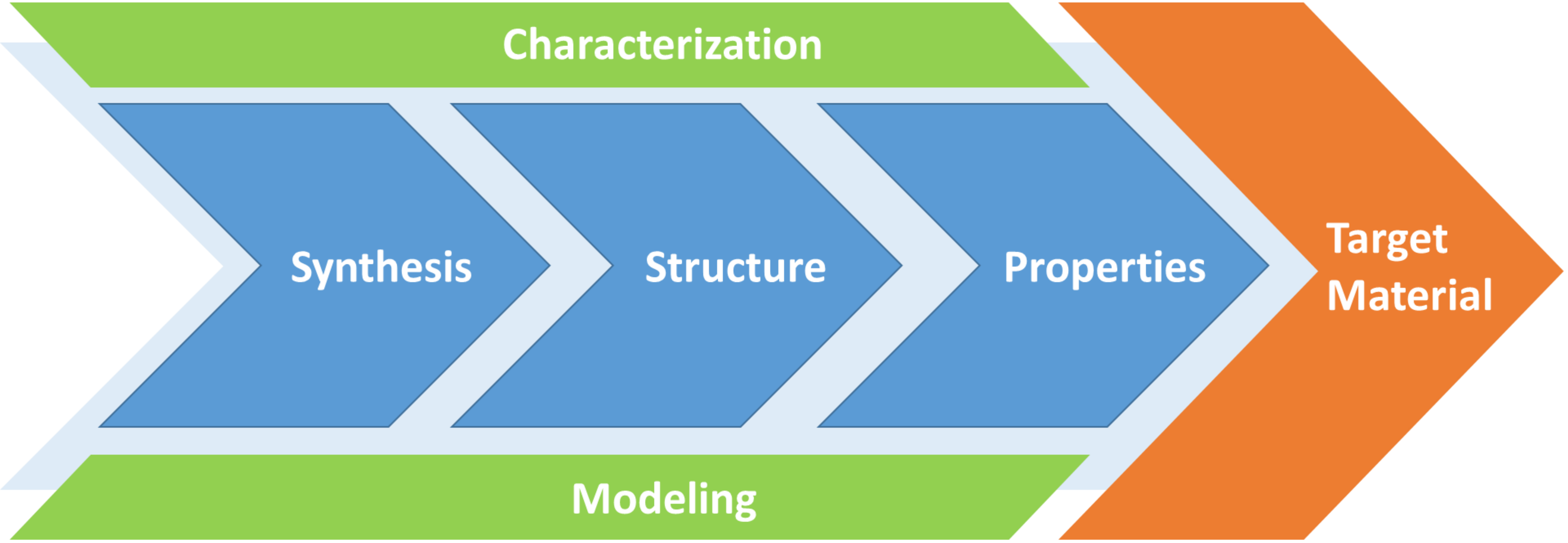
Functional polymers





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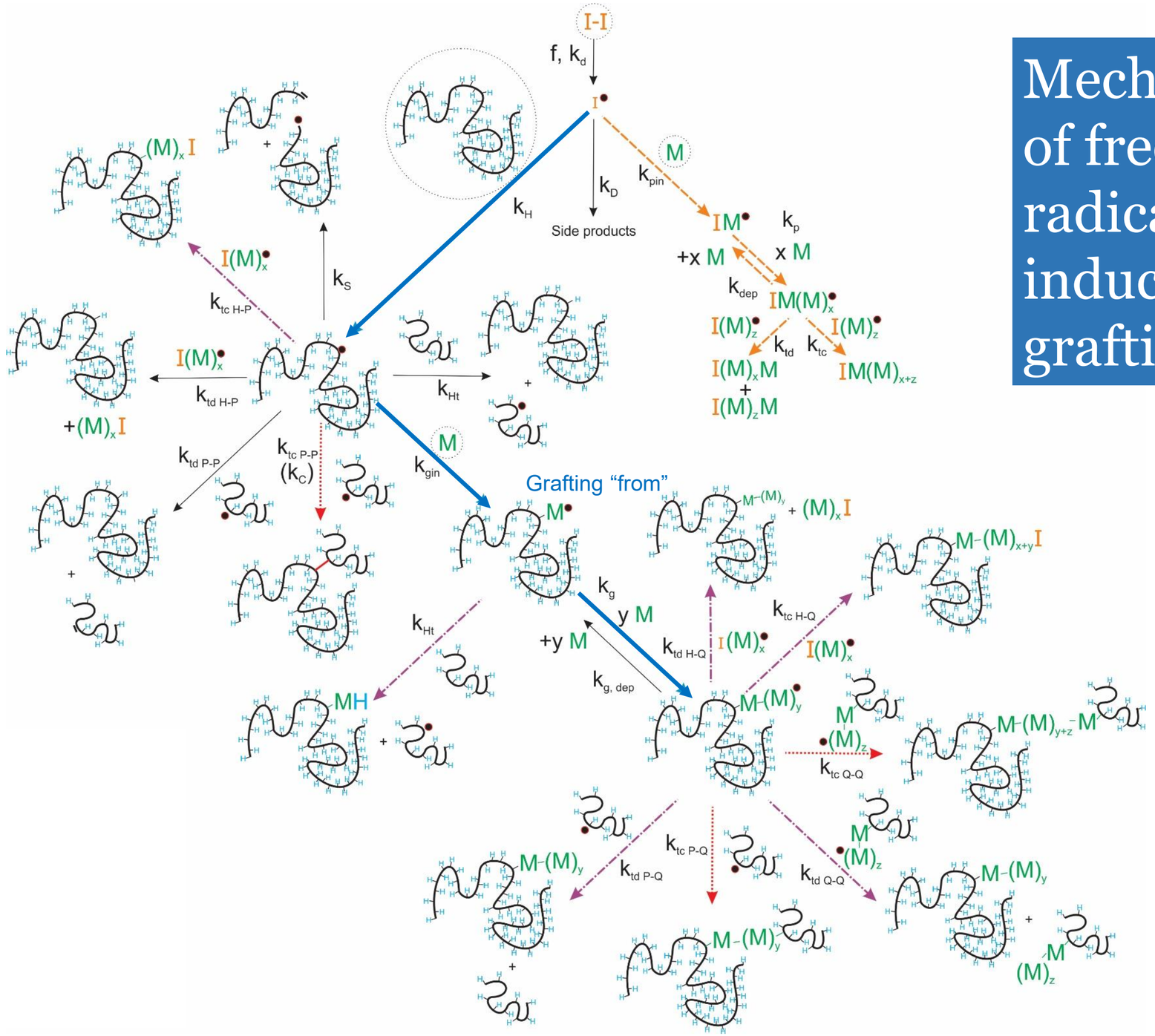
Mechanism of free-radical induced grafting



