MMAtwo

Second Generation MethylMethAcrylate

Concepts of Chemical Recycling: Part 1

Dr. Yoshi W. Marien

GHENT UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

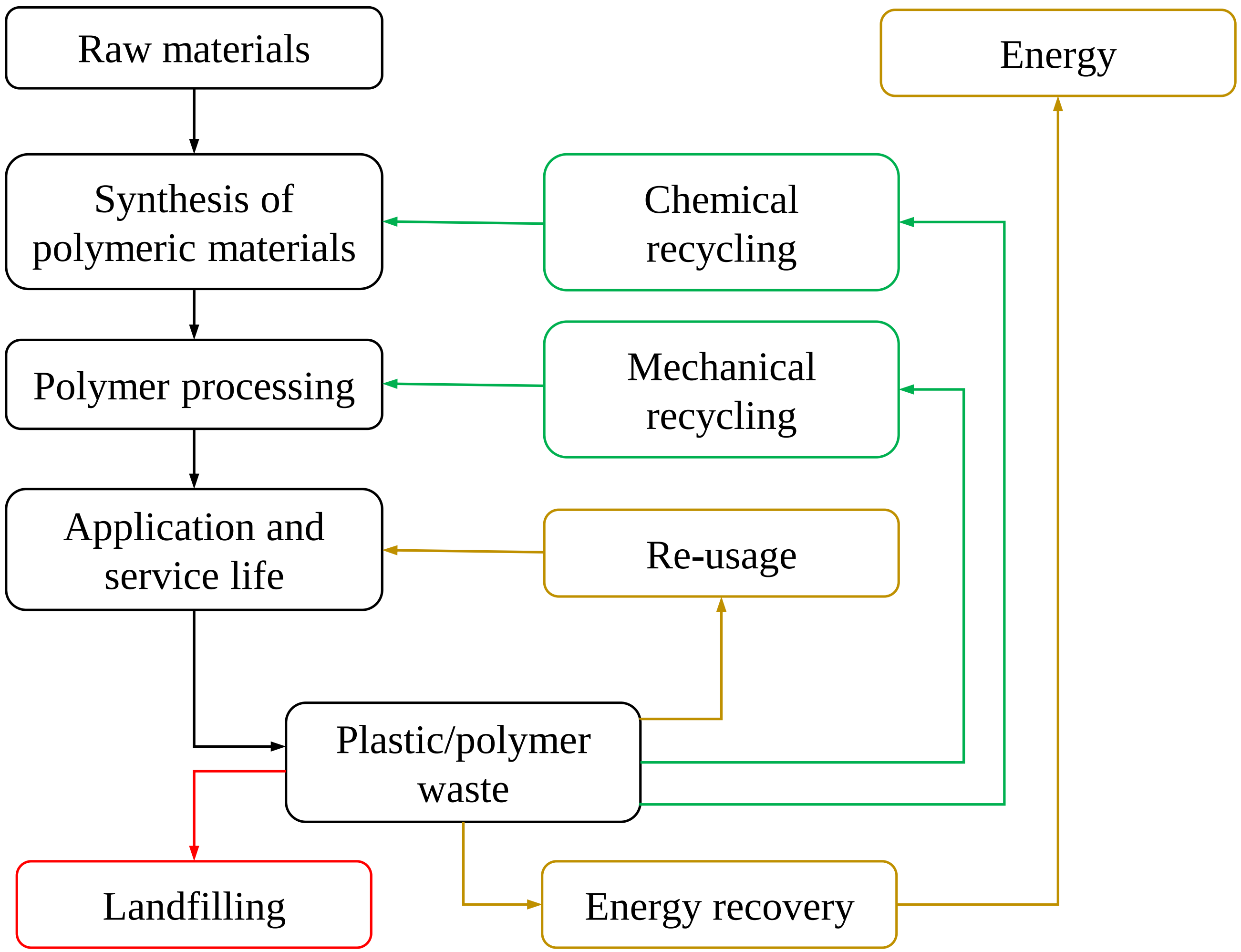
MMAtwo workshop

15/09/2020

DOI: 10.13140/RG.2.2.36058.98241

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 820687.

Introduction



Moens *et al.*, Polymers 2020, 12, 1667
Ragaert *et. al.*, Waste Management 2017, 69, 24

Outline

- Introduction
- Overview of depolymerization kinetic models
- Application of matrix based kinetic Monte Carlo to PMMA depolymerization
  - The role of defects & functionalities to initiate depolymerization
  - How defects & functionalities are introduced during free radical polymerization
  - Modeling of free radical polymerization
  - Modeling of depolymerization
- Conclusions

Depolymerization kinetic models

- **Global conversion based models**
- **Global average chain length based models**
- **Elementary reaction step based models**

Global conversion based models

$$\frac{d\alpha}{dt} = kf(\alpha) = A\,exp\left(-\frac{E}{RT}\right)f(\alpha)$$

α: conversion

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = \frac{d\alpha}{dT}\beta$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\,exp\left(-\frac{E}{RT}\right)f(\alpha)$$

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln[A\,f(\alpha)] - \frac{E}{RT}$$

$$\left[\frac{d\ln\left(\frac{d\alpha}{dT}\right)}{d\left(\frac{1}{T}\right)}\right]_{\alpha} = -\left[\frac{E}{R}\right]_{\alpha} + \left[\frac{d\ln\left(f(\alpha)\right)}{d\left(\frac{1}{T}\right)}\right]_{\alpha}$$

Moens *et al.*, Polymers 2020, 12, 1667

Depolymerization kinetic models

- **Global conversion based models**

$$\left[\frac{d\ln\left(\frac{d\alpha}{dT}\right)}{d\left(\frac{1}{T}\right)}\right]_{\alpha} = -\left[\frac{E}{R}\right]_{\alpha} + \left[\frac{d\ln\left(f(\alpha)\right)}{d\left(\frac{1}{T}\right)}\right]_{\alpha}$$

- **Global average chain length based models**

$$\ln\left(1-\frac{1}{x_{n,0}}\right)-\ln\left(1-\frac{1}{x_n}\right)=k_{ir}t$$

- **Elementary reaction step based models**
  - **Deterministic**
  - **Stochastic**

Deterministic elementary reaction based models

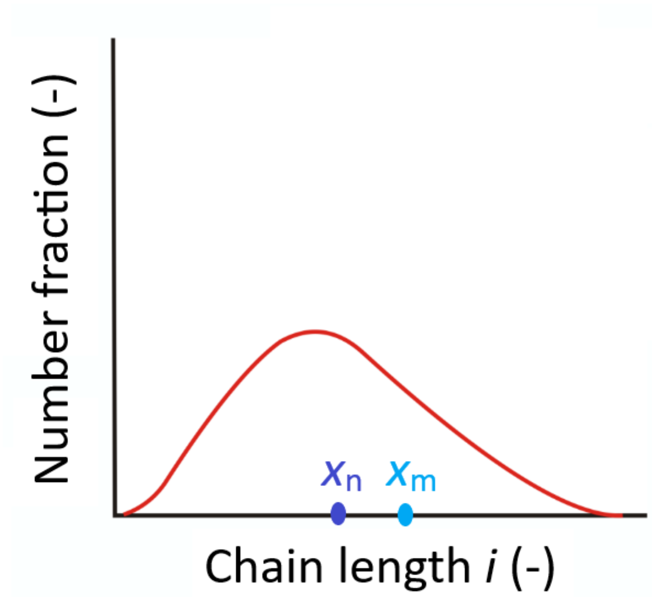
$$P_i \xrightarrow{k_f} R_{i-j} + R_j$$

Population balances

$$\frac{d[P_i]}{dt} = -(i-1)k_f[P_i] + \cdots \qquad i = 1, i_{max}$$

Balances for moments only

$$\frac{d\mu_m}{dt} = -k_f(\mu_{m+1} - \mu_m) + \cdots \qquad m = 0, 1, 2$$



$$x_n = \frac{\mu_1}{\mu_0} \quad x_m = \frac{\mu_2}{\mu_1} \quad Đ = \frac{x_m}{x_n}$$

