UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

A tracking of the complete microstructural evolution of individual polymer chains during polymer modification reactions

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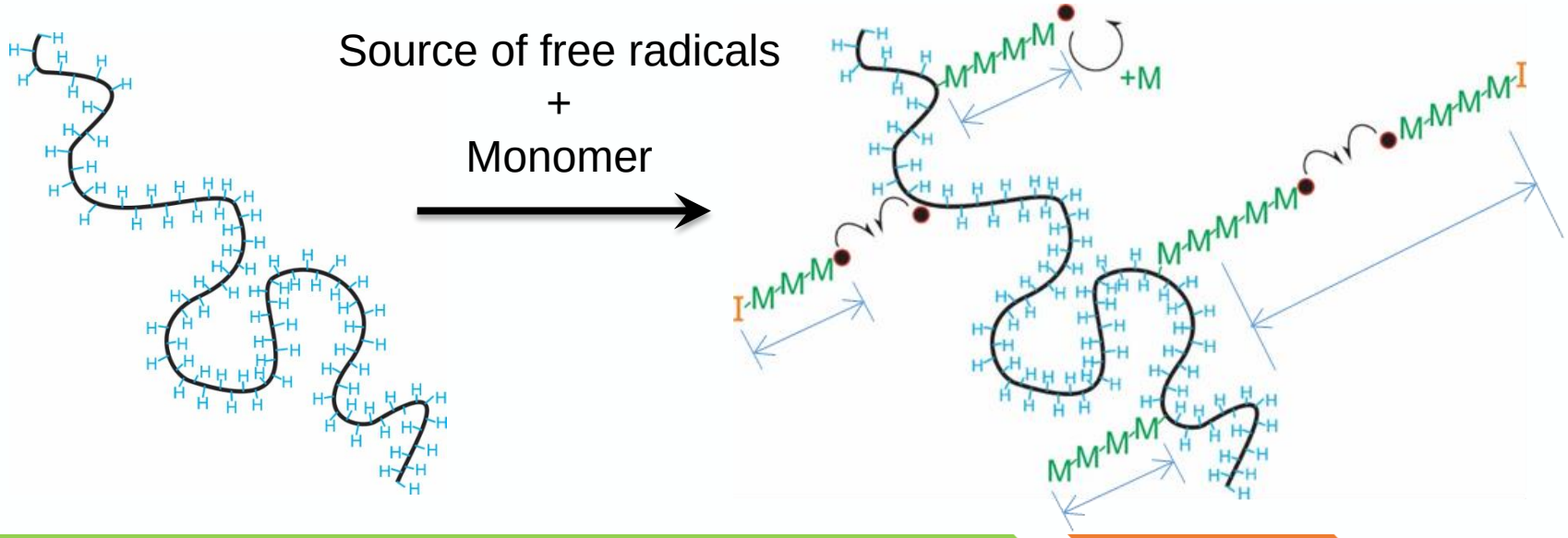
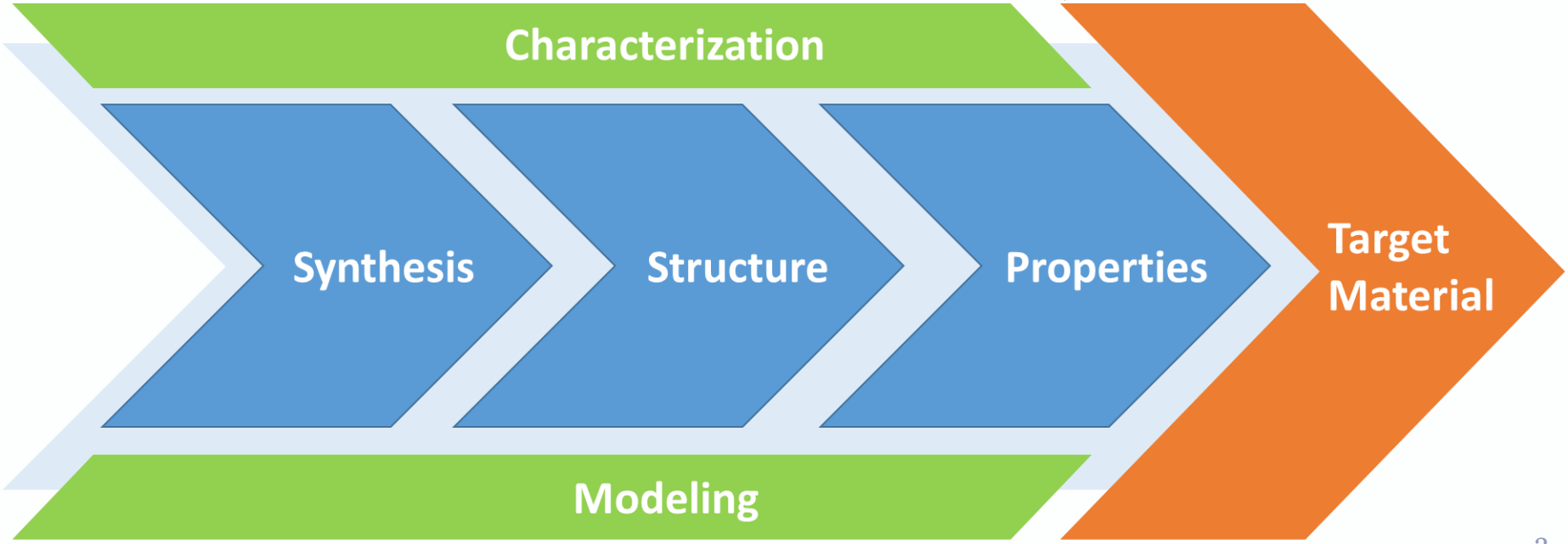
Outline

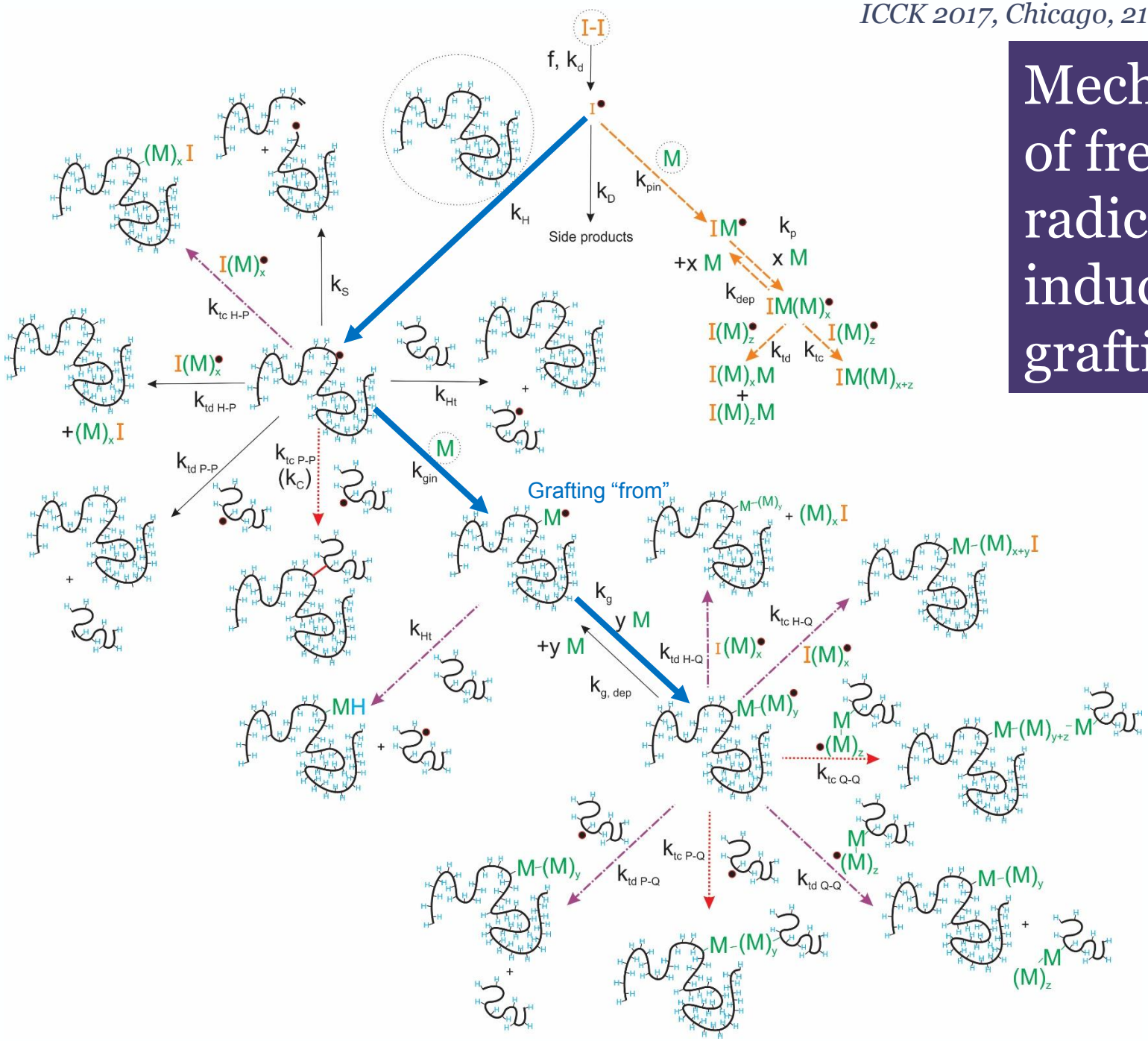
- Functional polymers
- Modeling by *k*MC
- Model development: Module A and Module B
- Results (Module A and Module B)
- Effect of diffusional limitations
- Conclusions