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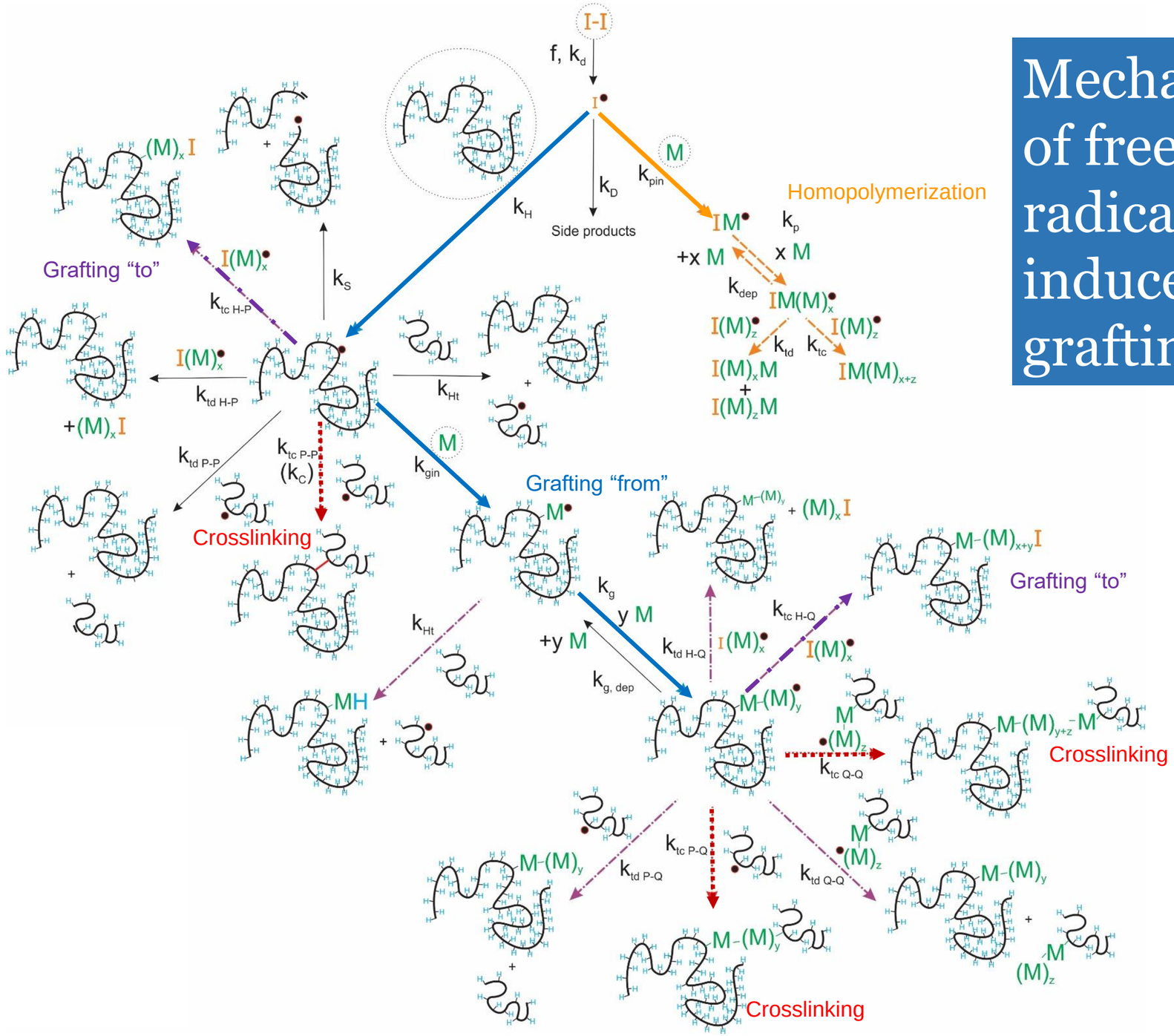
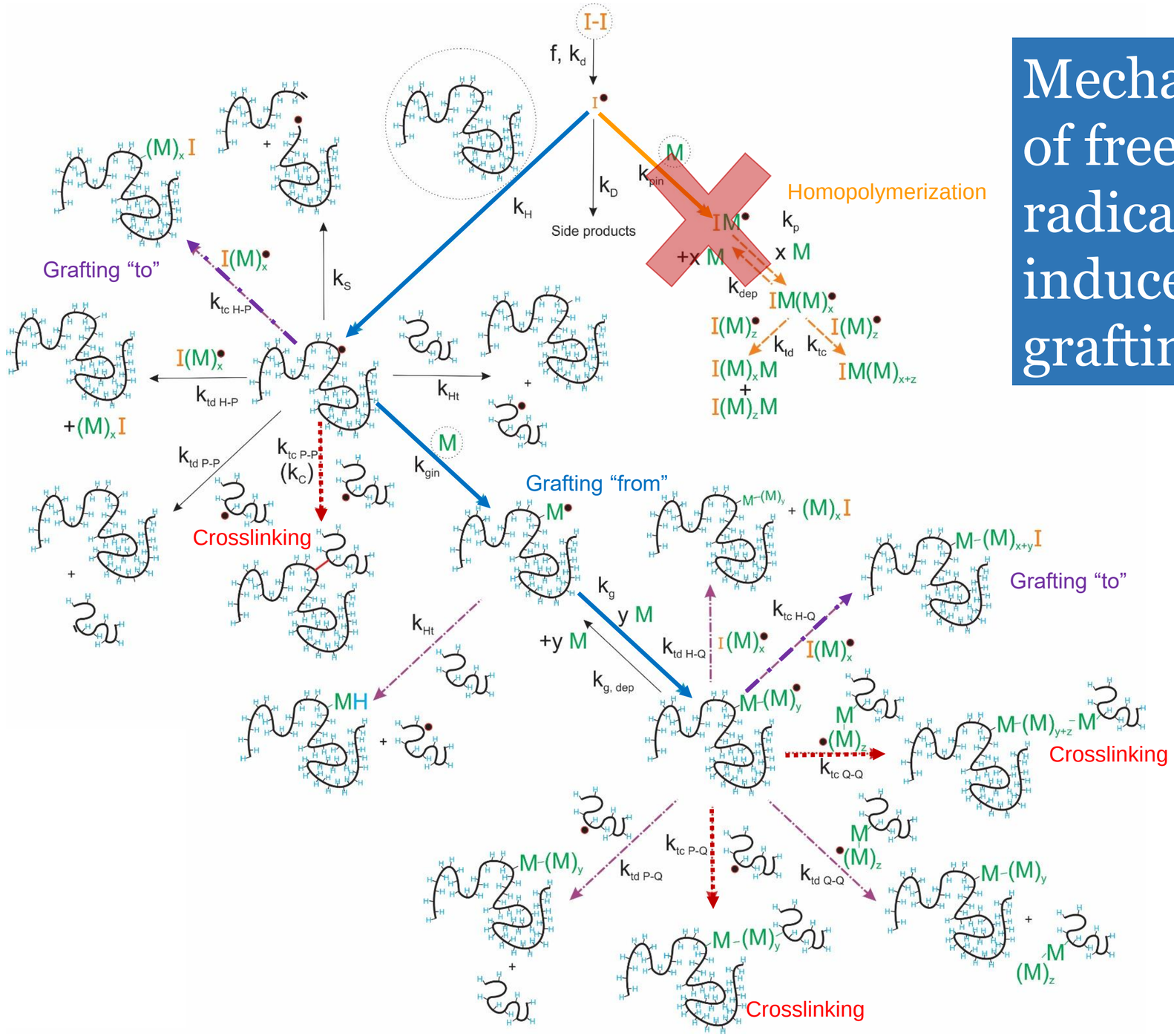
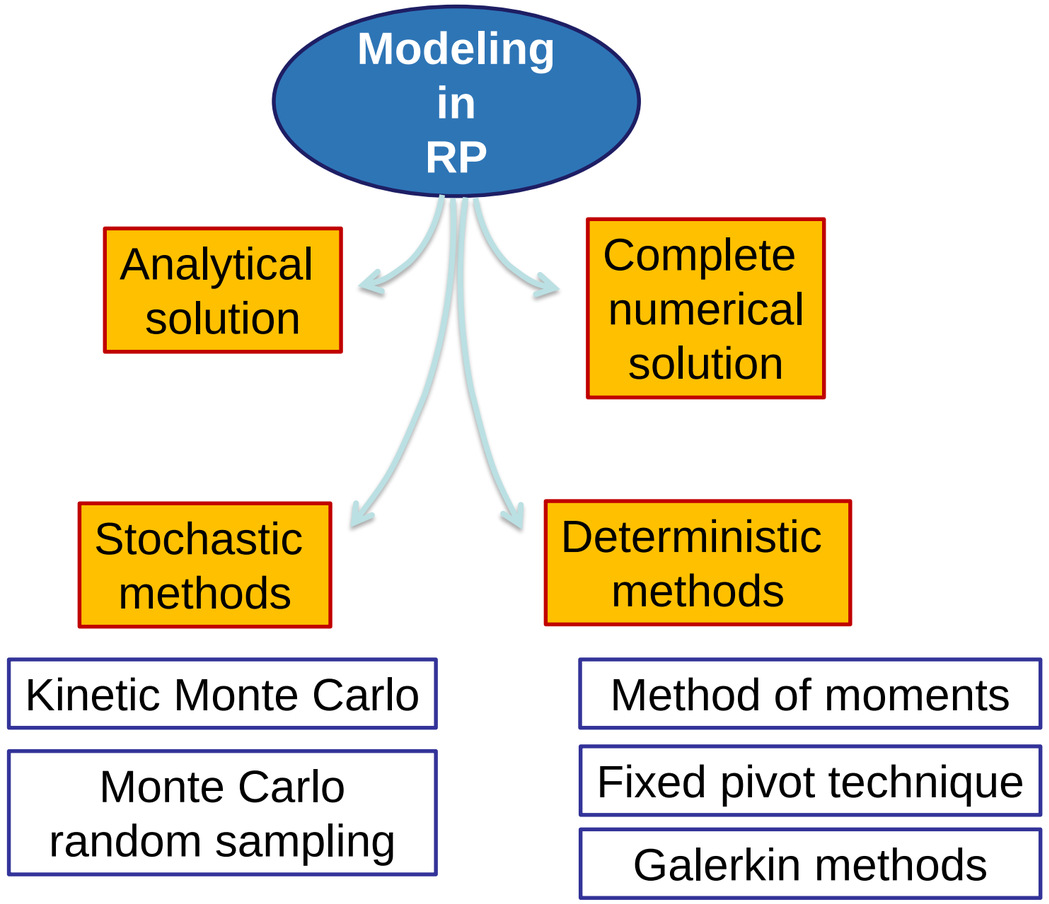
Mechanism of free-radical induced grafting



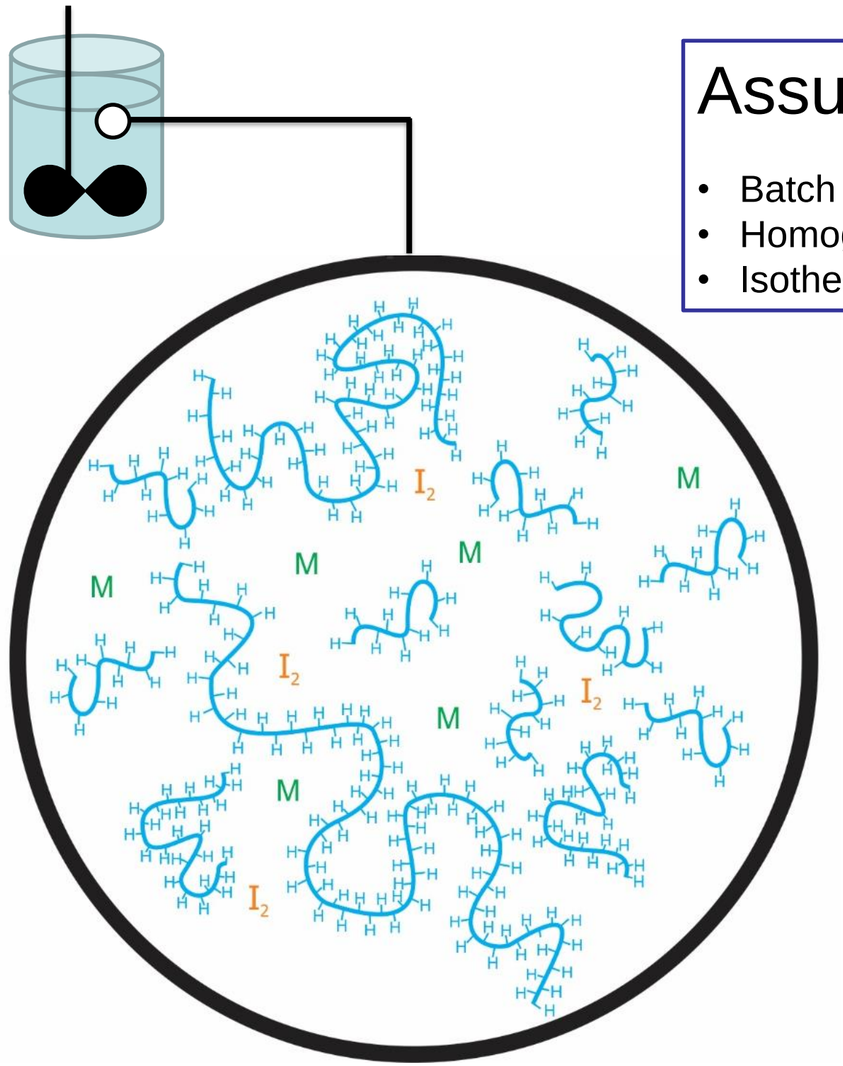
Mechanism of free-radical induced grafting