Depolymerization kinetic models

- Global conversion based models

$$\left[\frac{d\ln\left(\frac{d\alpha}{dT}\right)}{d\left(\frac{1}{T}\right)}\right]_{\alpha} = -\left[\frac{E}{R}\right]_{\alpha} + \left[\frac{d\ln\big(f(\alpha)\big)}{d\left(\frac{1}{T}\right)}\right]_{\alpha}$$

- Global average chain length based models

$$\ln\left(1-\frac{1}{x_{n,0}}\right) - \ln\left(1-\frac{1}{x_n}\right) = k_{ir}t$$

- Elementary reaction step based models
  - Deterministic
  - Stochastic
    - ✓ Tree based kinetic Monte Carlo
    - ✓ Matrix based kinetic Monte Carlo

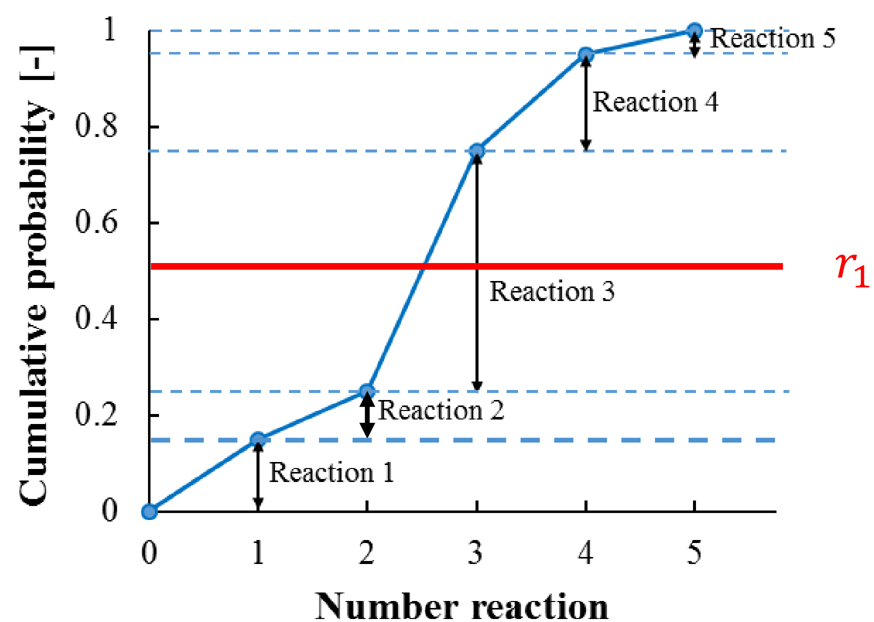
Stochastic elementary reaction based models

- Stochastic sampling of reactions via kinetic Monte Carlo (*k*MC)
- Probability P to sample reaction υ is proportional to its microscopic reaction rate R [s^{-1}]

$$R(\upsilon) = k^{\upsilon}_{app,MC} n_A n_B$$

$$P(\upsilon) = R(\upsilon)\left[\sum_{\upsilon} R(\upsilon)\right]^{-1}$$

$$\sum_{\upsilon=1}^{\upsilon=\mu-1} P(\upsilon) < r_1 \le \sum_{\upsilon=1}^{\upsilon=\mu} P(\upsilon)$$