Functional polymers





Mechanism of free-radical induced grafting



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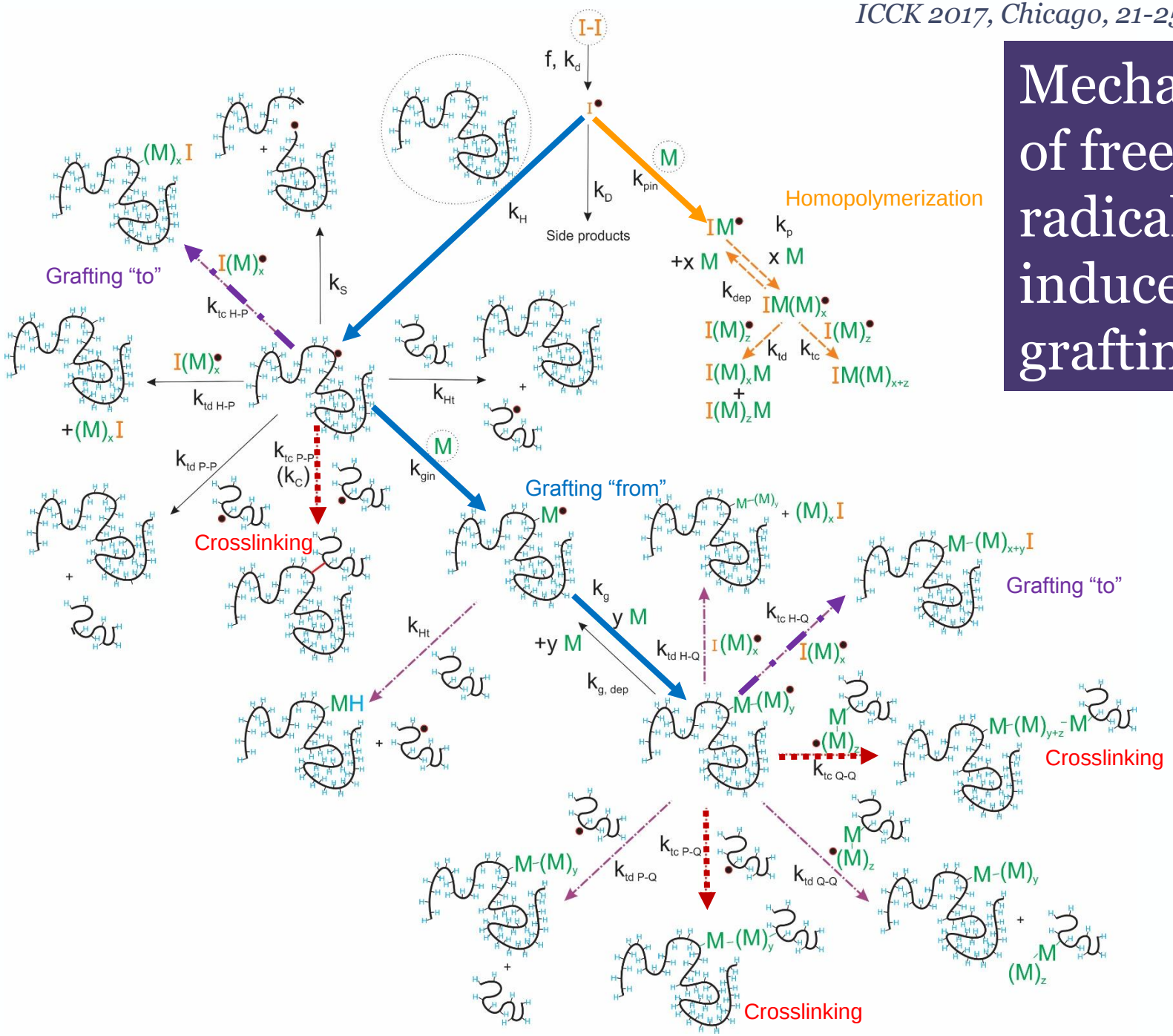
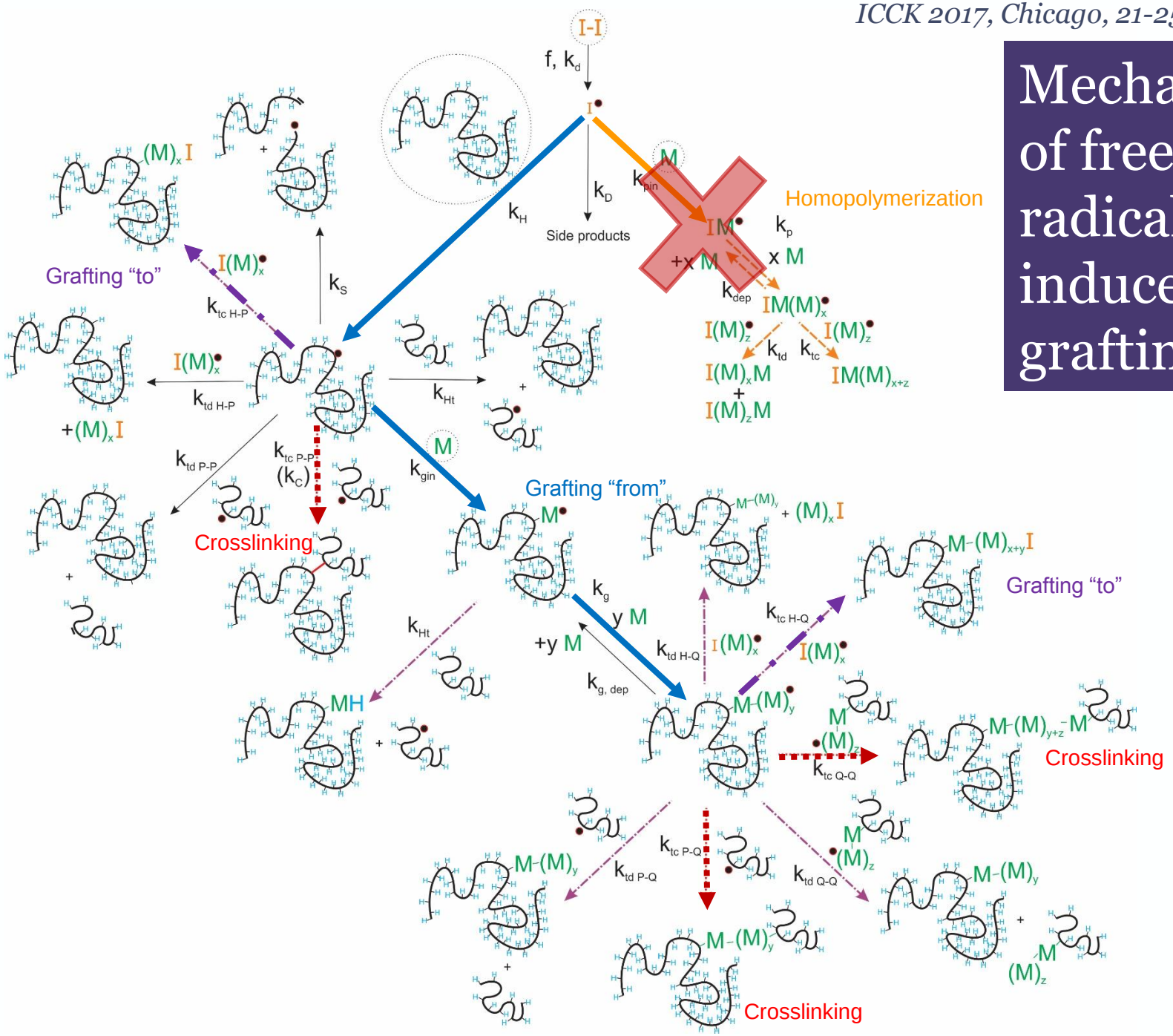