Kinetic Monte Carlo in Reactive Processes



Kinetic Monte Carlo (*k*MC)



Assumptions:

- Batch reaction
- Homogeneous phase
- Isothermal conditions

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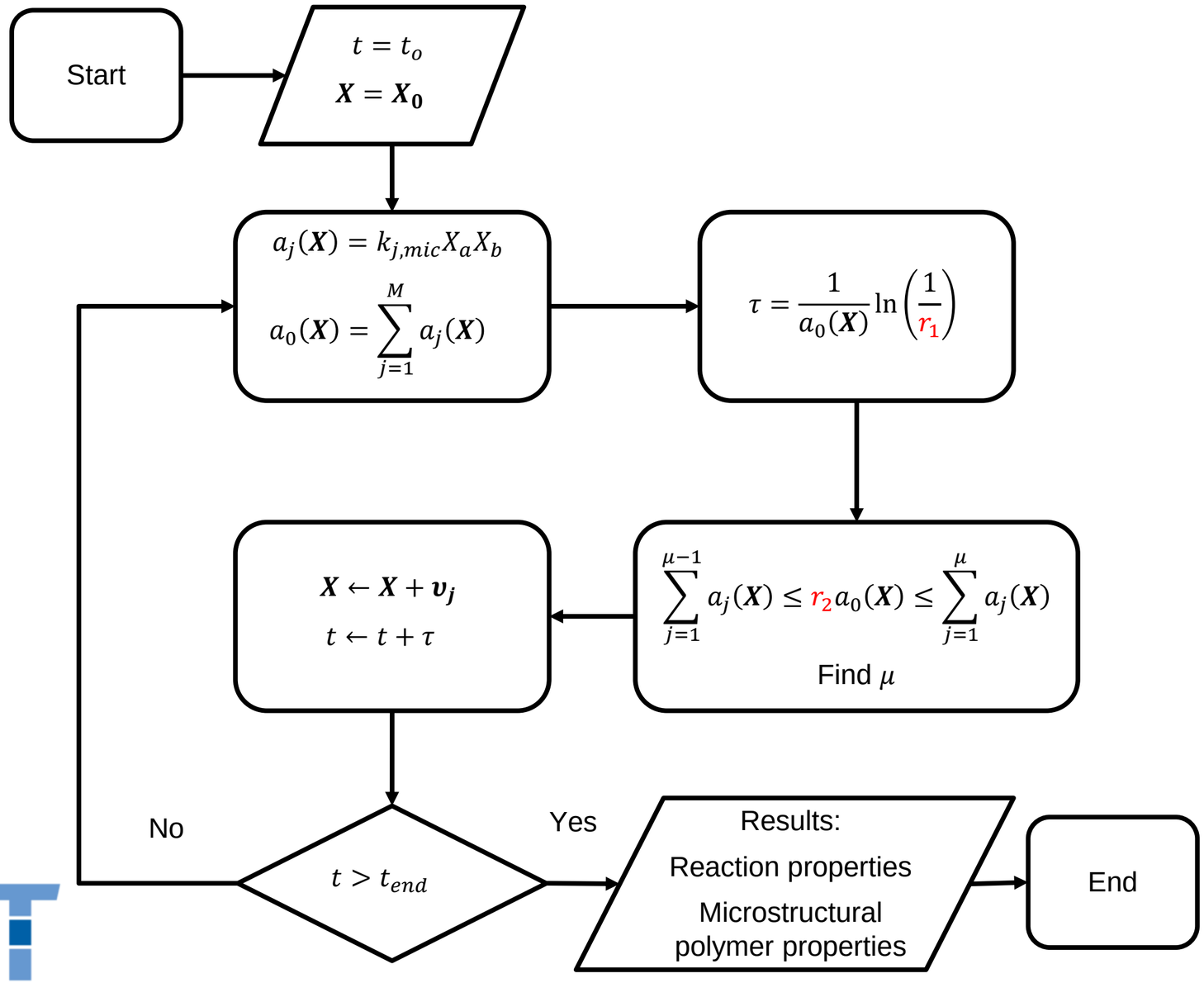
Kinetic Monte Carlo (*k*MC) Algorithm



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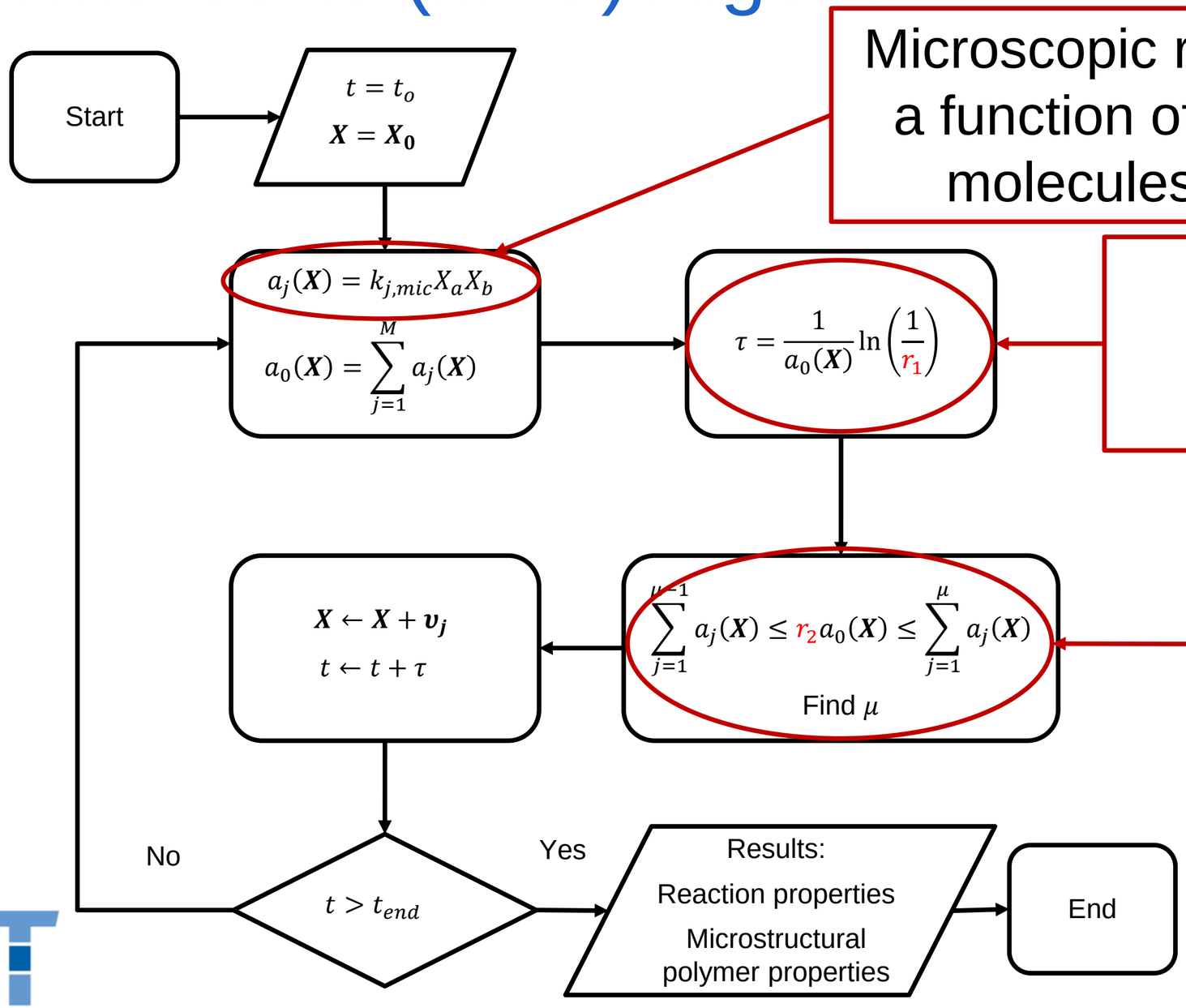
Kinetic Monte Carlo (*k*MC) Algorithm



Microscopic reaction rates as a function of the number of molecules of reactants

When will a reaction take place?

Which reaction will take place?