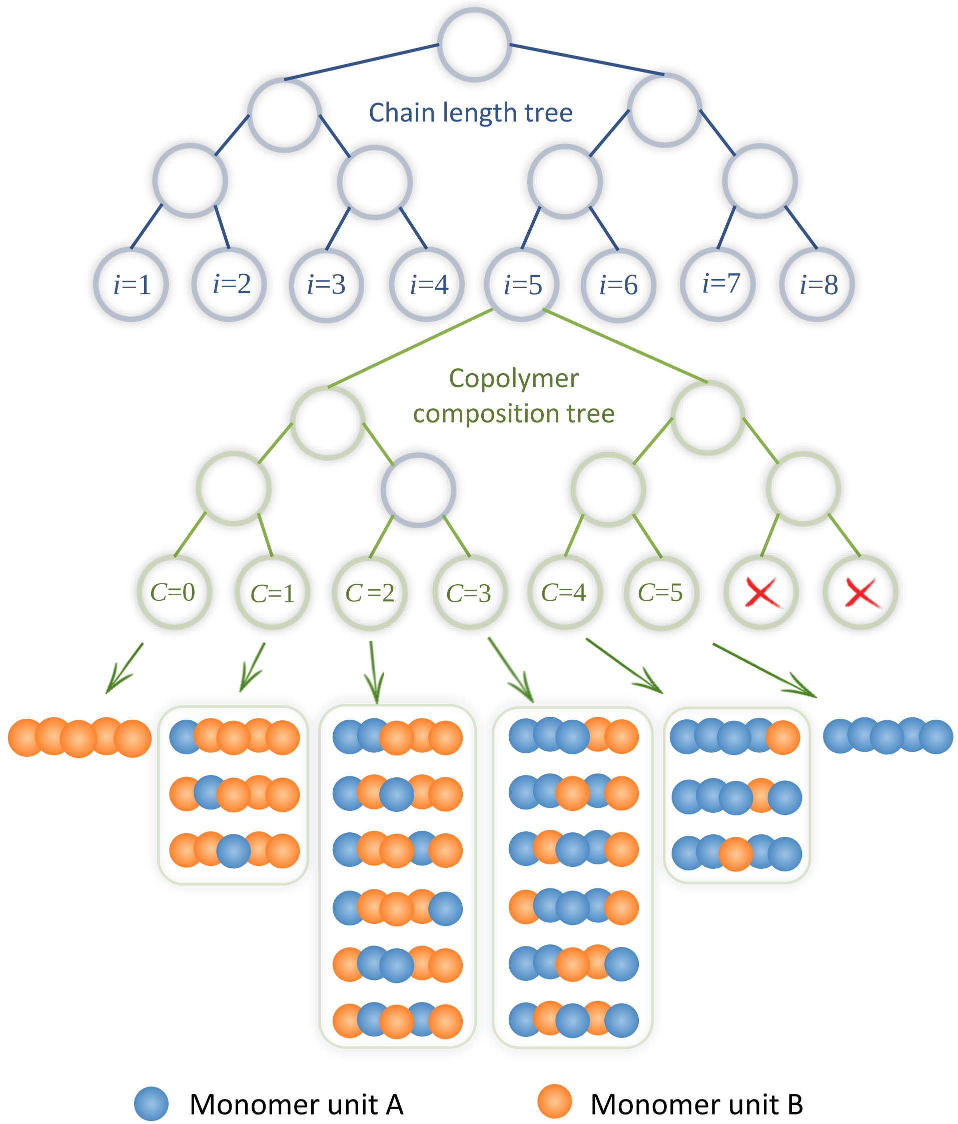


- Update of reaction time via

$$t = t + \frac{ln\left(\frac{1}{r_2}\right)}{\sum_{\upsilon} R(\upsilon)}$$

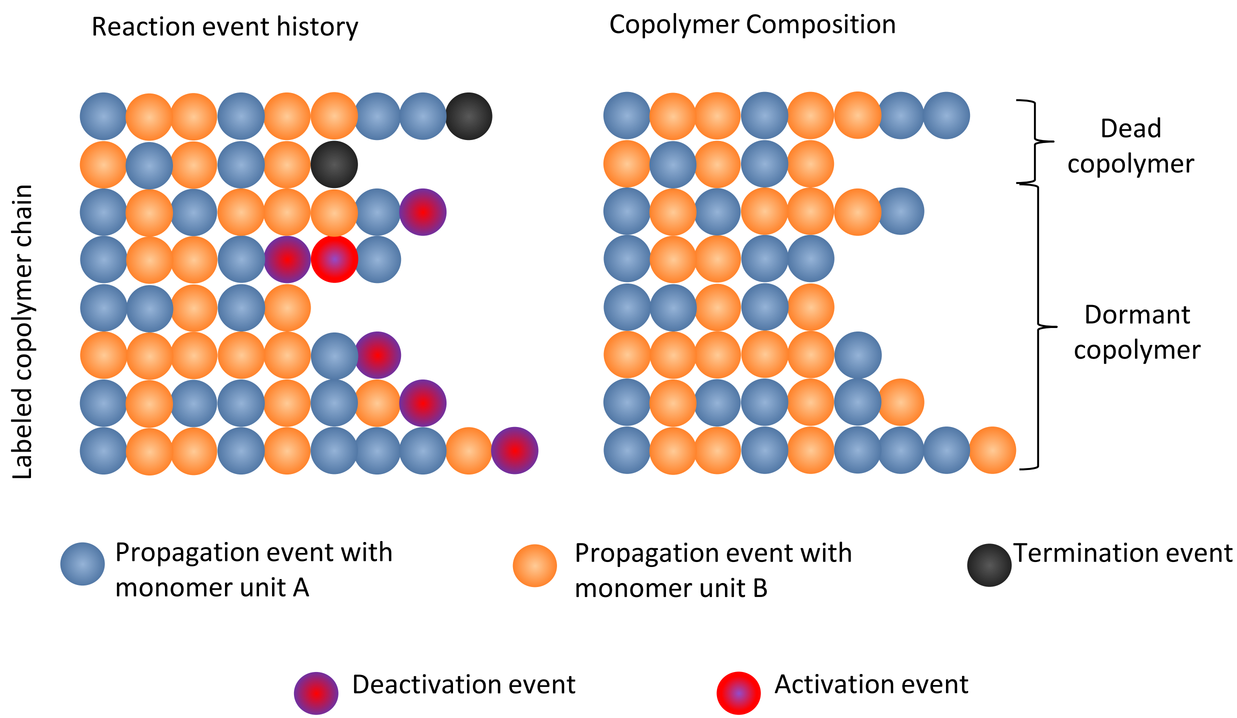
Van Steenberge *et al.*, Macromolecules 2012, 45, 8519

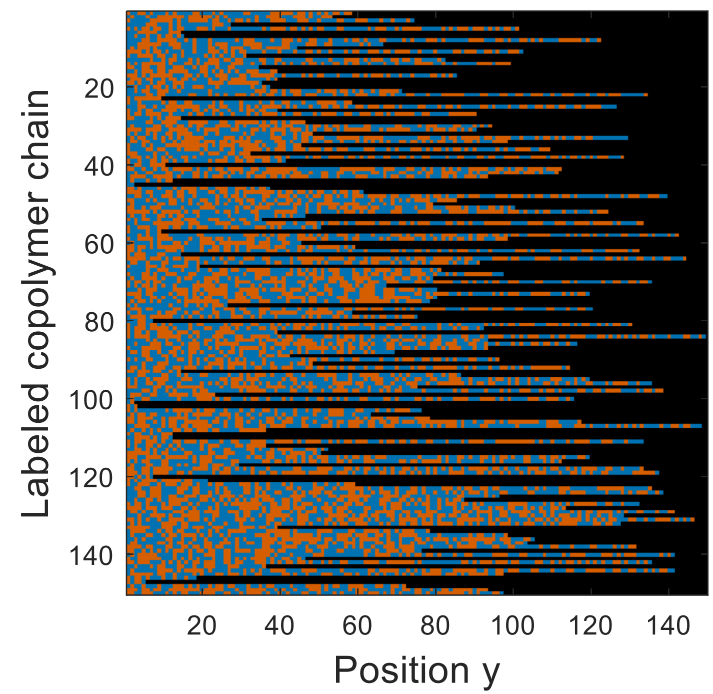
Tree based kMC



Van Steenberge *et al.*, Chem. Eng. Sci. 2014, 110, 185
Trigilio *et. al.*, Ind. Eng. Chem. Res. 2020, doi.org/10.1021/acs.iecr.0c03888

Matrix based kMC





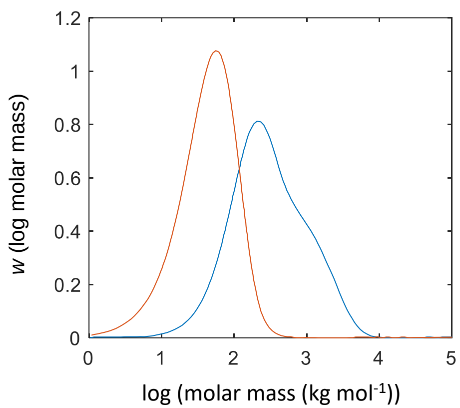
Van Steenberge *et al.*, Macromolecules 2012, 45, 8519
Trigilio *et. al.*, Ind. Eng. Chem. Res. 2020, doi.org/10.1021/acs.iecr.0c03888

