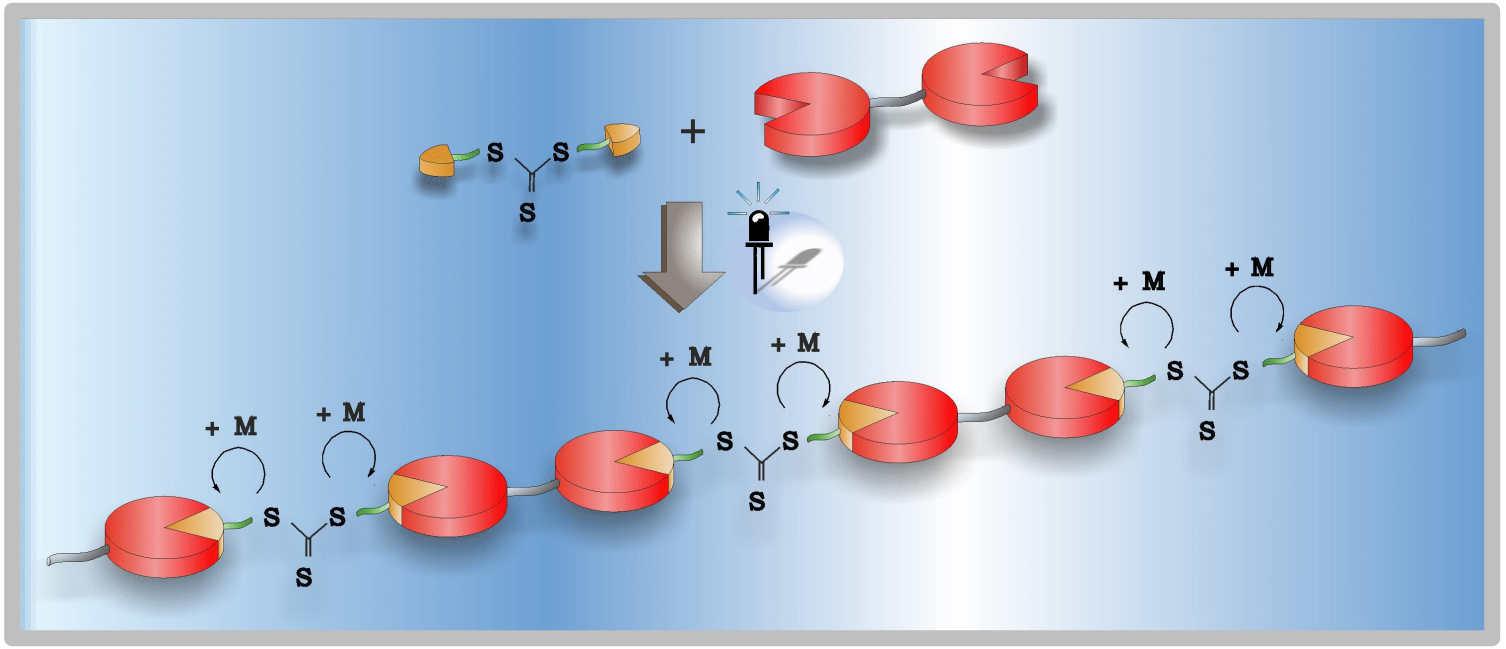
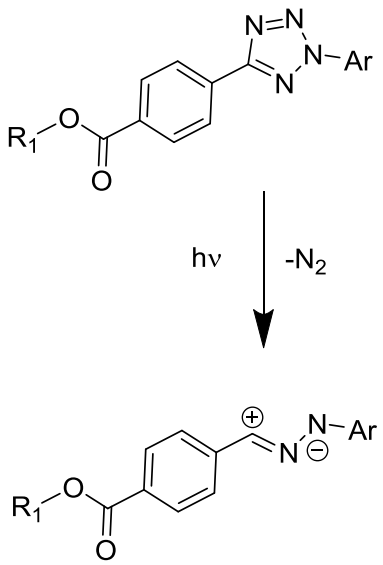


T. Gegenhuber, L. De Keer, A. S. Goldmann, P.H.M. Van Steenberge, M.F. Reyniers, D. R. D´hooge, C. Barner-Kowollik

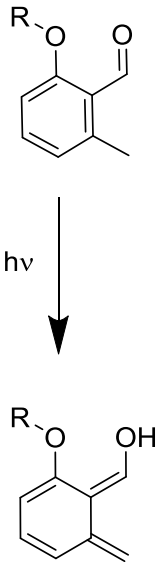
STEP-GROWTH POLYMERS AS MACRO CHAIN TRANSFER AGENTS – AN EXPERIMENTAL AND THEORETICAL STUDY

The Road into the Light?