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Update of the number of molecules

Update of the number of molecules

Non-macromolecular species

$$I \xrightarrow{f, k_d} 2\ R^*_{in}$$

Reactant

$X_I = X_I - 1$

Product

$X_{R^*_{in}} = X_{R^*_{in}} + 2$

$X_{R^*_{in}} = X_{R^*_{in}}$

Efficiency factor f

This increment of +2 will be executed only with a probability *f* every time this reaction event is sampled

Macromolecular species

$$R^*_n + M \xrightarrow{k_p} R^*_{n+1}$$

Reactant

$X_M = X_M - 1$

$X_{R^*_n} = X_{R^*_n} - 1$

Product

$X_{R^*_{n+1}} = X_{R^*_{n+1}} + 1$

$$r_p = k_{p,mac}[M] \sum_{n=1}^{N} [R^*_n]$$

Every update for macromolecular species would require to make a sum of N elements

Usually, N→∞

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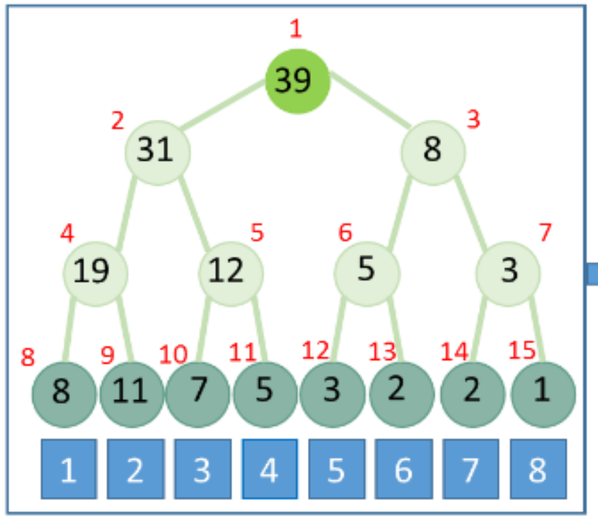
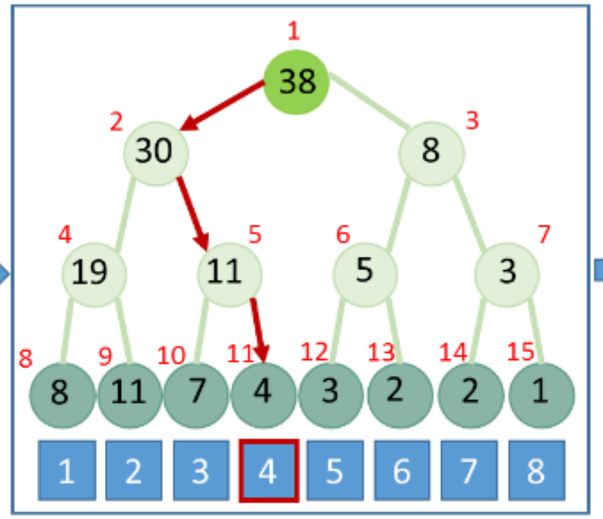
Binary trees

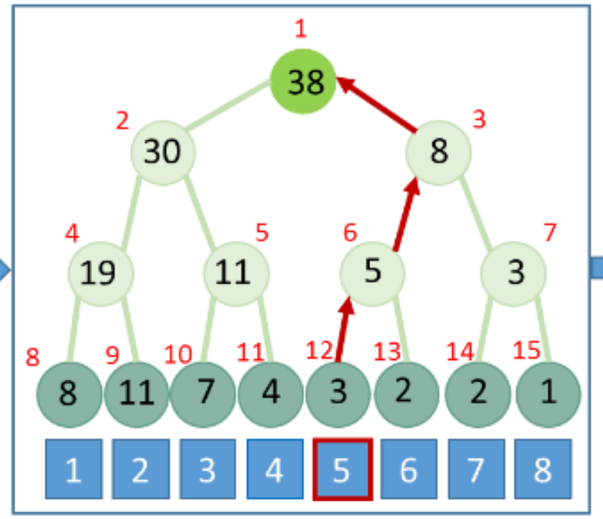
Homopropagation $R_n^* + M \xrightarrow{k_p} R_{n+1}^*$



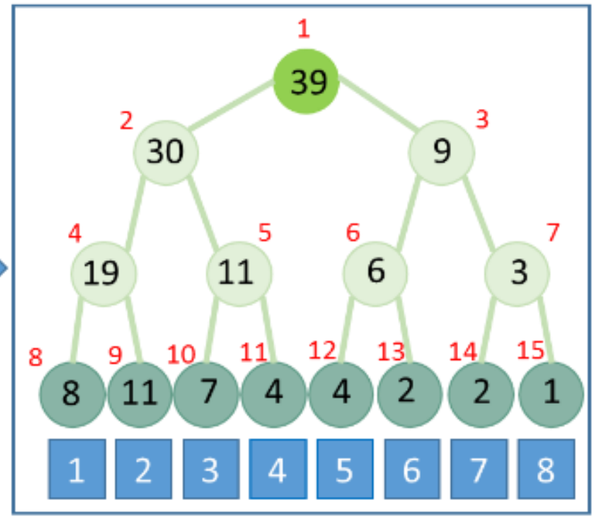
Initial *state* for the chain-length binary tree of macroradicals.



Semi-updated *state* for the chain-length binary tree of macroradicals, considering the consumption of one macromolecule of the randomly selected chain length "*n*" during monomer propagation.



Jump to one chain length forward in the binary tree of macroradicals and selection of the path upwards to the *root node* in order to update the *state* of the binary tree due to the product formation during monomer propagation.



Updated state for the chain-length binary tree of macroradicals, considering the consumption of one macromolecule of the randomly selected chain length "*n*" and formation of one macroradical with chain length "*n+1*" .

Reactant consumption
n=4

Product formation
n=5

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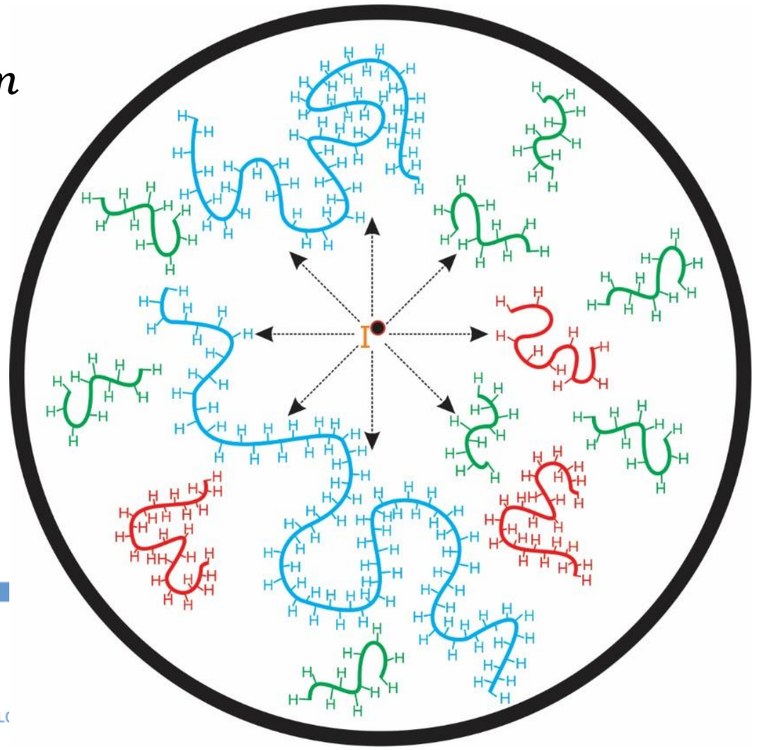
Sampling based on mass fraction

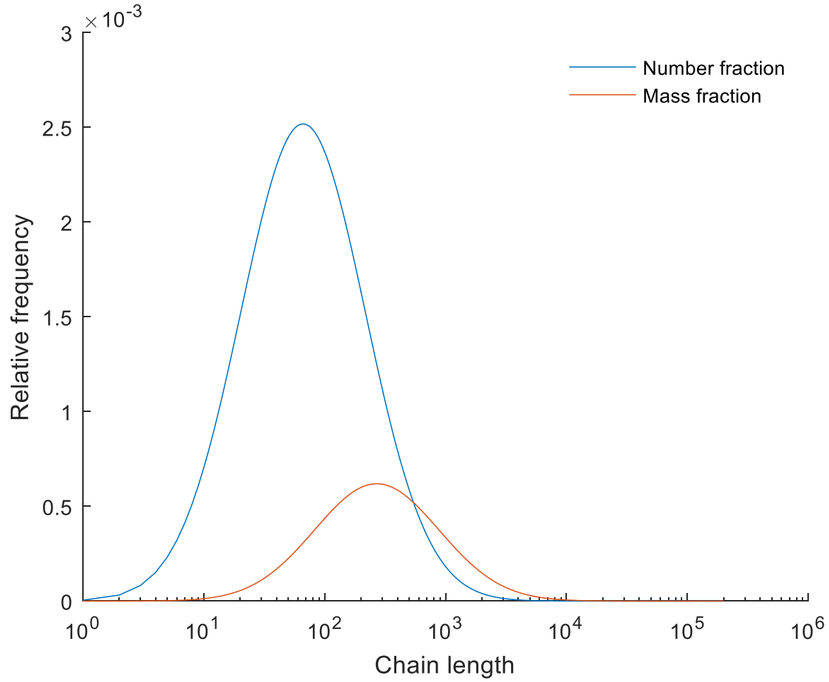
$$R_H = \underbrace{k_H n} C_{P_n} C_{R_{in}^\bullet}$$