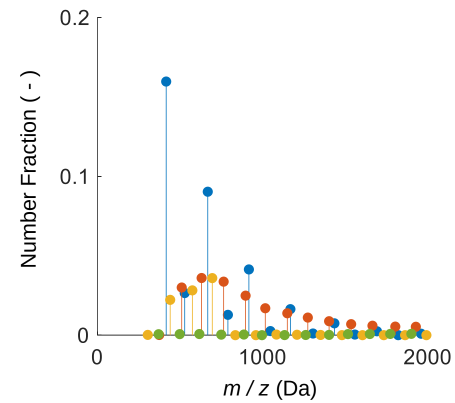
Tree vs. matrix based kMC

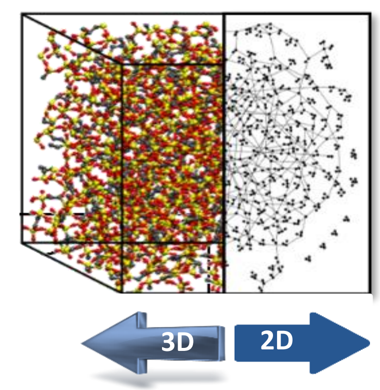
Univariate tree based

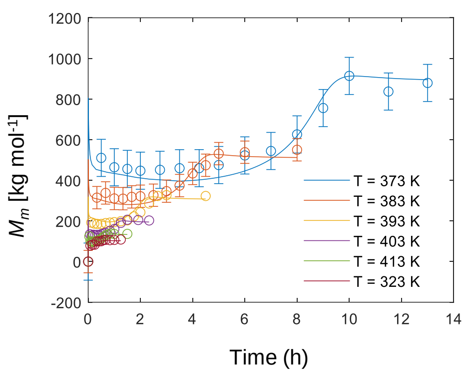
Bivariate tree based

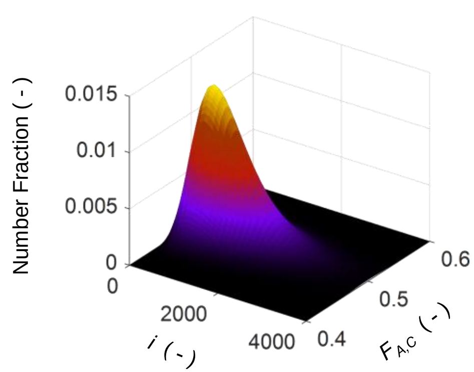
Matrix based

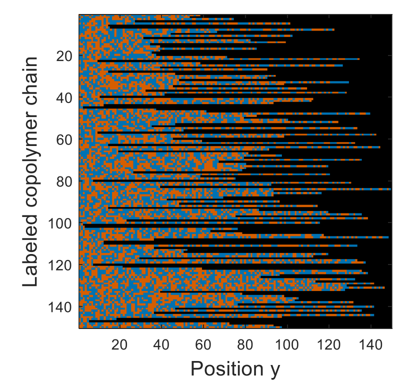












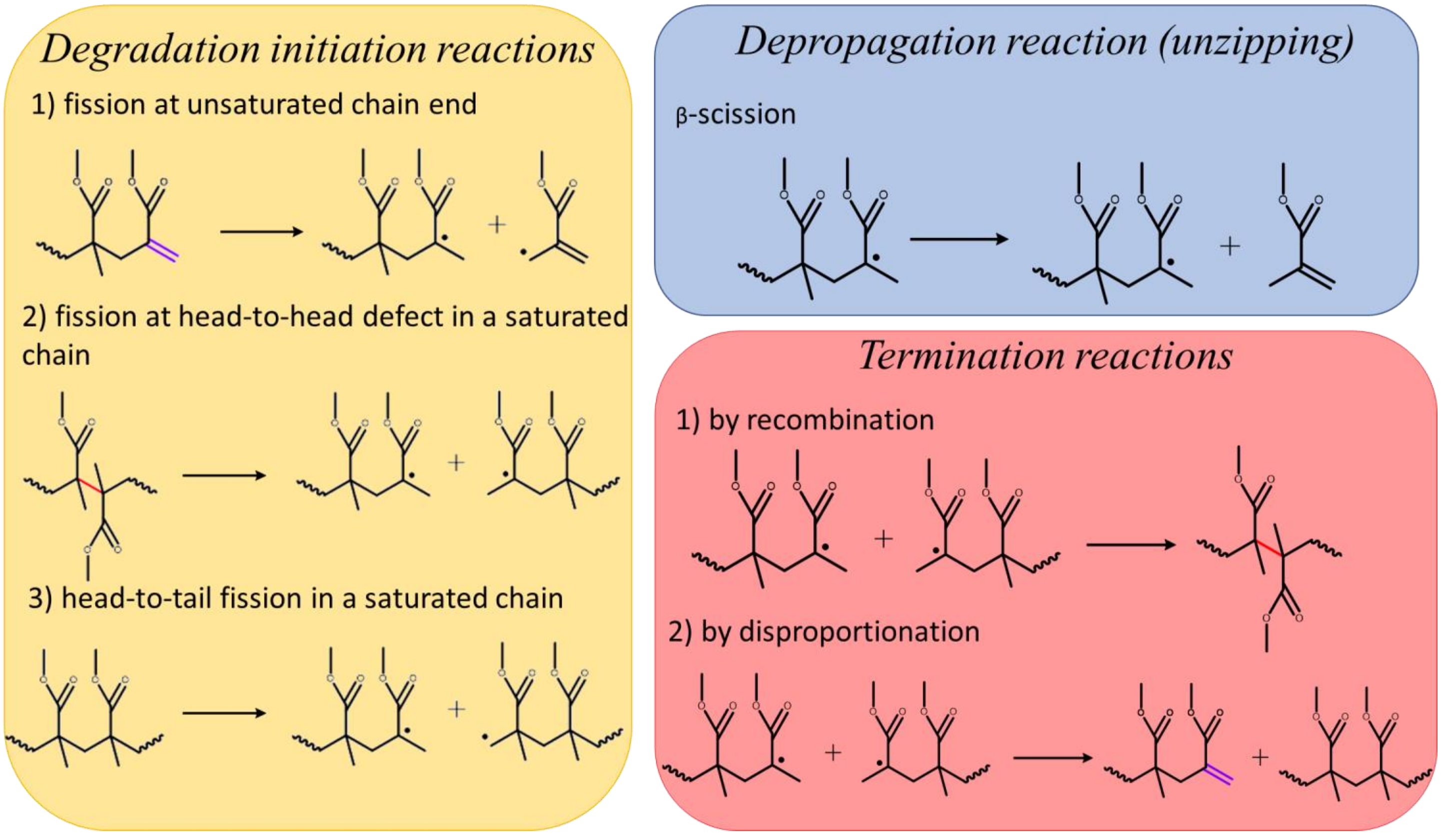
Complexity and macromolecular structural detail

D‘hooge *et al.*, Prog. Polym. Sci. 2016, 58, 59
Trigilio *et. al.*, Ind. Eng. Chem. Res. 2020, doi.org/10.1021/acs.iecr.0c03888

Outline

- Introduction
- Overview of depolymerization kinetic models
- Application of matrix based kinetic Monte Carlo to PMMA depolymerization
  - The role of defects & functionalities to initiate depolymerization
  - How defects & functionalities are introduced during free radical polymerization
  - Modeling of free radical polymerization
  - Modeling of depolymerization
- Conclusions

PMMA depolymerization reactions

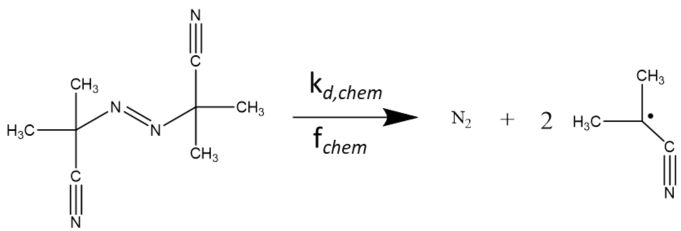


Initiation of depolymerization depends on the presence of structural defects and functionalities → also chain-by-chain visualization of polymerization needed

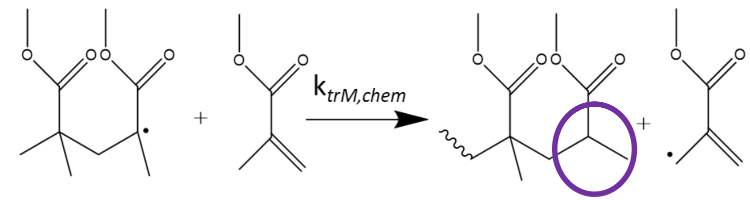
Moens *et al*., Polymers 2020, 12, 1667
De Smit *et. al*., Reac. Chem. Eng. 2020, 10.1039/D0RE00266F