Mechanism of free-radical induced grafting

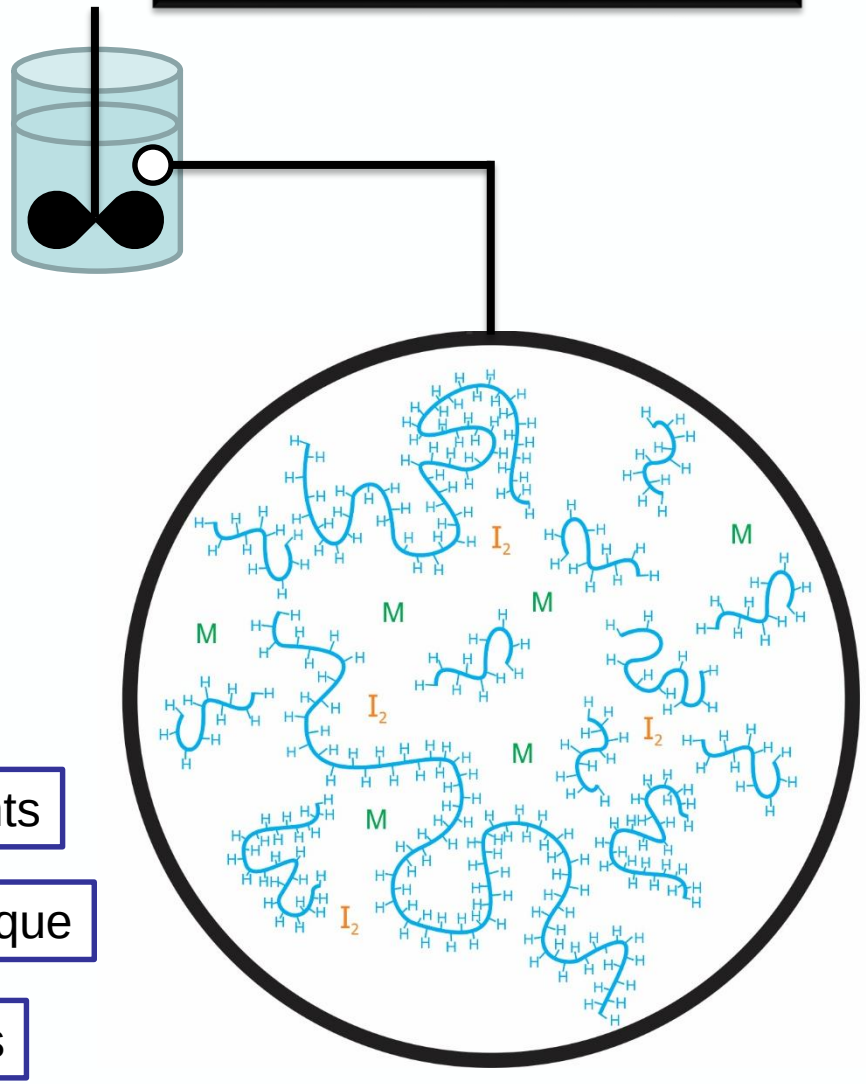


Kinetic Monte Carlo in PRE

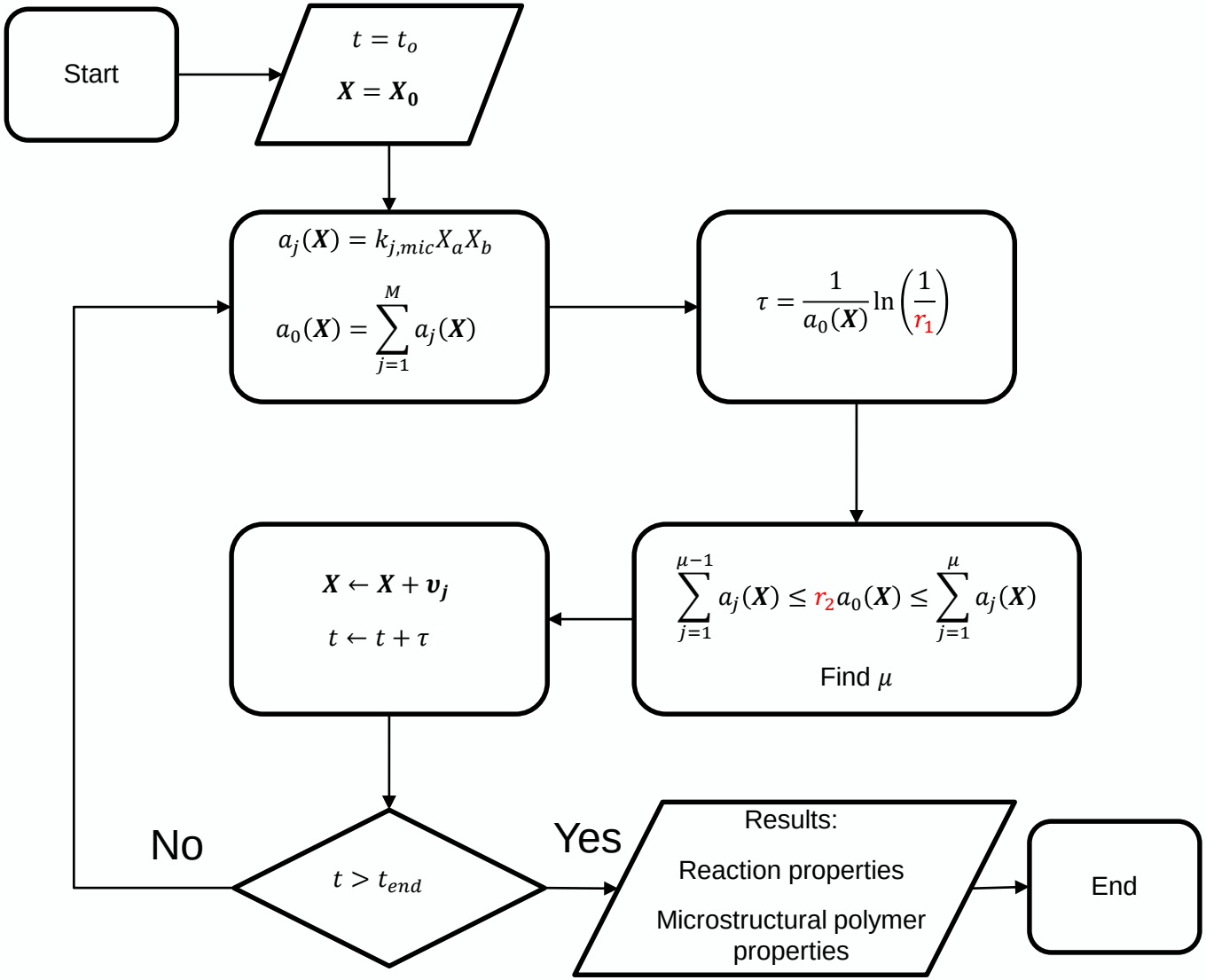
Modeling in PRE

- Analytical solution
- Complete numerical solution
- Stochastic methods
  - Kinetic Monte Carlo
  - Monte Carlo random sampling
- Deterministic methods
  - Method of moments
  - Fixed pivot technique
  - Galerkin methods