Monomer units

Random sampling base on mass fraction

$$m_{P_n} = nC_{P_n}$$





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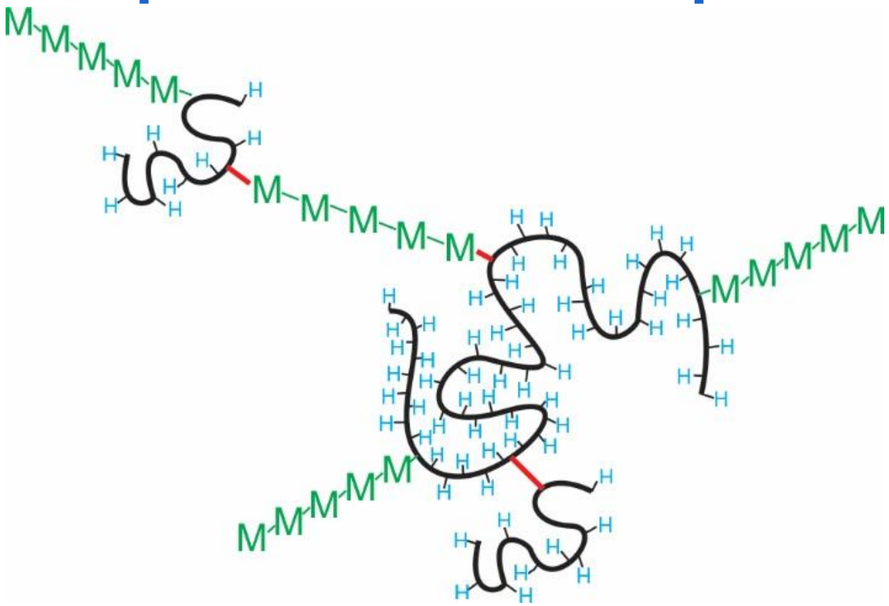
Description of complex architectures



Complex architecture:
Several ***grafted chains*** and several ***crosslinking points*** per macromolecule

It is possible to track average properties of the reactive system, as ***average grafting "from" density***, ***average grafting "to" density,*** ***average crosslinking density***, etc., but the information for the ***distribution*** of this properties is mixed and difficult to track.

It is not possible to calculate the ***chain length*** of ***every graft*** or the ***chain length*** of the **vinyl *segments between crosslinking points***

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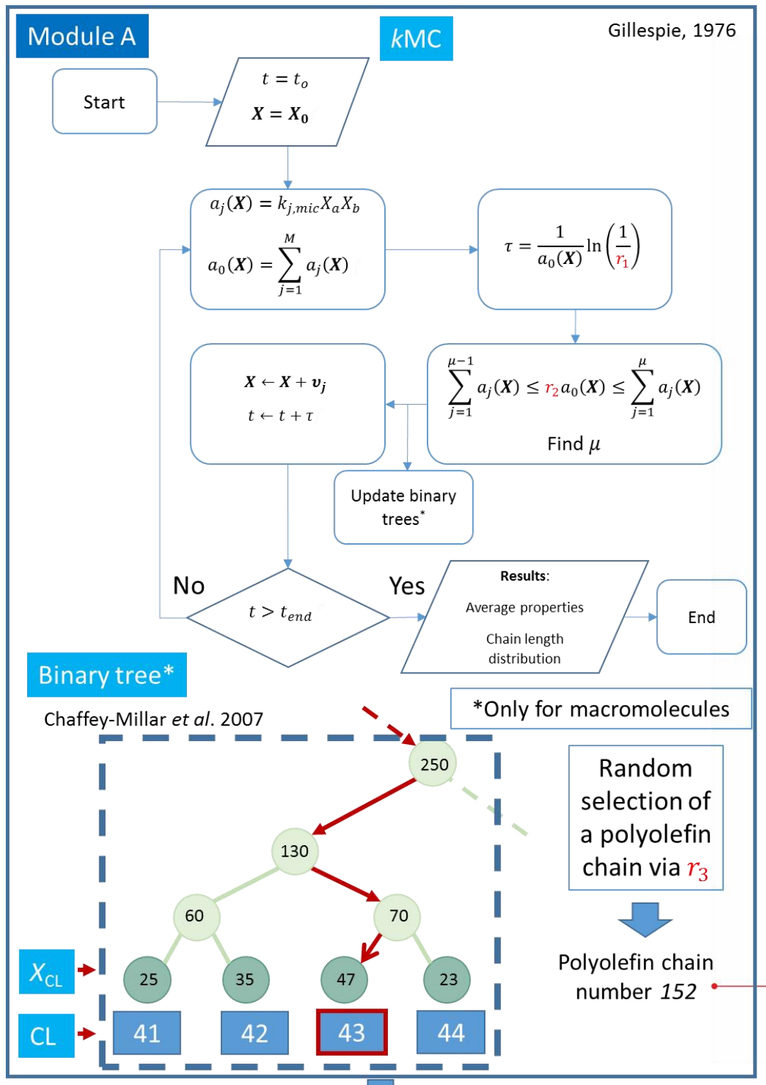
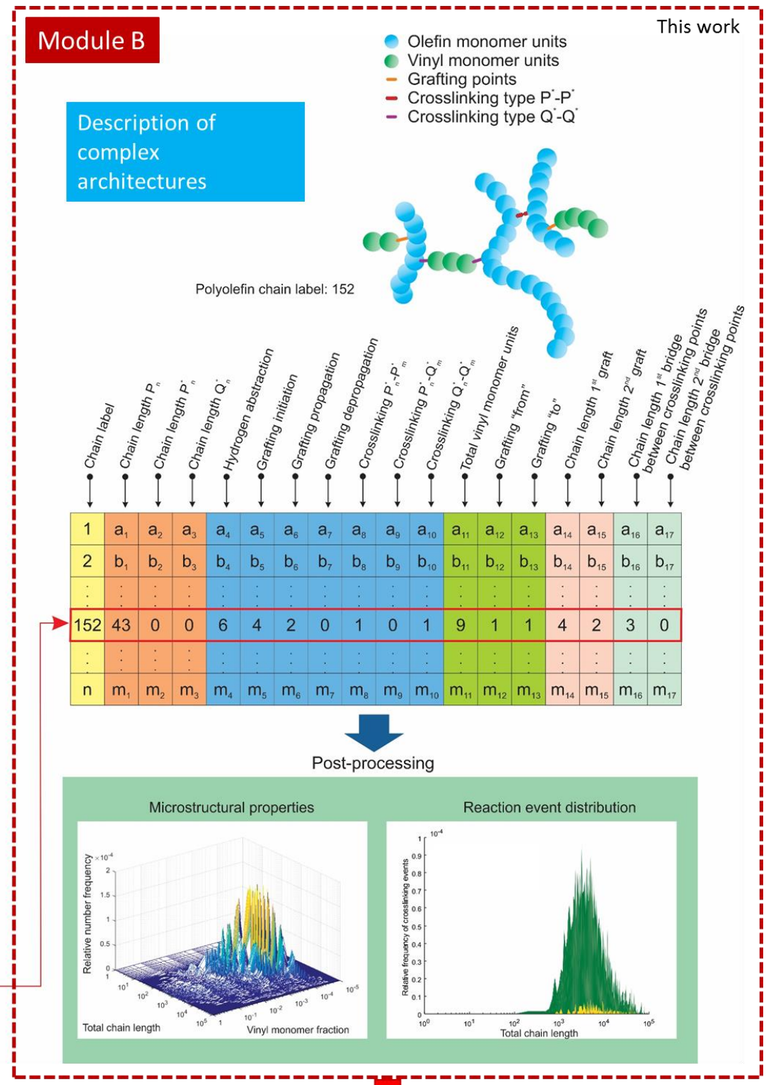
*k*MC simulation: Module A and B





Reaction rate, grafting selectivity and grafting yield
full CLD of the macromolecular species
average grafting "from" density,
average grafting "to" density,
average chain length of grafts, etc. (approximate),
no ***distribution*** of the properties of the grafted chains

Number of grafted chains in each macromolecule of polyolefin
Number of crosslinking points in every macromolecule
Chain length of every graft in every functionalized polyolefin
Chain length of every vinyl segment comprised between crosslinking points
Total CLD of grafted chains

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Arrays in Module B

	Chain length $P_n^{\cdot}$	Chain length $P_n^{\cdot}$	Chain length $Q_n^{\cdot}$	Hydrogen abstraction	Grafting initiation	Grafting propagation	Grafting depropagation	Crosslinking $P_n^{\cdot}$-$P_m^{\cdot}$	Crosslinking $P_n^{\cdot}$-$Q_m^{\cdot}$	Crosslinking $Q_n^{\cdot}$-$Q_m^{\cdot}$	Total vinyl monomer units	Grafting "from"	Grafting "to"	Chain length 1st graft	Chain length 2nd graft	...	Chain length n^{th} graft	Chain length 1st bridge between crosslinking points	Chain length 2nd bridge between crosslinking points	...	Chain length n^{th} bridge between crosslinking points
1	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
2	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
3	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
4	15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
5	15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
6	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
100000	500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
100001	500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
100002	500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
n	m	0	0	0	0	0	0	0	0	0	0	0	0	0	0	...	0	0	0	...	0