MMA free radical polymerization reactions

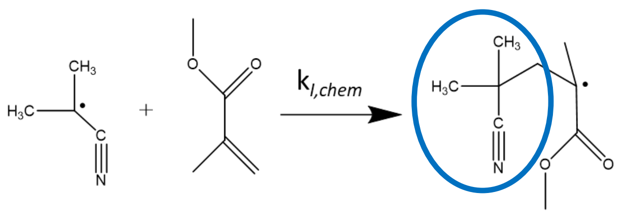
Initiator dissociation



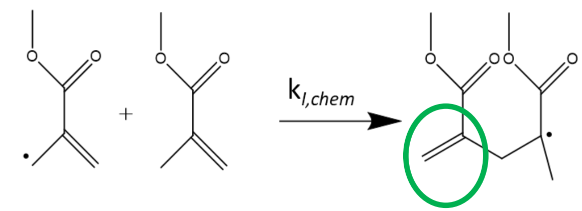
Chain transfer to monomer



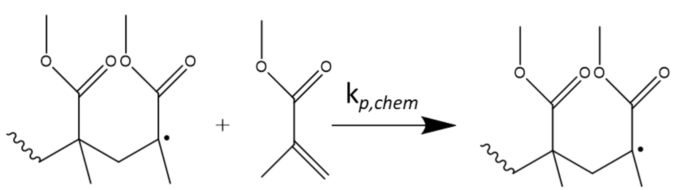
Chain initiation initiator radical



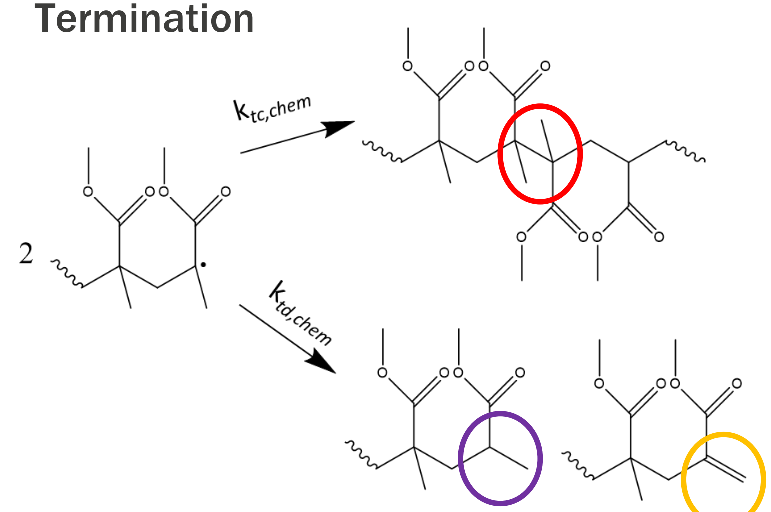
Chain initiation monomeric radical



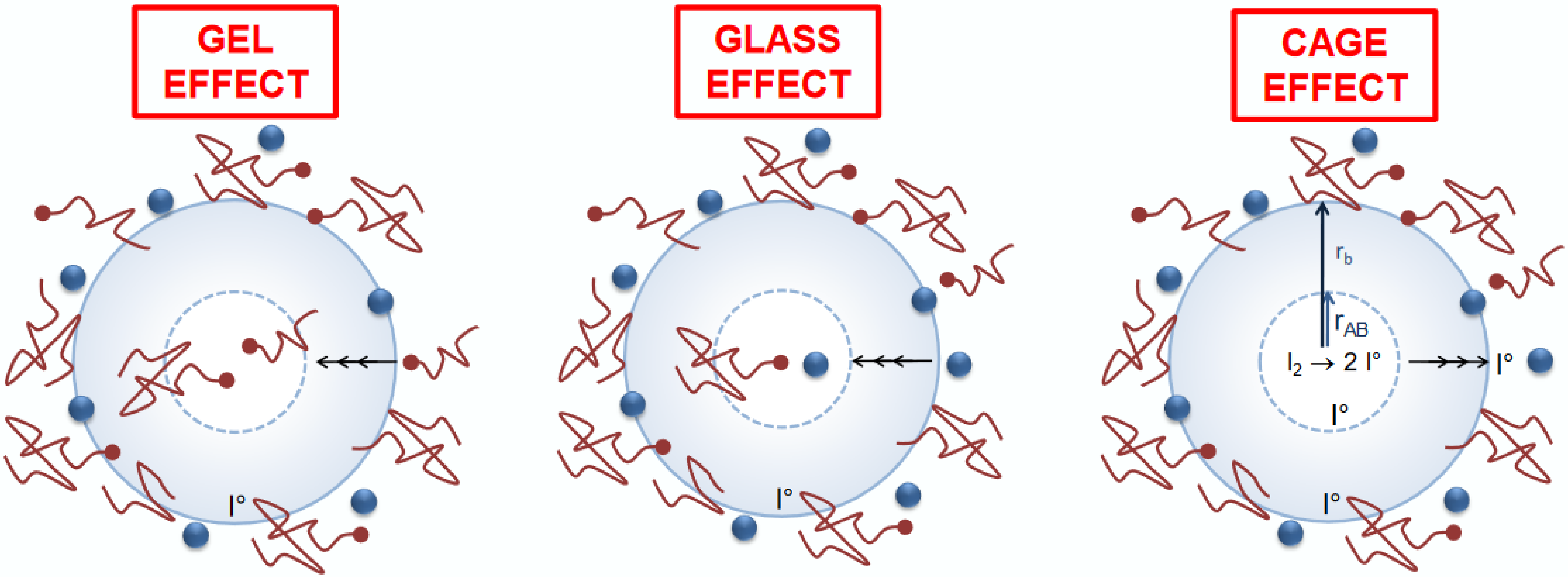
Propagation



Termination

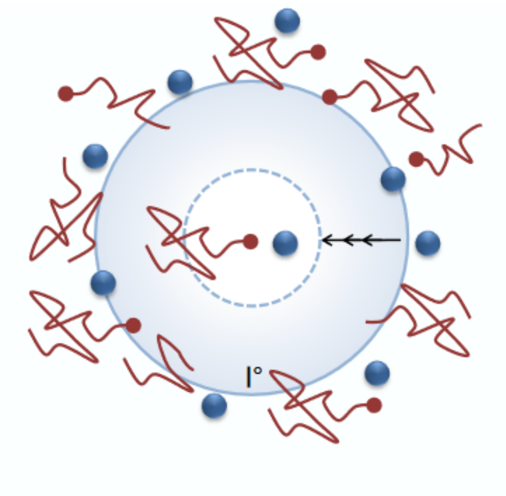


Diffusional limitations in FRP



Buback *et. al.*, Macromol. Chem. Phys. 1994, 195, 2117
Achilias *et. al.*, Macromol. Theory. Simul. 2007, 16, 319
D'hooge *et al.*, Macromol. React. Eng. 2009, 3, 185

Glass effect



Parallel encounter pair model

$$\frac{1}{k^i_{p,app}} = \frac{1}{k^i_{p,chem}} + \frac{1}{k^i_{p,diff}}$$

Smoluchowski equation

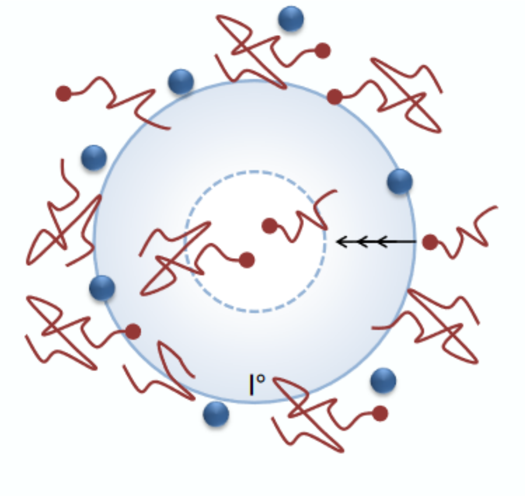
$$k^i_{p,diff} = k_{p,diff} = 4\pi\sigma_p N_A D_{tr,M}$$

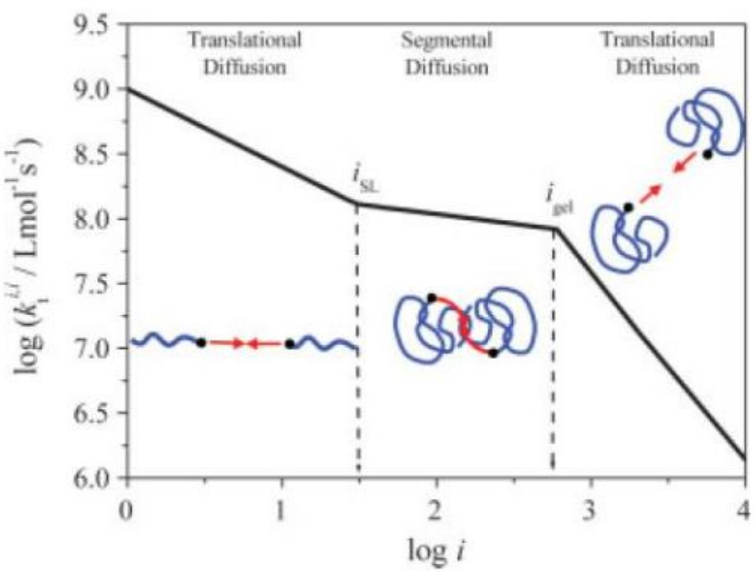
Free volume theory

$$D_{tr,M} = D_{M,0}\, e^{-\frac{E_{a,M}}{RT}} \left(-V^*_M M_{j,M} \frac{\frac{w_m}{M_{j,M}} + \frac{w_p}{M_{j,M}}}{V_{FH}/\lambda} \right)$$

Vrentas *et al.*, J. Polym. Sci. Part A-2, Polym. Phys. 1984, 22, 459

Gel effect





$$\text{for } i < i_{\text{gel}} \text{ and } i < i_{\text{SL}}:\ k_{\text{t,ii}}^{\text{app}} = k_{\text{t,11}}^{\text{app}}\, i^{-\alpha_{\text{s}}}$$

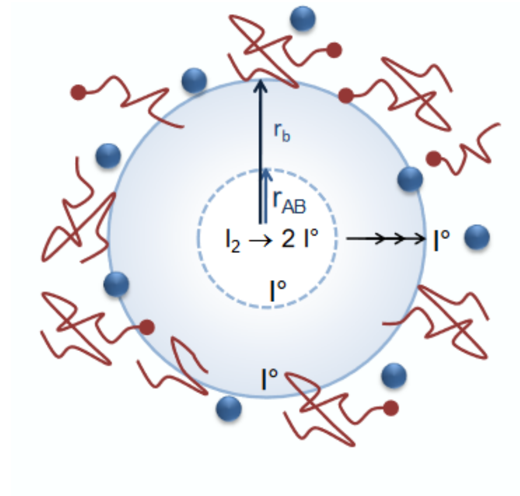
$$\text{for } i < i_{\text{gel}} \text{ and } i \geq i_{\text{SL}}:\ k_{\text{t,ii}}^{\text{app}} = k_{\text{t,11}}^{\text{app}}\, i_{\text{SL}}^{\alpha_{\text{l}}-\alpha_{\text{s}}}\, i^{-\alpha_{\text{l}}}$$

$$\text{for } i \geq i_{\text{gel}} \text{ and } i < i_{\text{SL}}:\ k_{\text{t,ii}}^{\text{app}} = k_{\text{t,11}}^{\text{app}}\, i_{\text{gel}}^{\alpha_{\text{gel}}-\alpha_{\text{s}}}\, i^{-\alpha_{\text{gel}}}$$

$$\text{for } i \geq i_{\text{gel}} \text{ and } i < i_{\text{SL}}:\ k_{\text{t,ii}}^{\text{app}} = k_{\text{t,11}}^{\text{app}}\, i_{\text{SL}}^{\alpha_{\text{l}}-\alpha_{\text{s}}}\, i_{\text{gel}}^{\alpha_{\text{gel}}-\alpha_{\text{l}}}\, i^{-\alpha_{\text{gel}}}$$