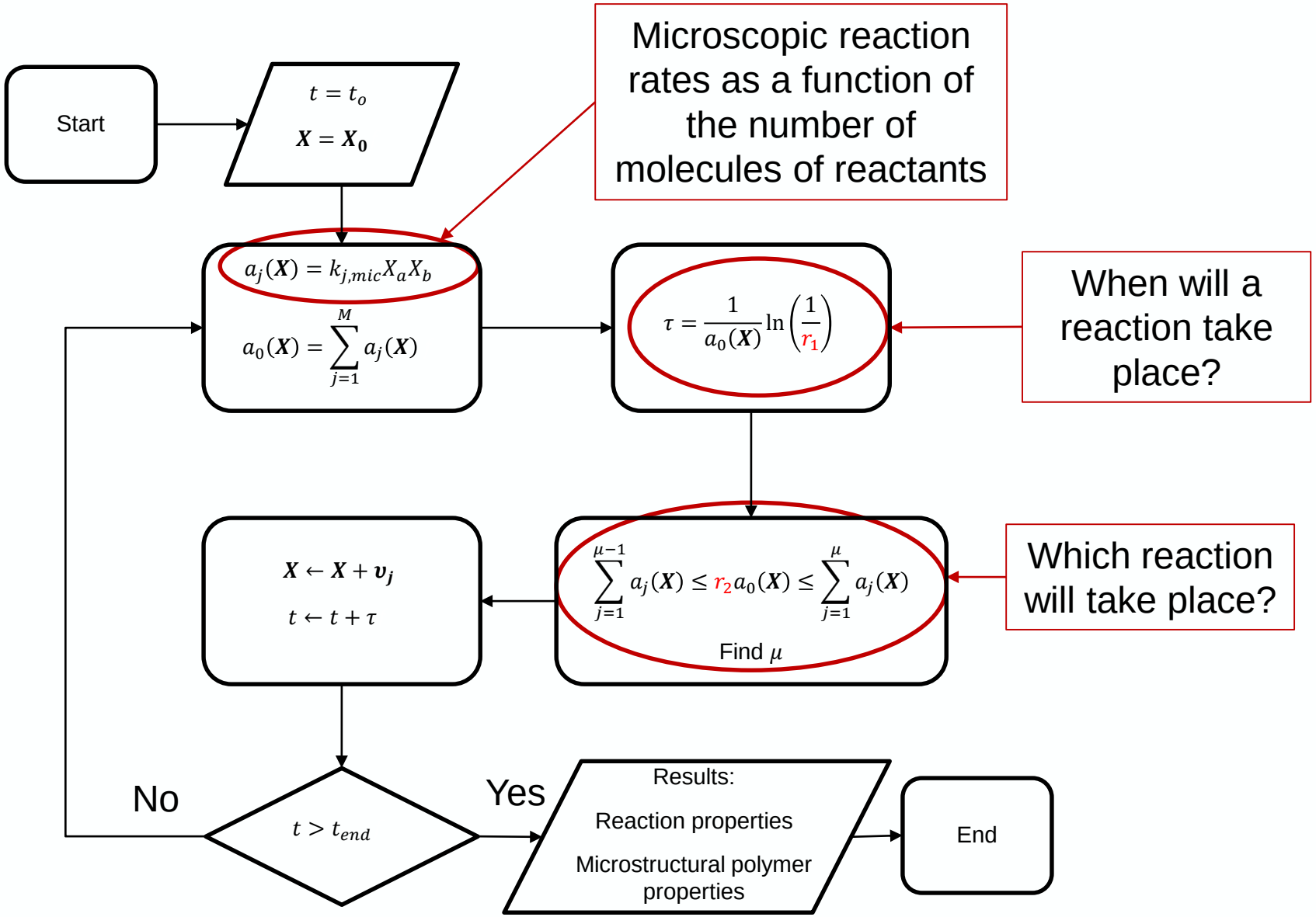
Kinetic Monte Carlo (*k*MC)



Kinetic Monte Carlo (*k*MC) Algorithm



Kinetic Monte Carlo (*k*MC) Algorithm



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

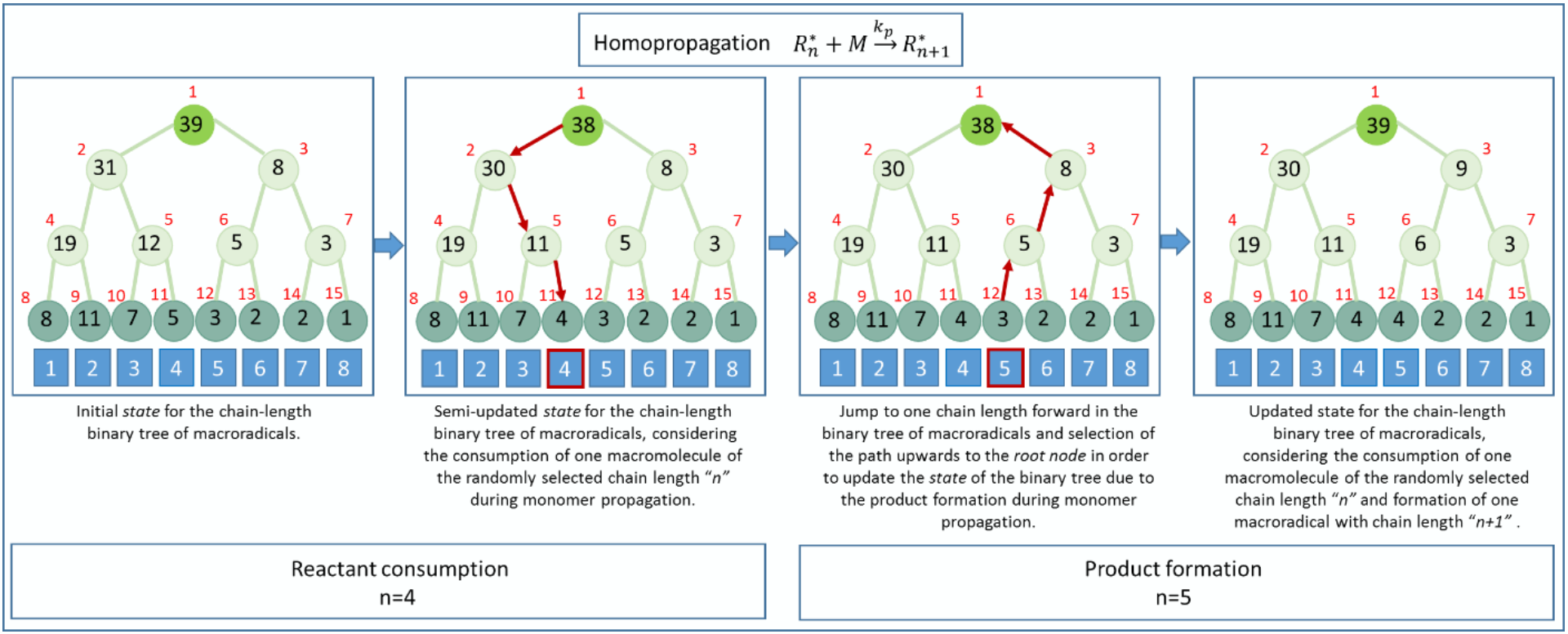
$X_{R^*_{n+1}} = X_{R^*_{n+1}} + 1$

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

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

Usually, $N \to \infty$

Binary trees



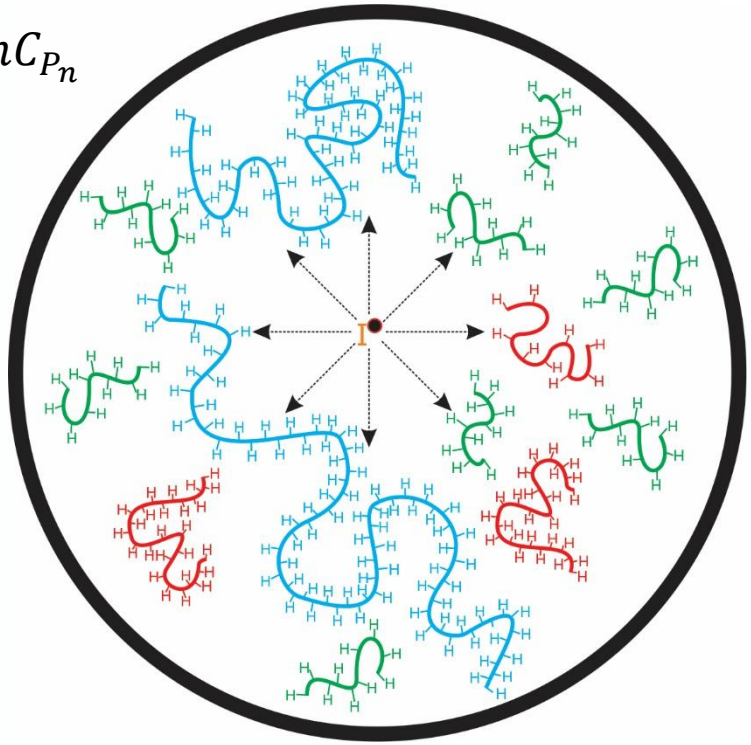
Sampling based on mass fraction

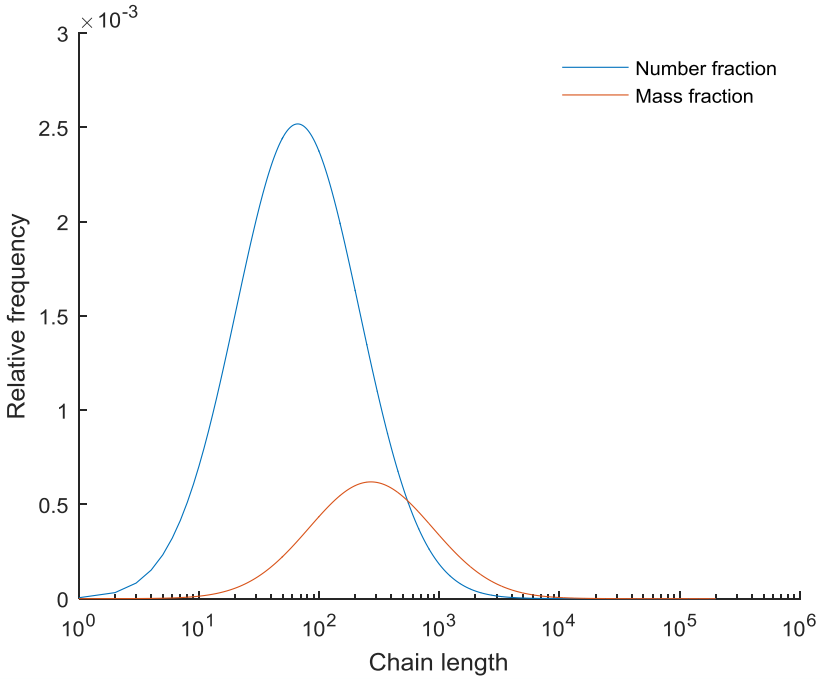
$$R_H = k_H \underbrace{nC_{P_n}} C_{R_{in}}\bullet$$