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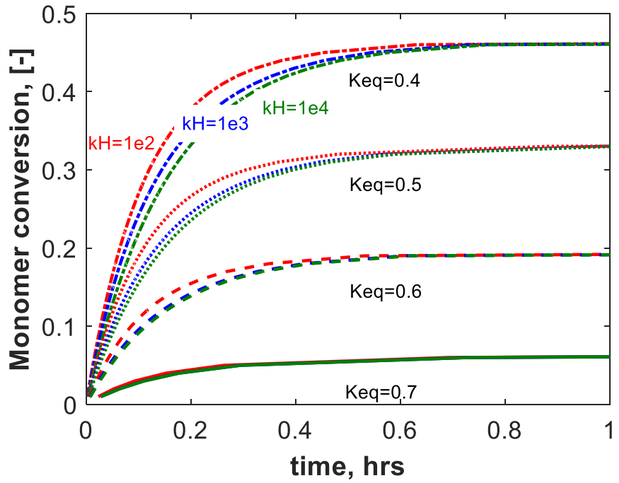
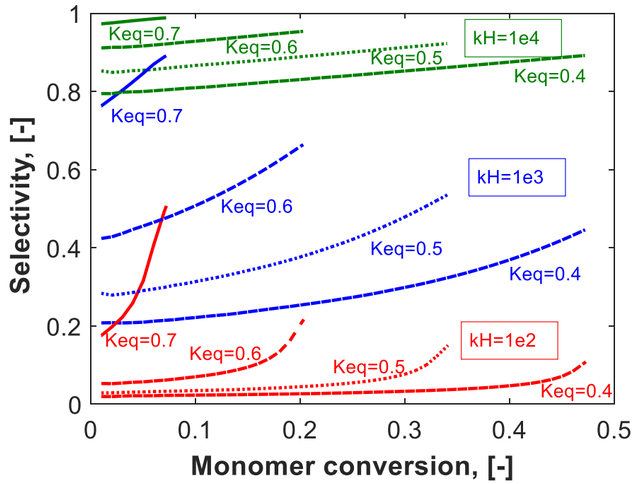
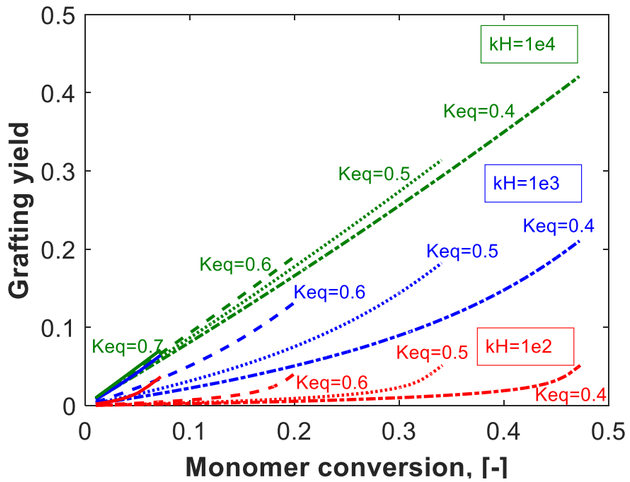
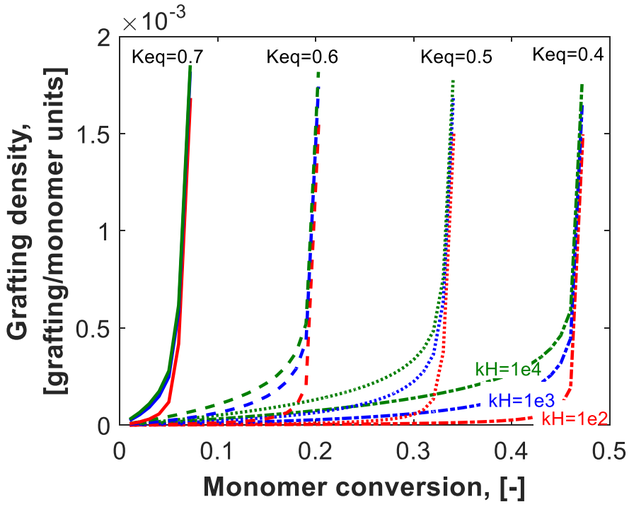
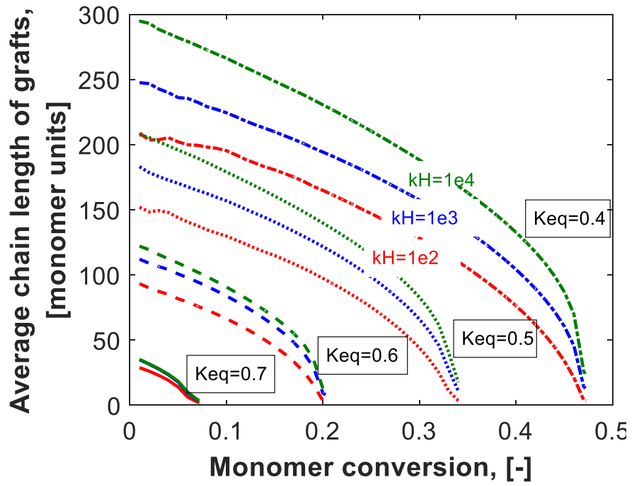
Results obtained with Module A

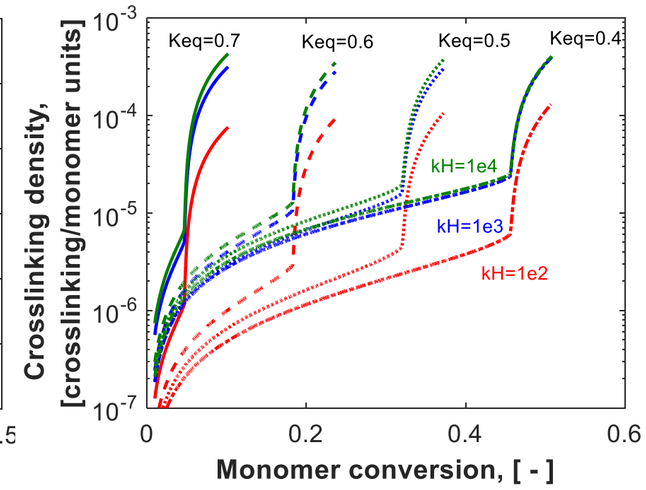












k_H (dm³·mol⁻¹·s⁻¹)

K_{eq} (mol·dm⁻³)

$$k_p^{eff} = k_p\left(1 - \frac{K_{eq}}{[M]}\right)$$

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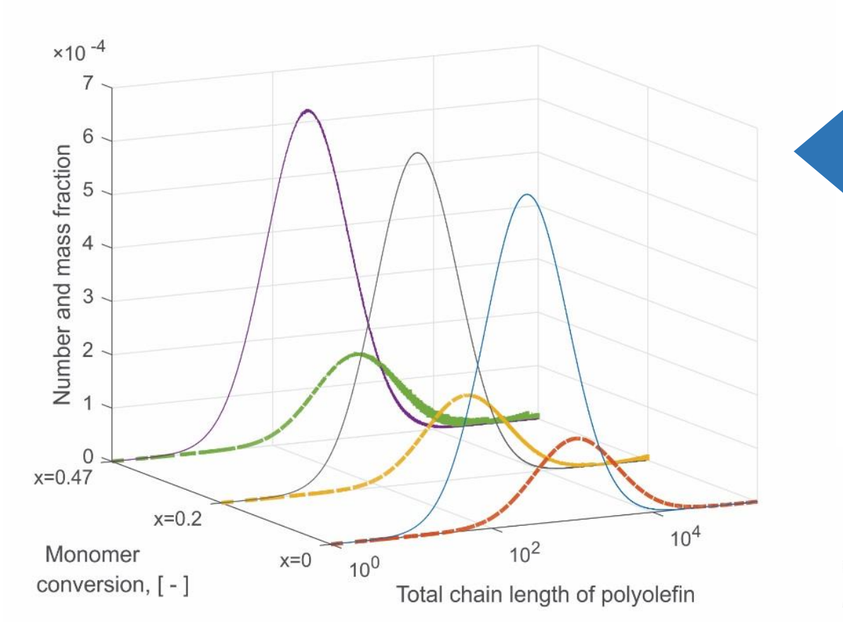
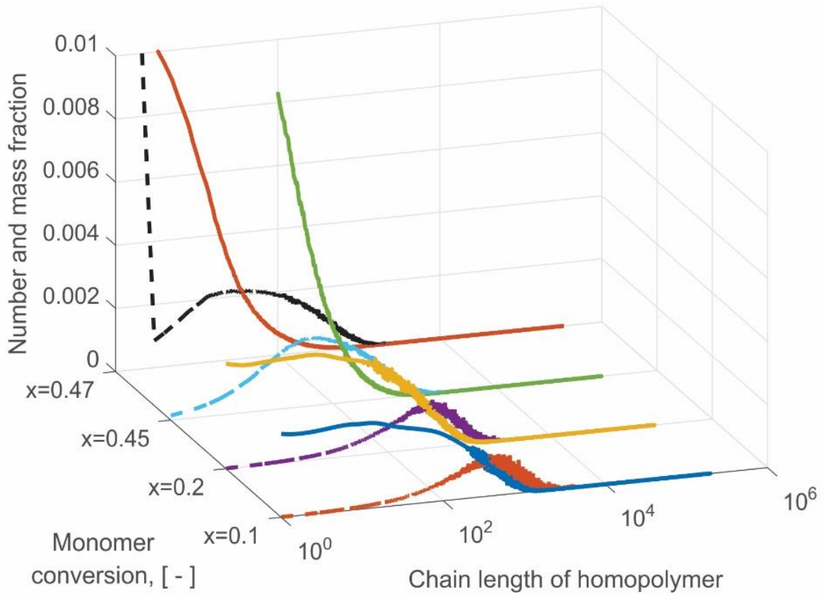
Results obtained with Module A