Johnston-Hall *et al.*, J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 3155

Cage effect



Apparent initiator efficiency as a function of monomer conversion

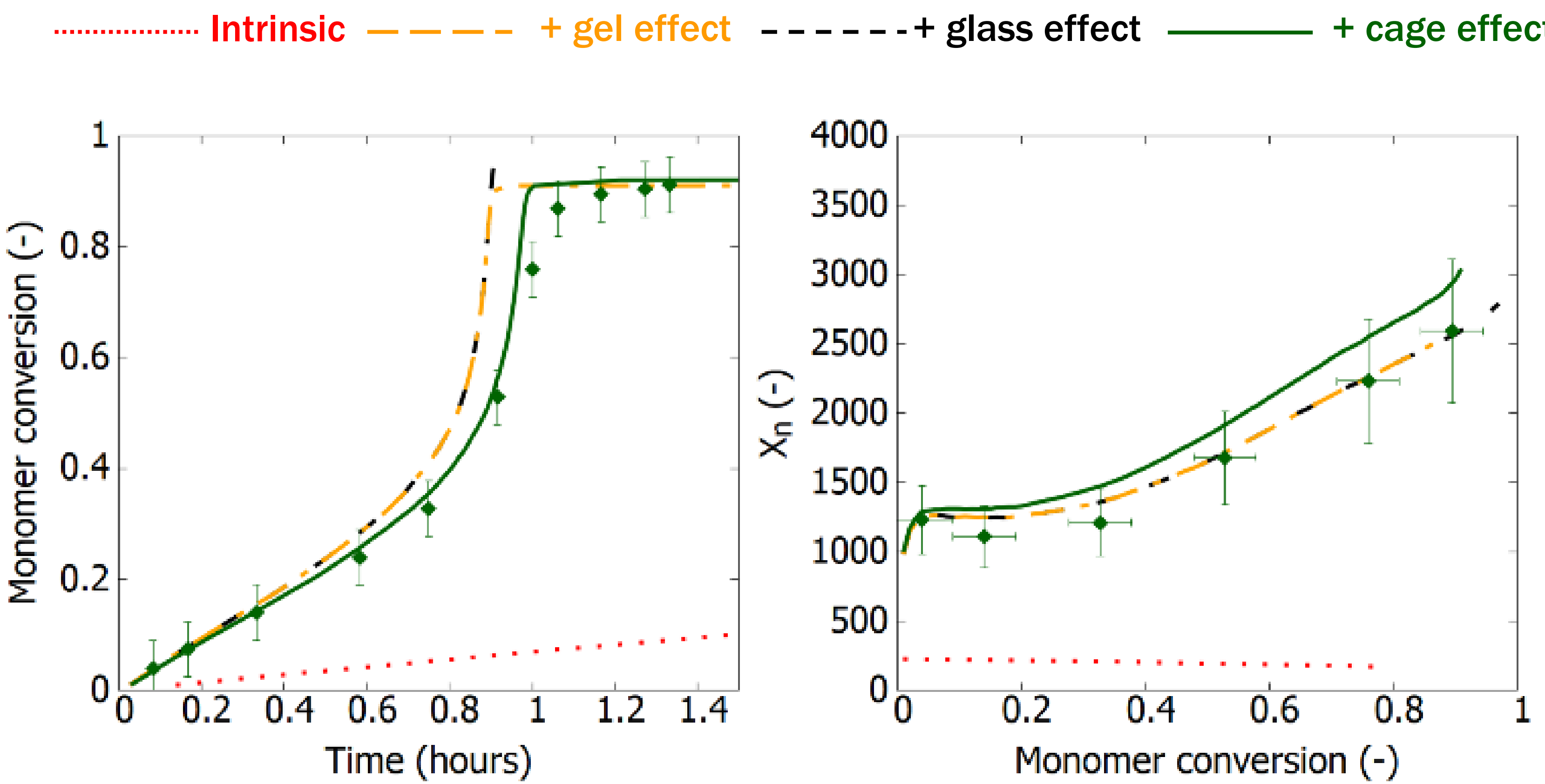
$$f_{app} = \frac{D_I}{D_I + D_{term}}$$

Free volume theory

$$D_I = D_{0,I}\, e^{-\frac{E_{a,I}}{RT}} \left(- \frac{w_m V_m^* \xi_{cp}/\xi_{mp} + w_p V_p^* \xi_{cp}}{V_{FH}/\lambda} \right)$$