Monomer units

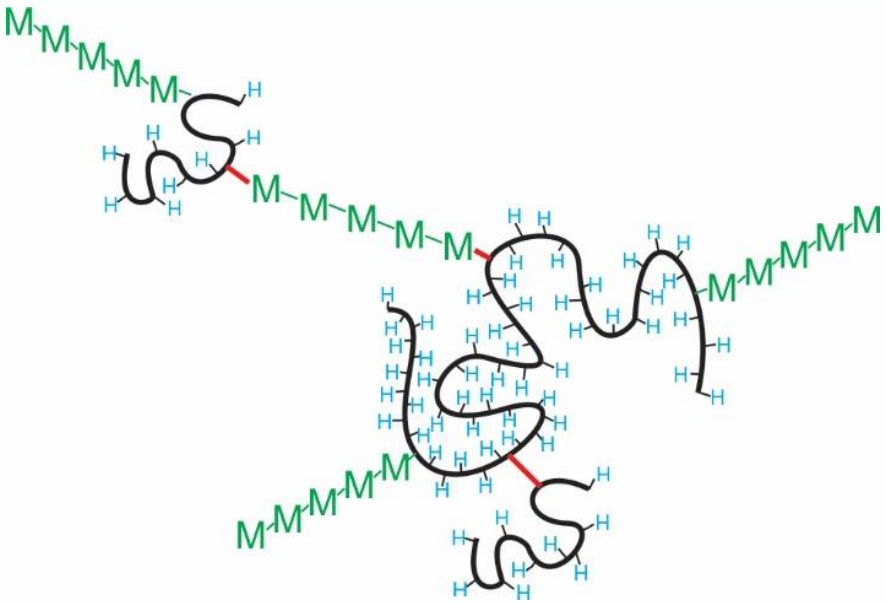
Random sampling base on mass fraction

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





Description of complex architectures

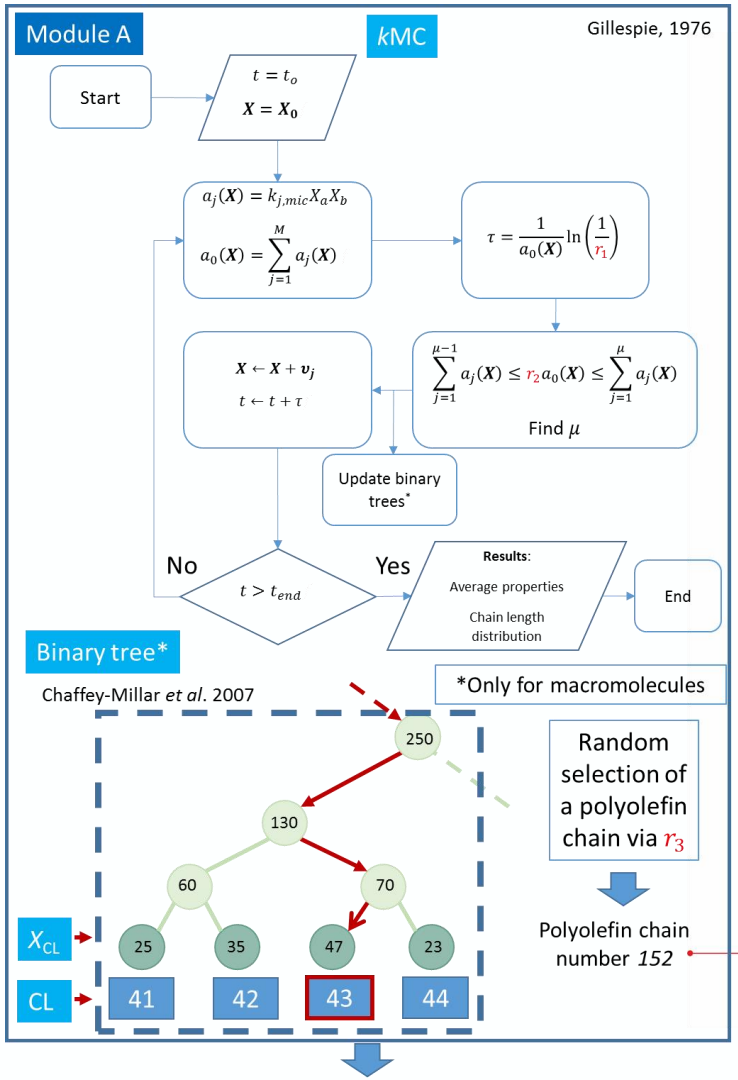


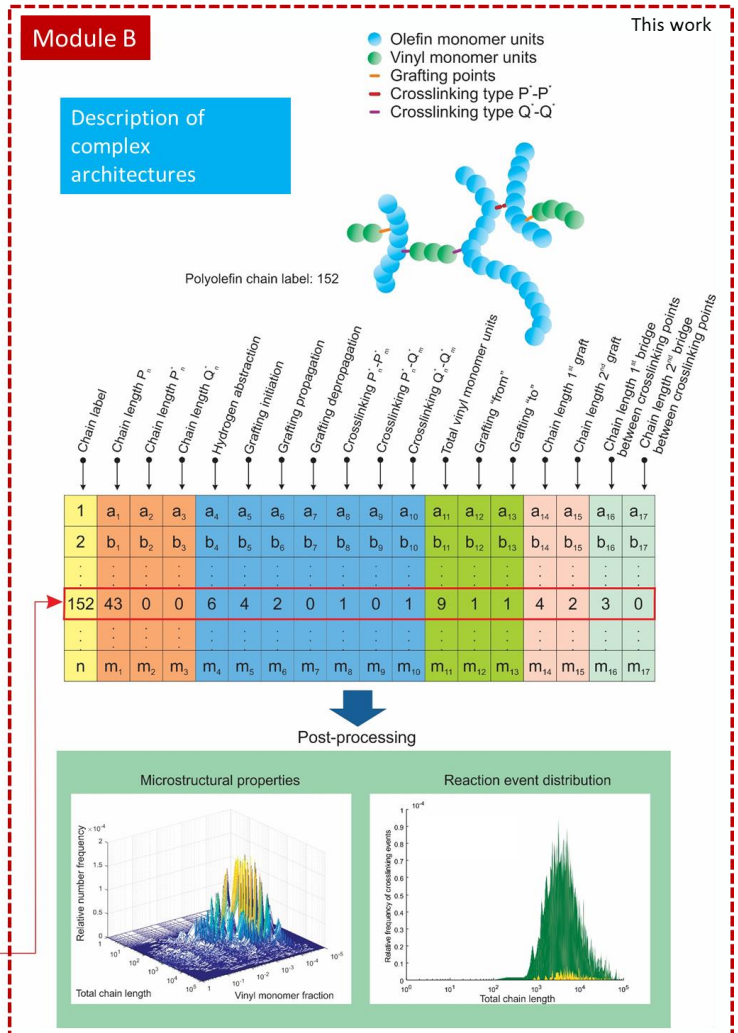
Complex architecture:
Several ***grafted chains*** and several ***crosslinking points*** per macromolecule

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***

*k*MC simulation: Module A and B

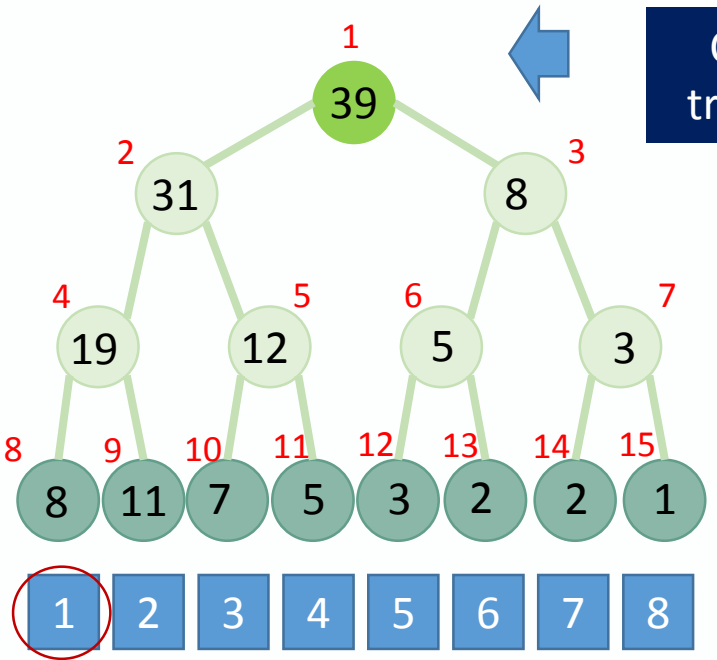




Reaction rate, grafting selectivity and grafting yield
full CLD of the macromolecular species
average grafting "from" density,
average grafting "to" density,
average chain length of grafts, etc. (approximate),
no ***distribution*** of the properties of the grafted chains