CLD of polyolefin

CLD of homopolymer



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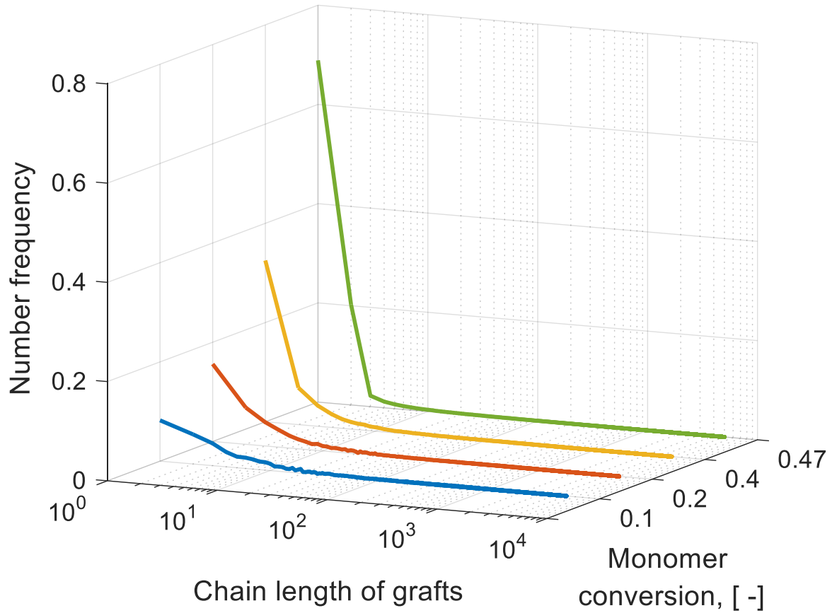
Results obtained with Module B



CLD of grafts

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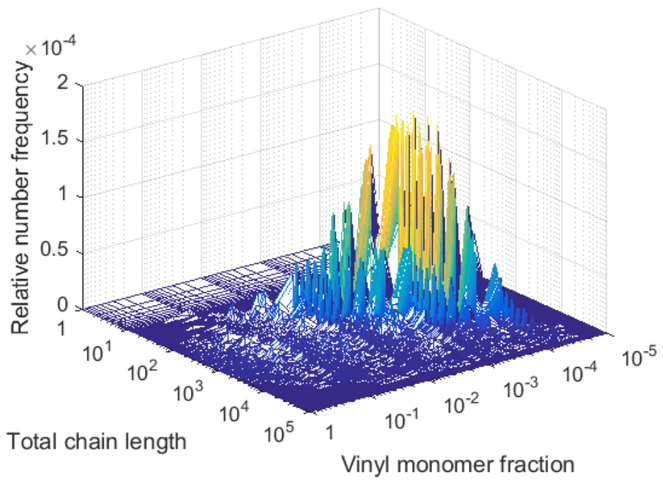
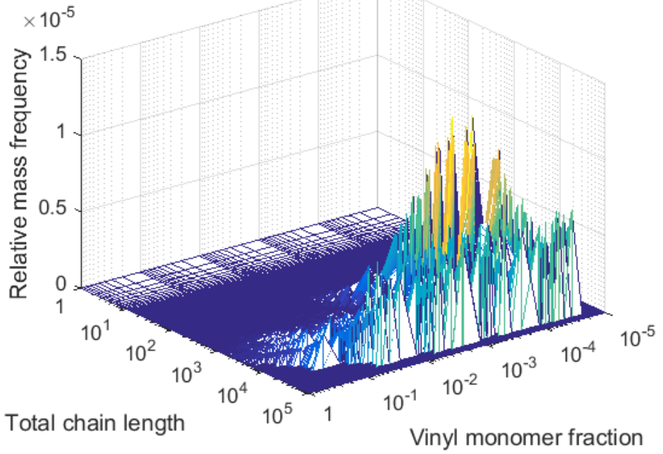
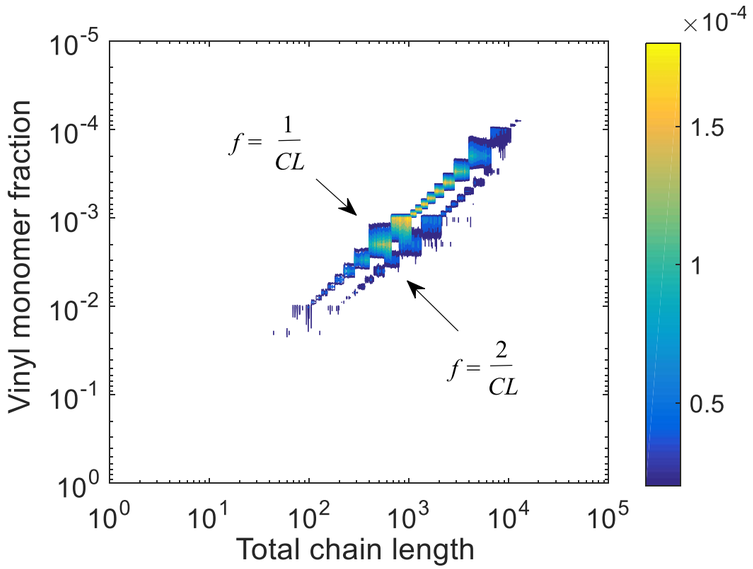
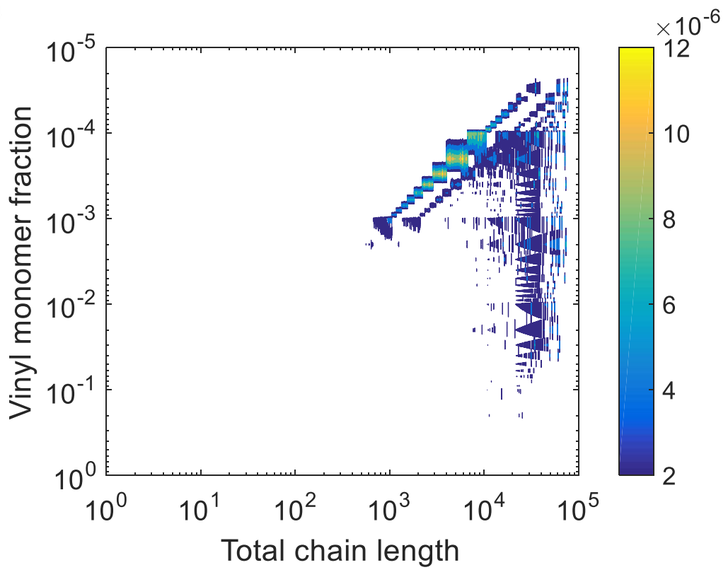
Results obtained with Module B

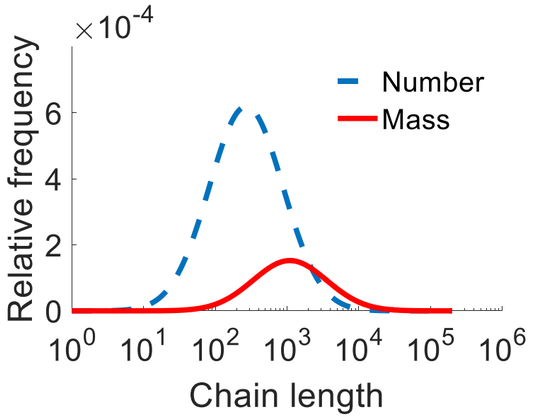
Bivariate distribution: Copolymer composition-CLD











Initial CLD of polyolefin

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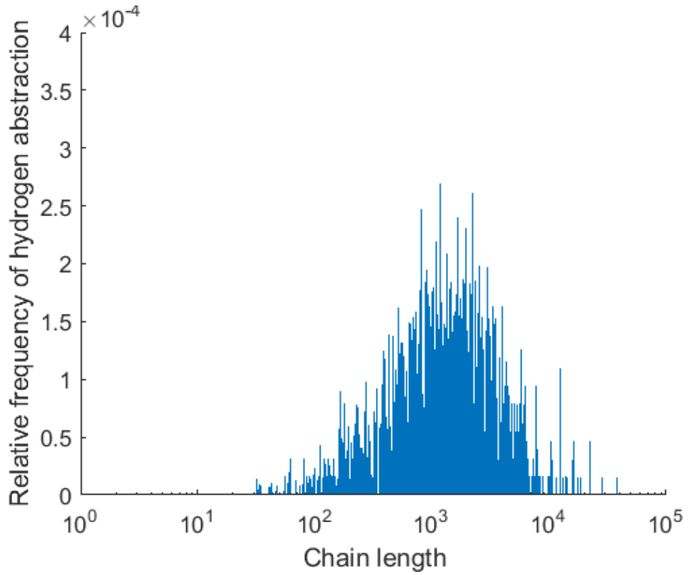
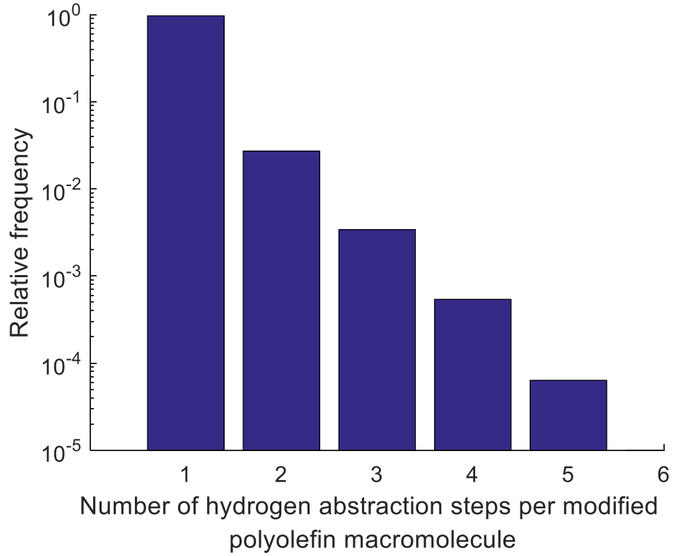
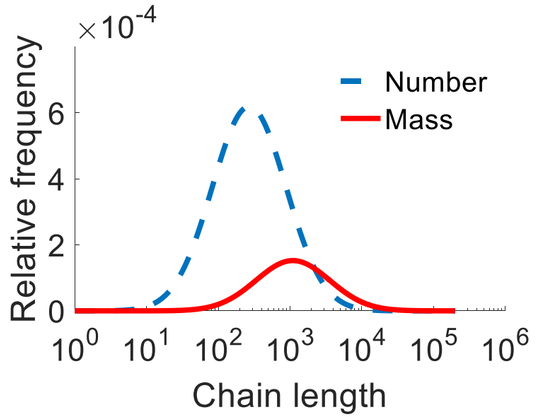
Results obtained with Module B