Buback *et al.*, Macromol. Chem. Phys. 1994, 195, 2117

Importance diffusional limitations in FRP

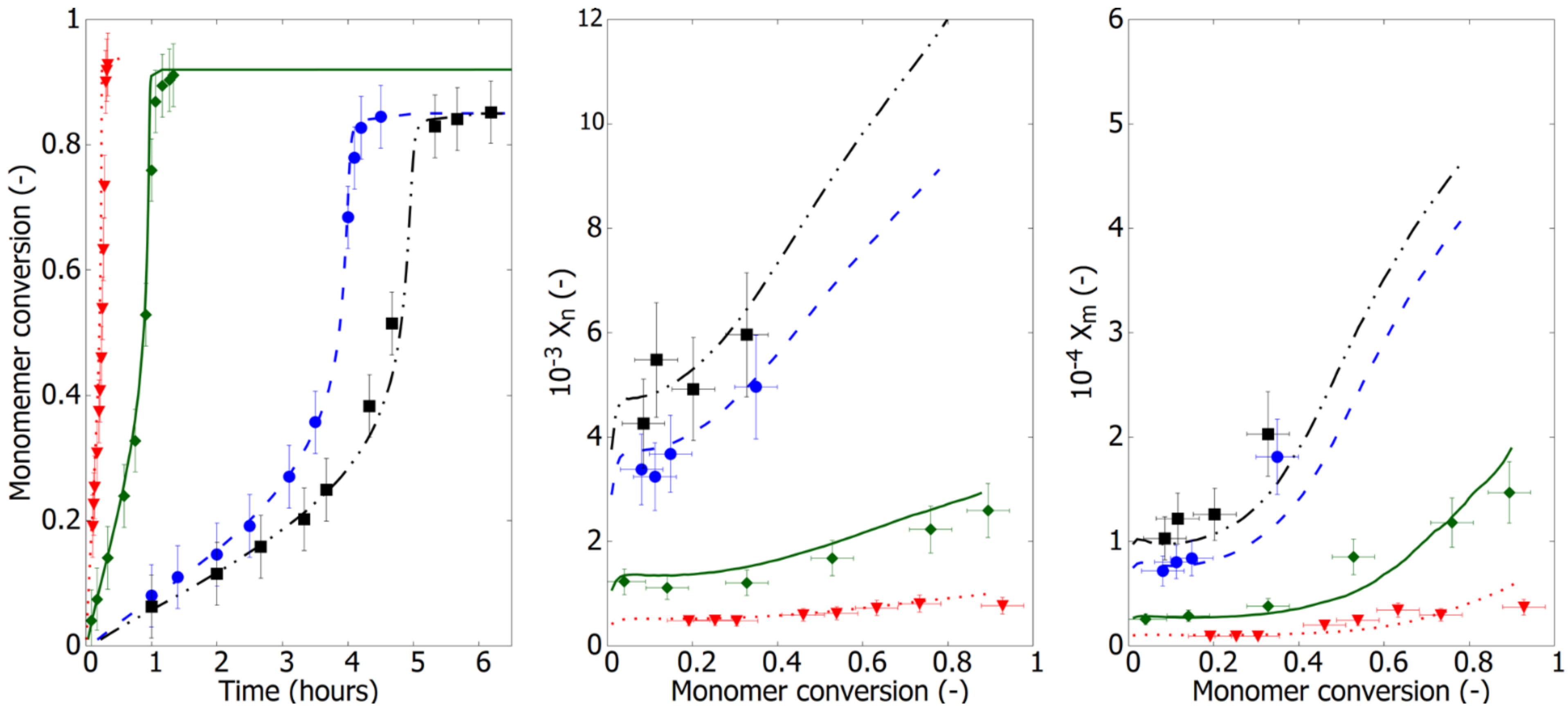


De Smit *et. al.*, Reac. Chem. Eng. 2020, 10.1039/D0RE00266F

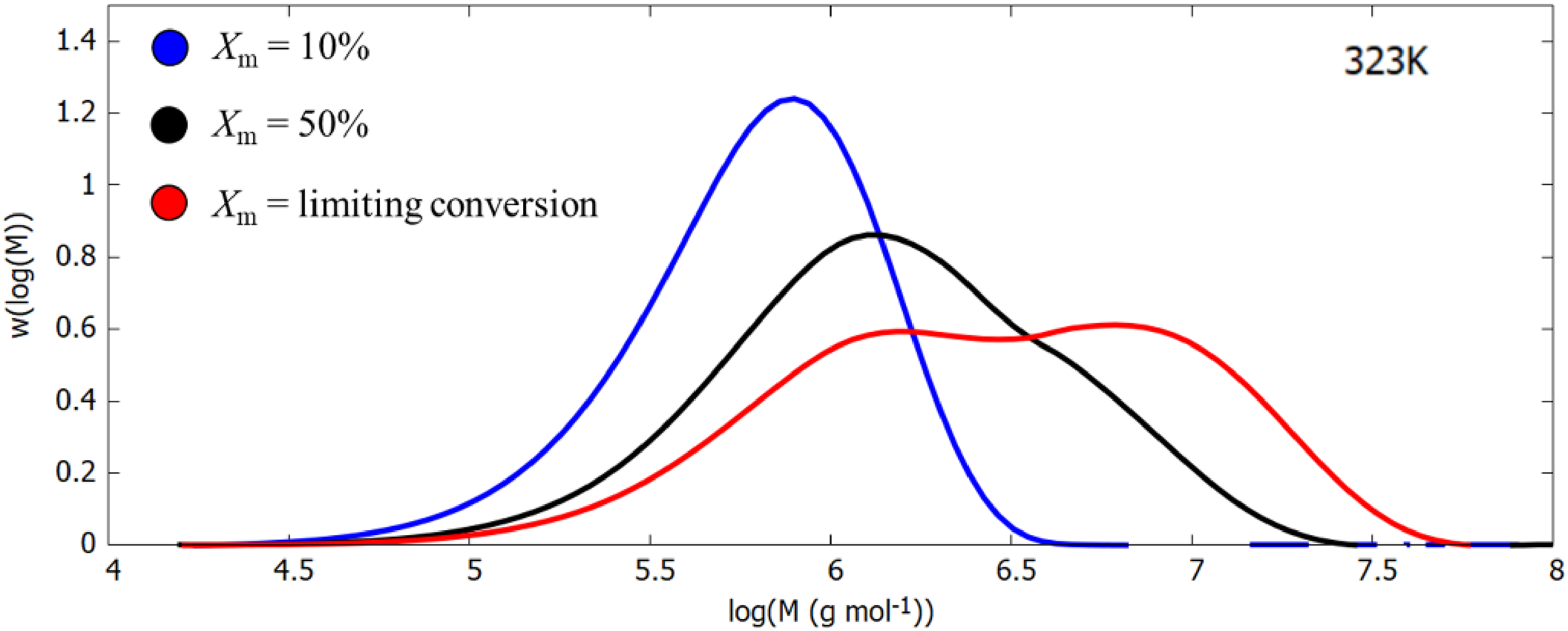
Model validation FRP

363 K and $[AIBN]_0:[MMA]_0=0.003$ | 343 K and $[AIBN]_0:[MMA]_0=0.003$

323 K and $[AIBN]_0:[MMA]_0=0.003$ | 323 K and $[AIBN]_0:[MMA]_0=0.002$

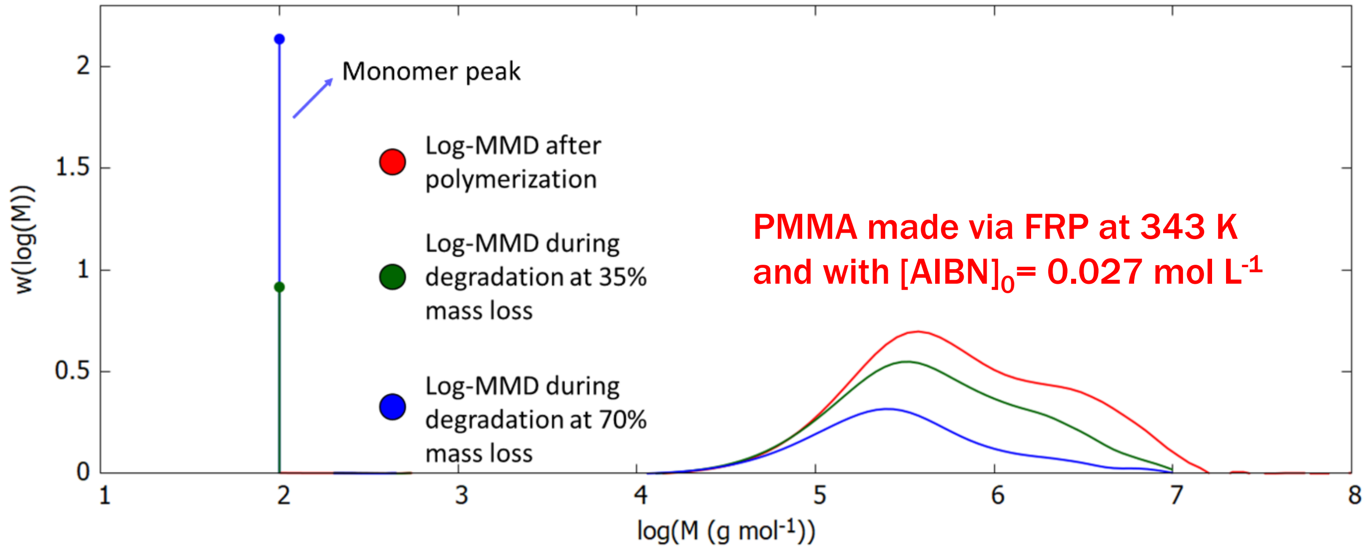


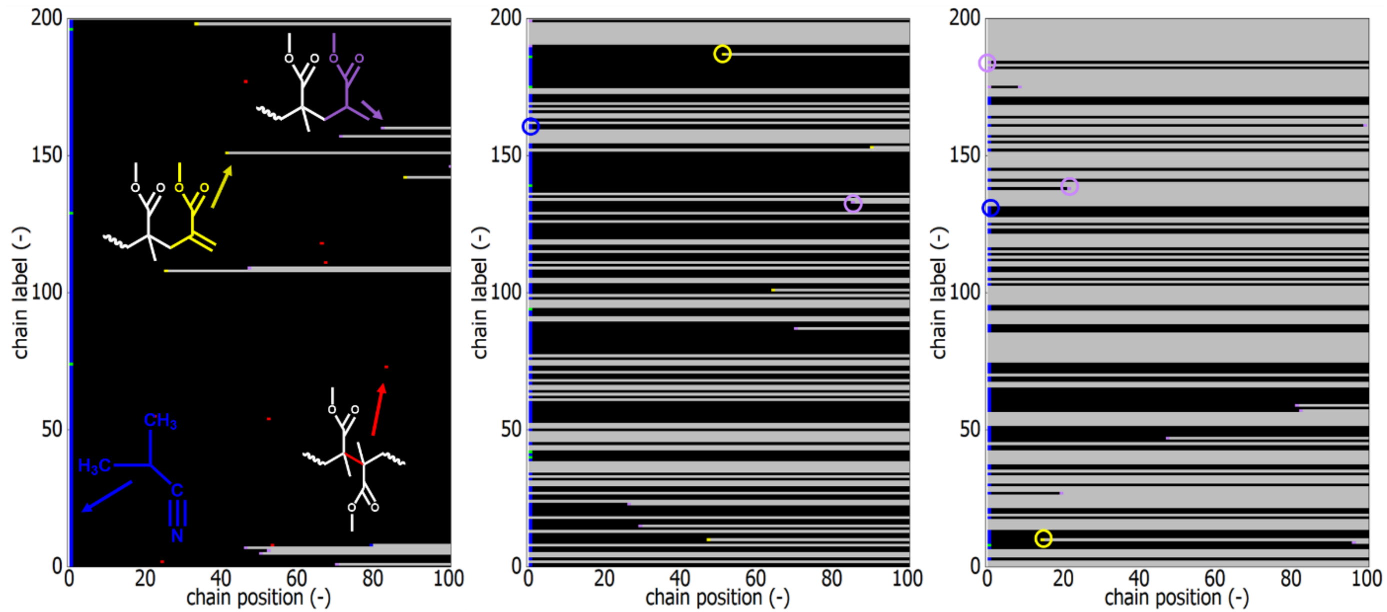
log-MMD evolution FRP



 De Smit *et. al.*, Reac. Chem. Eng. 2020, 10.1039/D0RE00266F

Depolymerization at 625 K

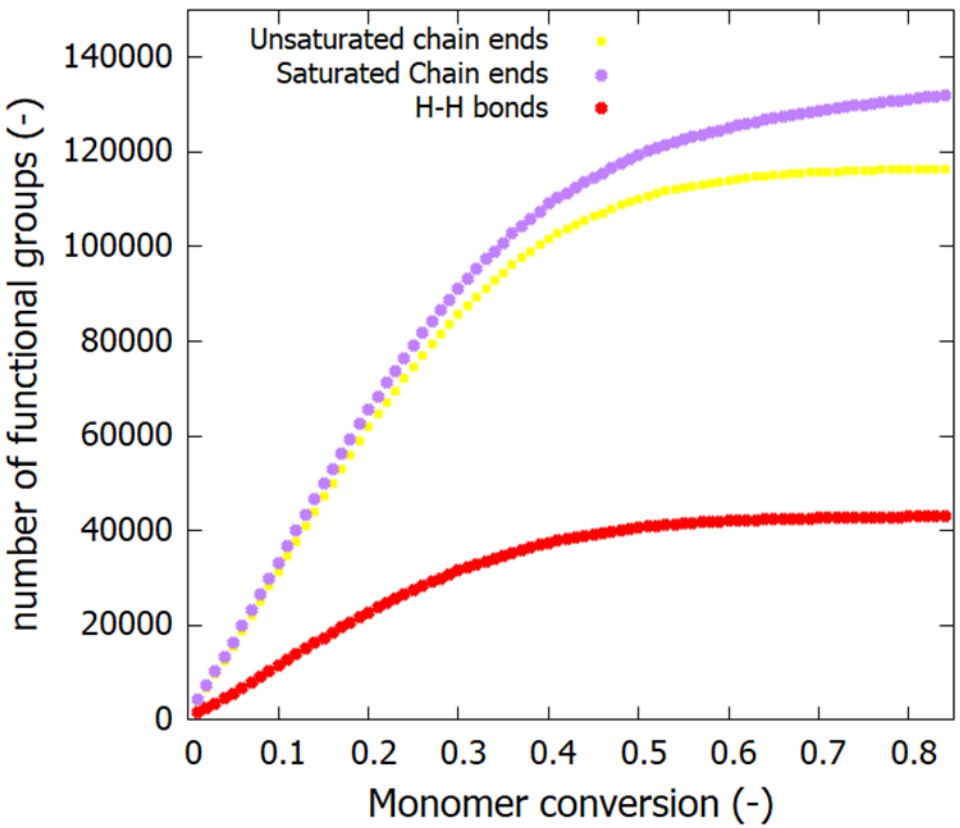




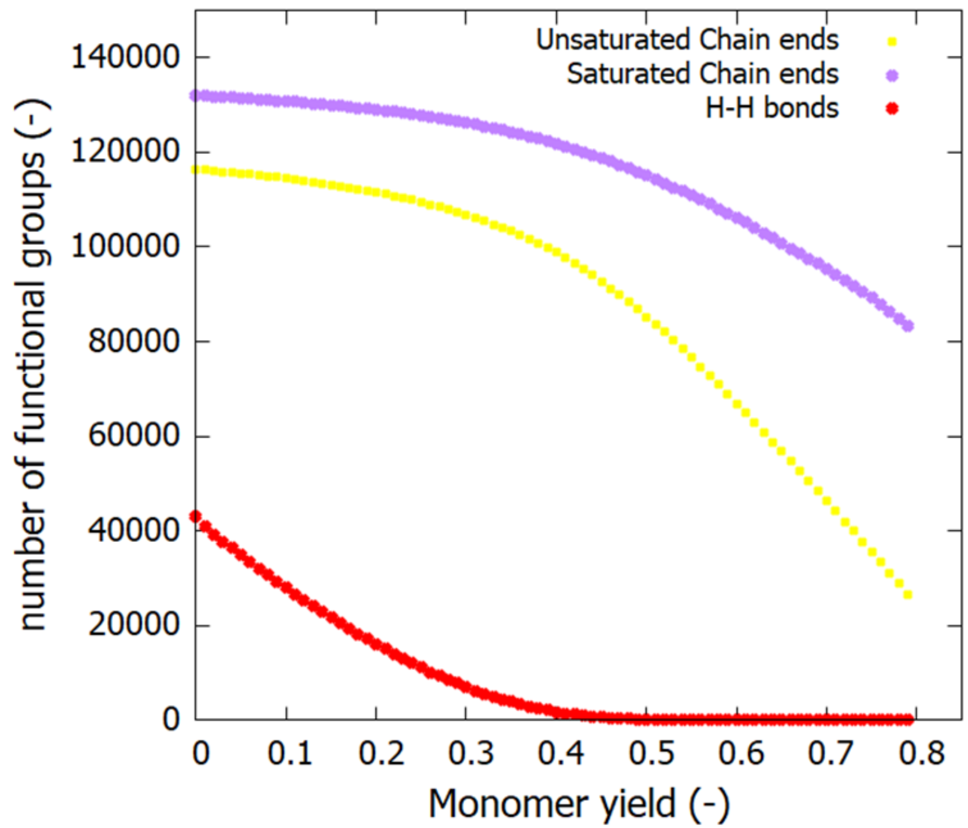
De Smit *et. al.*, Reac. Chem. Eng. 2020, 10.1039/D0RE00266F

Evolution of functionalities

Polymerization



Depolymerization



De Smit *et. al.*, Reac. Chem. Eng. 2020, 10.1039/D0RE00266F

Outline

- Introduction
- Overview of depolymerization kinetic models
- Application of matrix based kinetic Monte Carlo to PMMA depolymerization
    - The role of defects & functionalities to initiate depolymerization
    - How defects & functionalities are introduced during free radical polymerization
    - Modeling of free radical polymerization
    - Modeling of depolymerization
- Conclusions

Conclusions

- **Chemical recycling** (depolymerization) allows to recover monomeric building blocks
- Depolymerization processes are characterized by a **large number of competing elementary reactions** such as fission, scission and termination reactions
- **Elementary reaction step based models** are key to improve the knowledge of depolymerization mechanisms and kinetics
- **Matrix based kinetic Monte Carlo** tools allow to track individual chains during both polymerization and depolymerization
- The initial **molar mass distribution** and the presence of **defects and functionalities** strongly affect the depolymerization kinetics

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 820687.
The MMAtwo project results presented reflect only the author's view.
The Commission is not responsible for any use that may be made of the information it contains.