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

Link between binary trees and arrays



Chain-length binary tree for macroradicals

Array containing 8 macroradicals of ***chain length*** equal to 1, according to the information of the ***leaf node*** 8

Every ***leaf node*** provides the information of the ***chain length*** and the ***number of macromolecules*** with that specific chain length

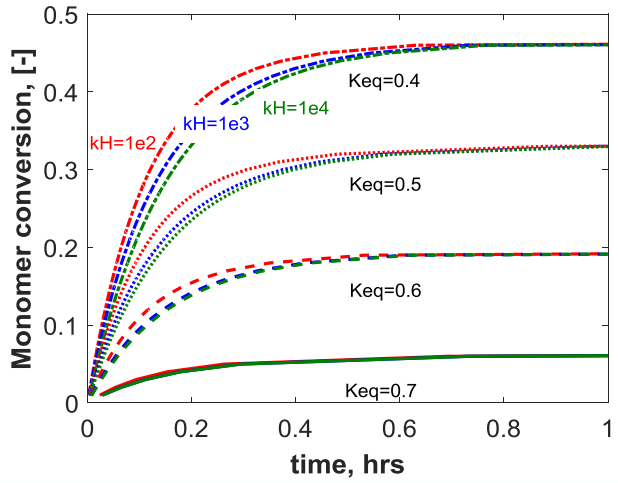
Chain-length array for macroradicals

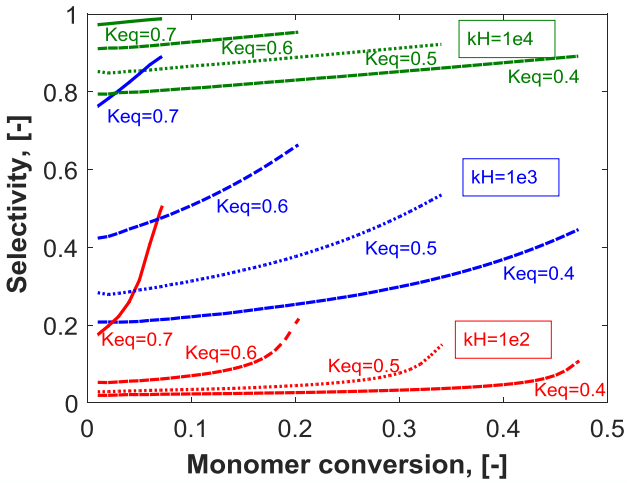
i	*CL_R*(i)*
1	1
2	1
3	1
4	1
5	1
6	1
7	1
8	1
9	2
10	2
11	2
12	2
13	2
14	2
15	2
16	2
17	2
18	2
19	2
.	.
.	.
.	.
39	8

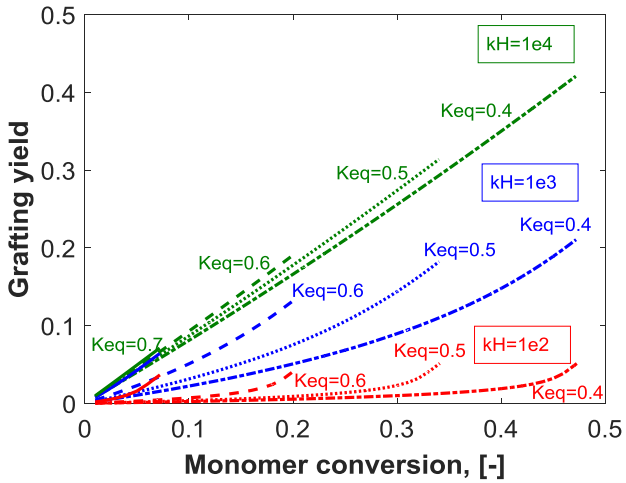
Arrays in Module B

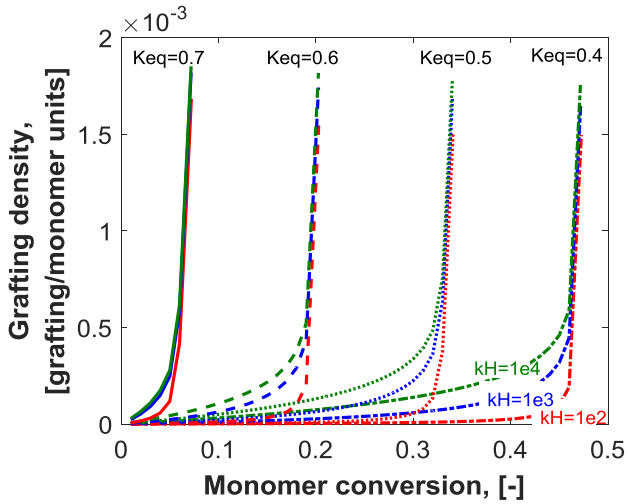
	Chain length P_n	Chain length $P^{\cdot}_n$	Chain length $Q^{\cdot}_n$	Hydrogen abstraction	Grafting initiation	Grafting propagation	Grafting depropagation	Crosslinking $P^{\cdot}_n$-$P^{\cdot}_m$	Crosslinking $P^{\cdot}_n$-$Q^{\cdot}_m$	Crosslinking $Q^{\cdot}_n$-$Q^{\cdot}_m$	Total vinyl monomer units	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

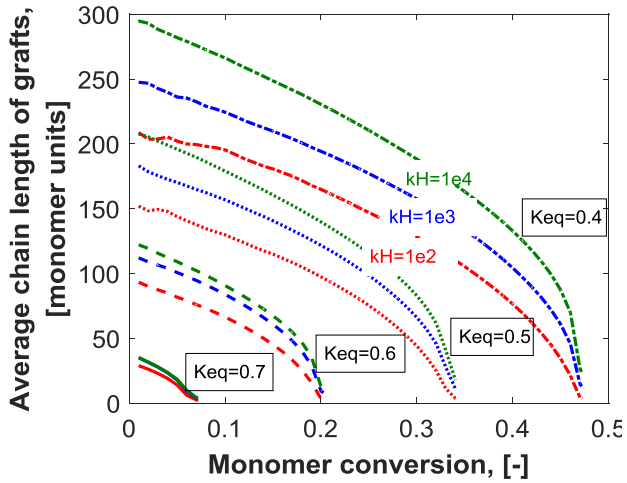
Results obtained with Module A

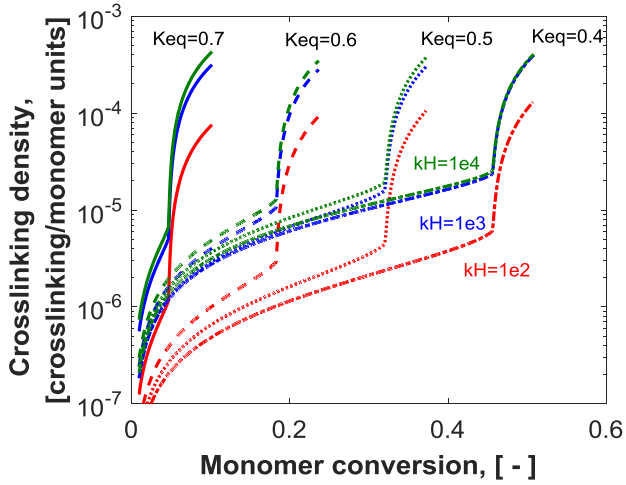








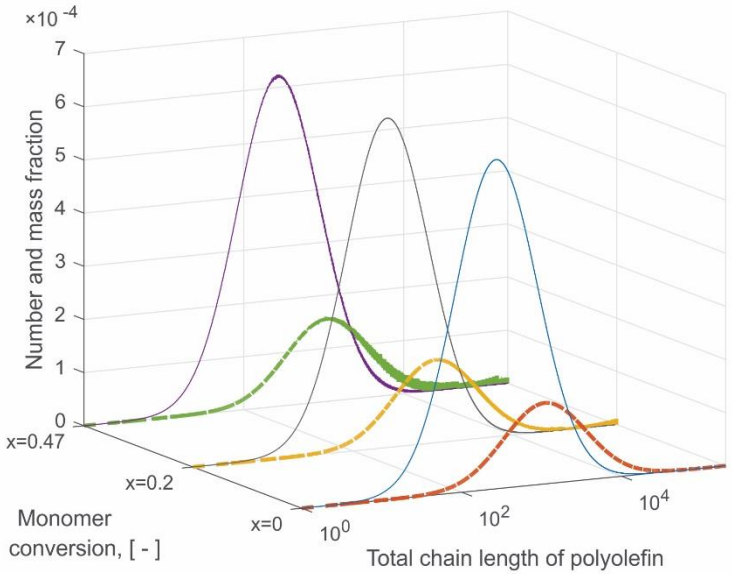




k_H (dm^3·mol^{-1}·s^{-1})
K_{eq} (mol·dm^{-3})