Reaction event distribution

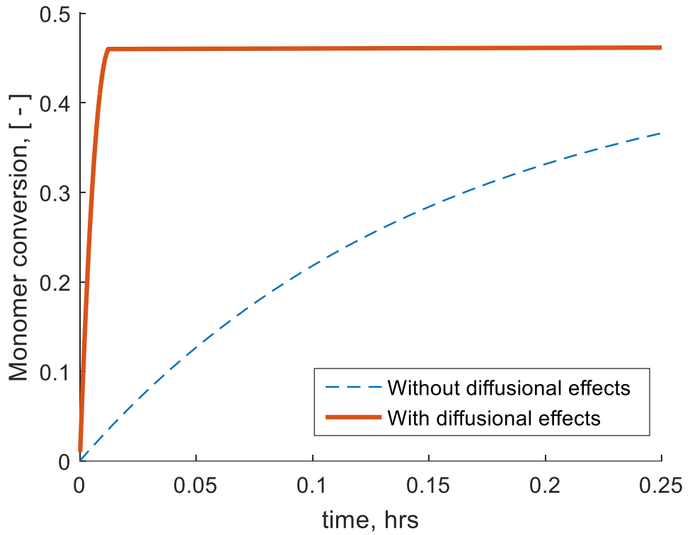


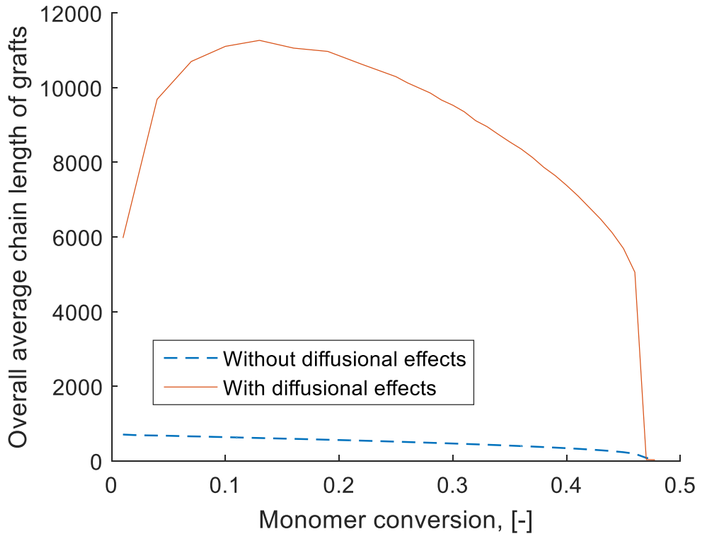


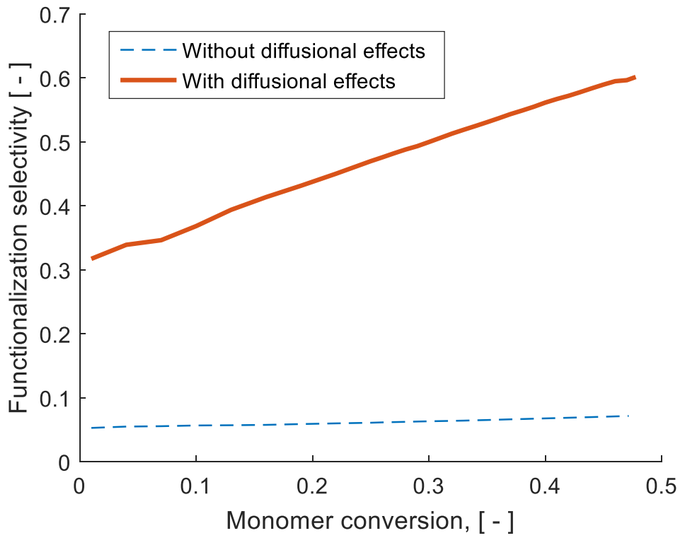


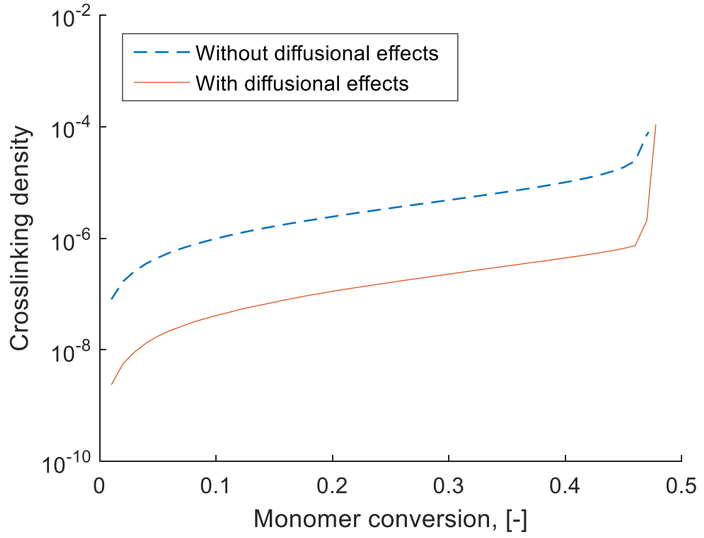
Initial CLD of polyolefin

Diffusional effects









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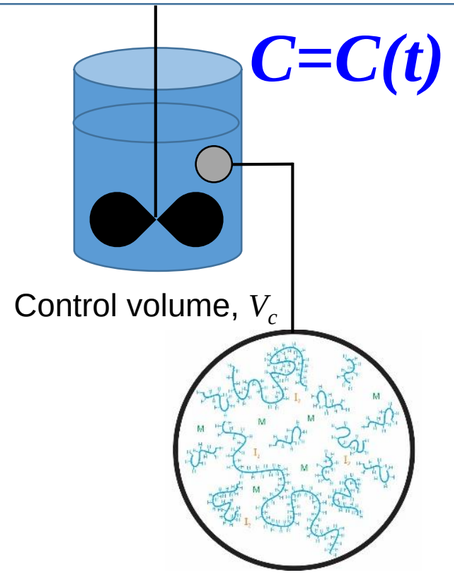
Extended model



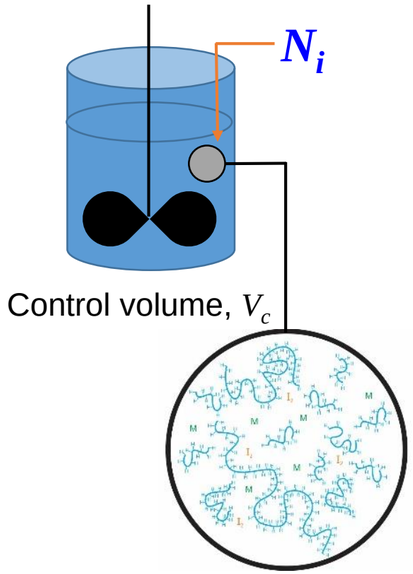
Assumptions:

- Batch reaction
- Homogeneous phase
- Isothermal conditions

$$\frac{dC_i}{dt} = R_{c_i}$$

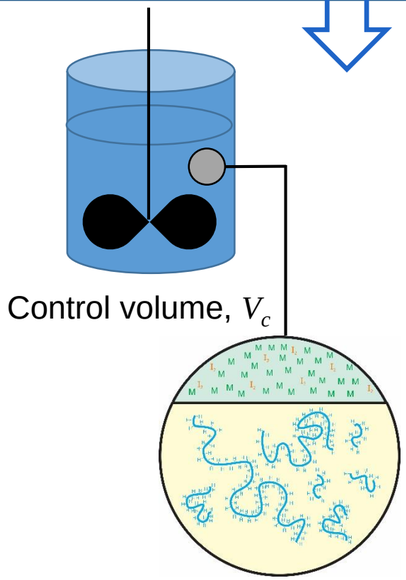
Present study focused on the **kinetics**.

Extended model currently accounts for **phase segregation** and **multiple injections**.



Semibatch process

$$\frac{dC_i}{dt} = R_{c_i} + R_a$$



Phase segregation

(accounting for mass transfer)

$$\frac{dC_i}{dt} = R_{c_i} + R_a$$

$$J_i = k_i^T \left[{c_i}^I \cdot k_{part\ i} - {c_i}^{II} \right]$$

$$k_{part\ i} = \frac{{c_i}^{II}{}_{eq}}{{c_i}^{I}{}_{eq}} \qquad k_i^T = A_{int} \cdot k_i^{ov}$$

Concluding remarks

- Comprehensive model for the description of microstructural properties of individual chains with complex topology was developed.
- A mass-weighted CLD needs to be considered to properly account for the chain length dependence of the hydrogen abstraction reactivity.
- Diffusional limitations need to be accounted for to accurately represent the grafting kinetics.

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Acknowledgments

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

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