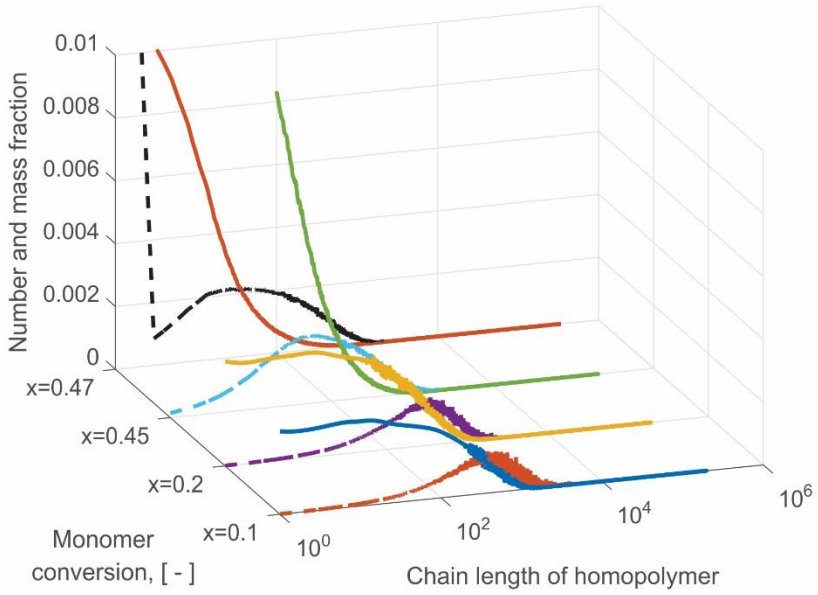
$$k_p^{eff} = k_p\left(1 - \frac{K_{eq}}{[M]}\right)$$

Results obtained with Module A



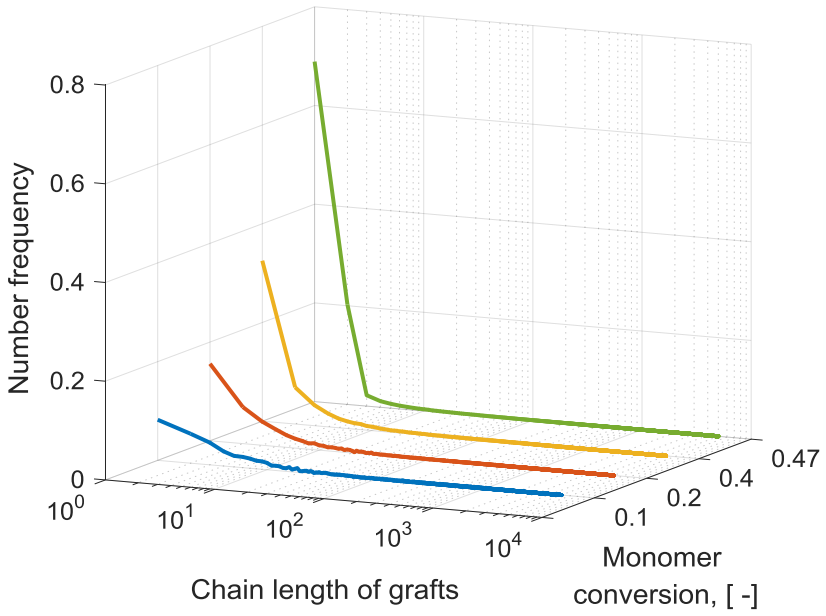
CLD of polyolefin

CLD of homopolymer



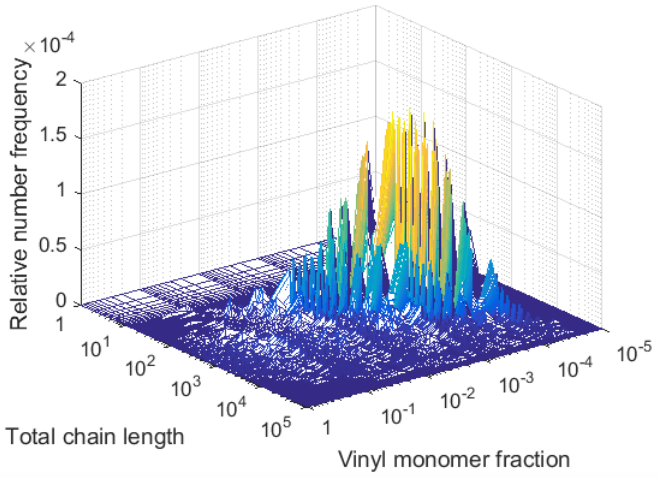
Results obtained with Module B

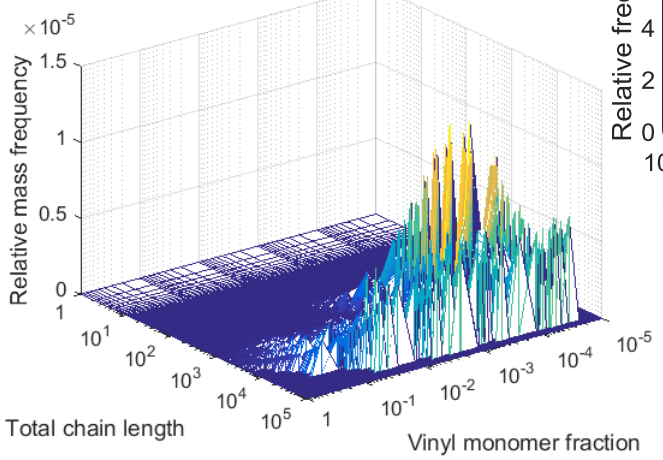
CLD of grafts

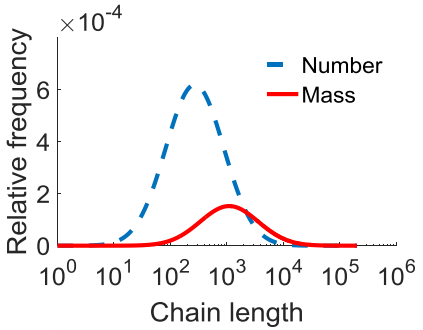


Results obtained with Module B

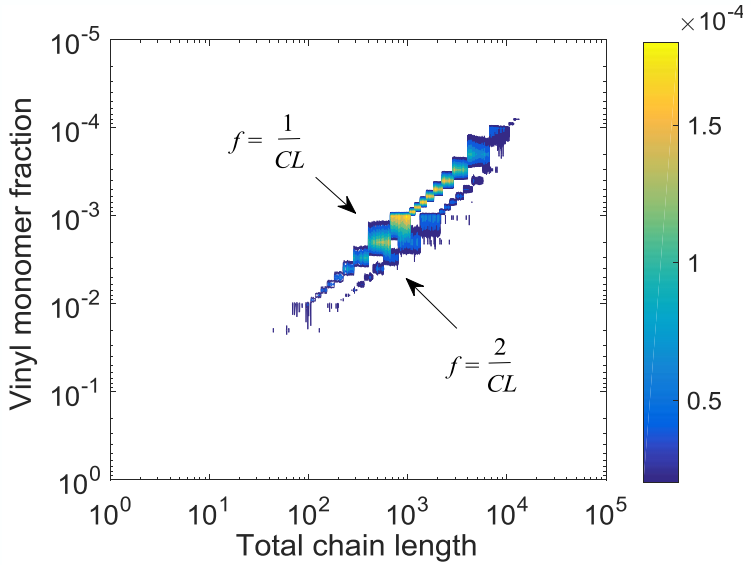
Bivariate distribution: Copolymer composition-CLD

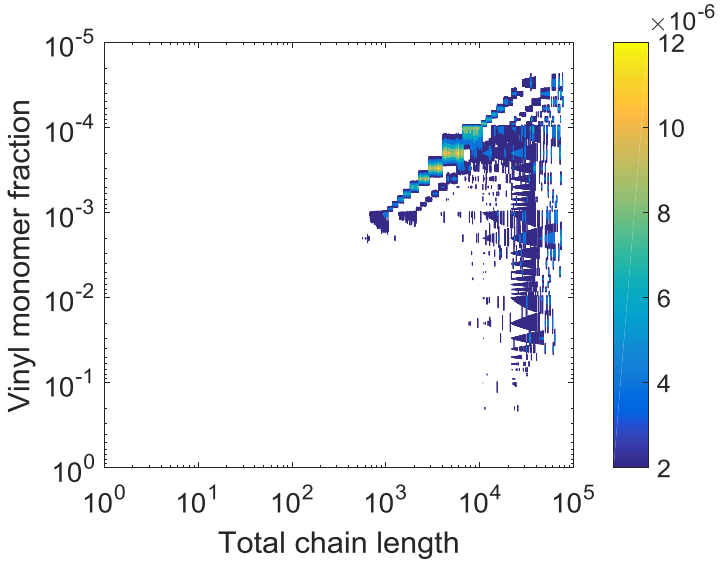






Initial CLD of polyolefin

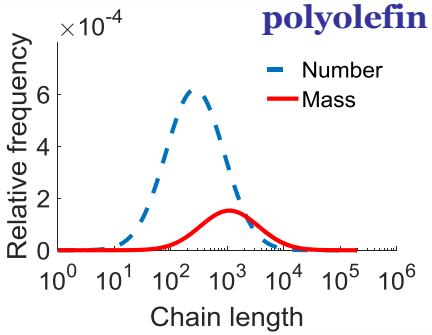


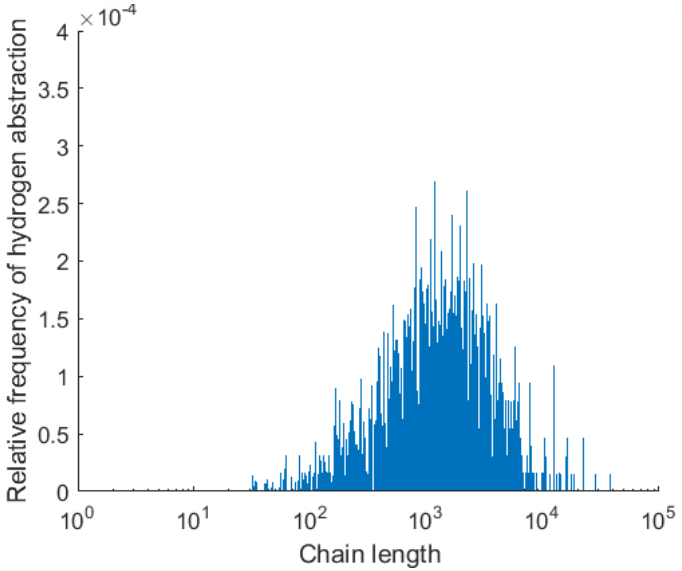


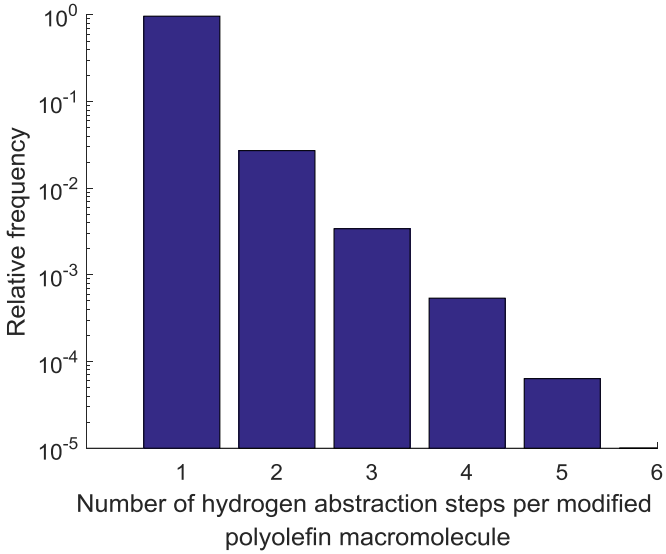
Results obtained with Module B

Reaction event distribution

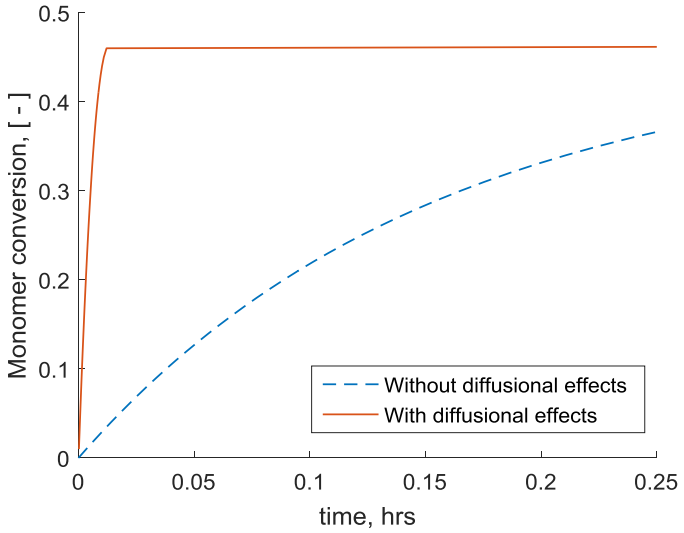
Initial CLD of polyolefin

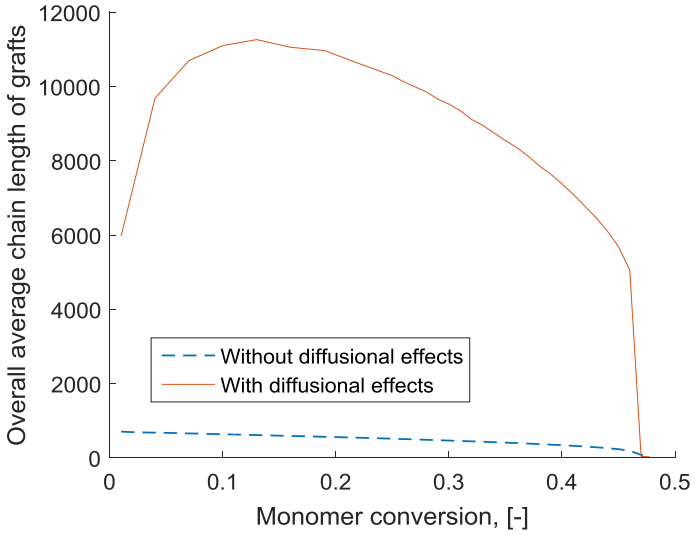


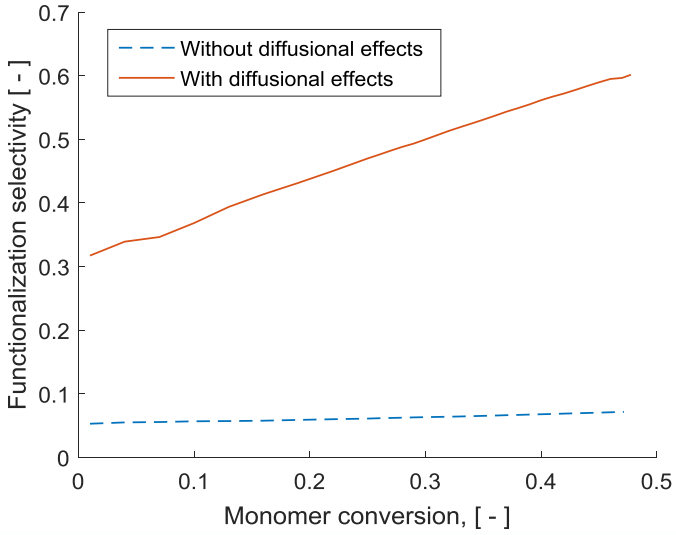


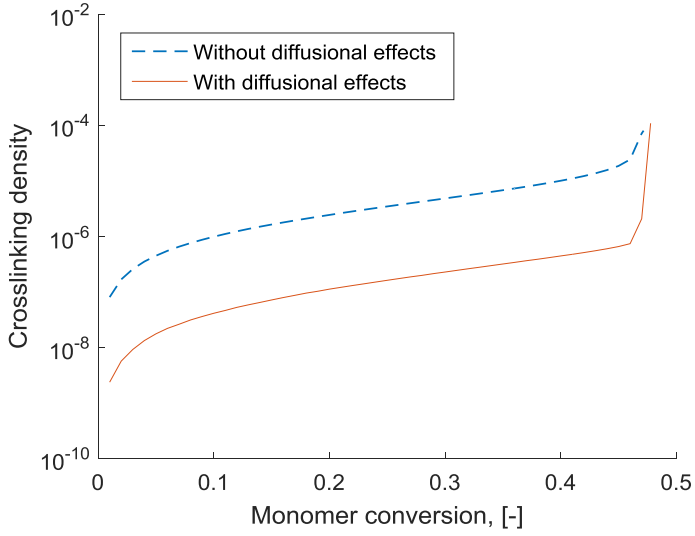


Diffusional effects









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.