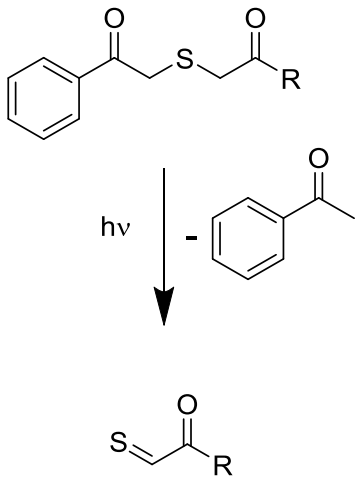
And if You feel that You can´t go on,
in the Light You will find the Road.
(“In the Light“, Physical Graffiti, Led Zeppelin © 1975)



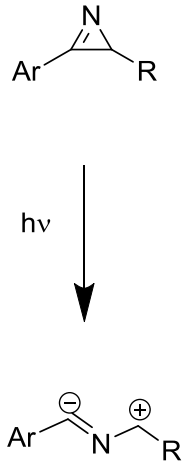
Tetrazole to Nitrile-imine



Methyl-Benzaldehyde to ”Photoenol“



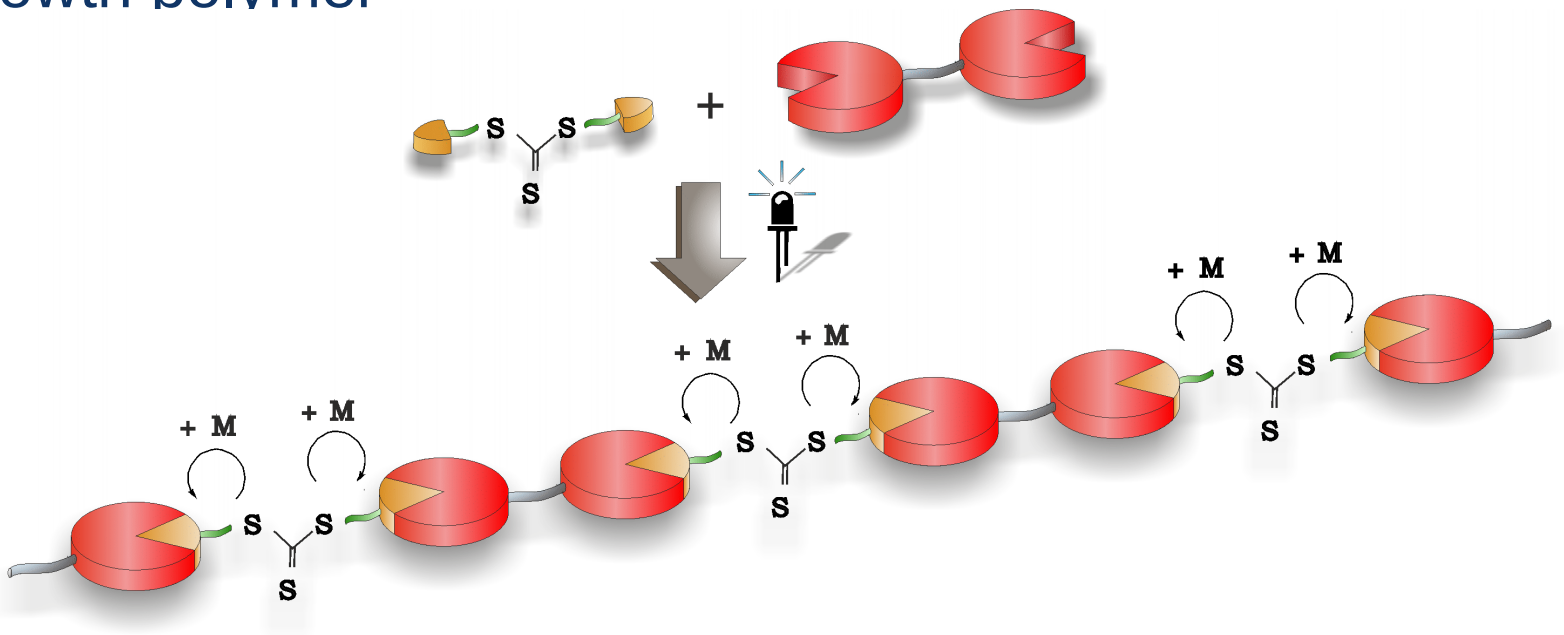
Phenacylsulfide to Thioaldehyde

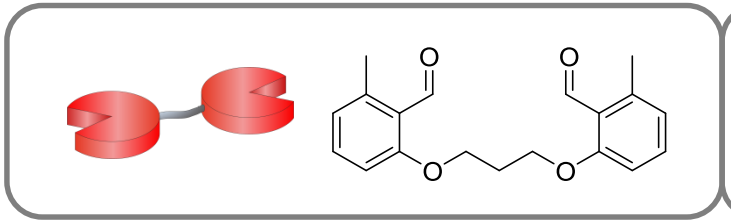


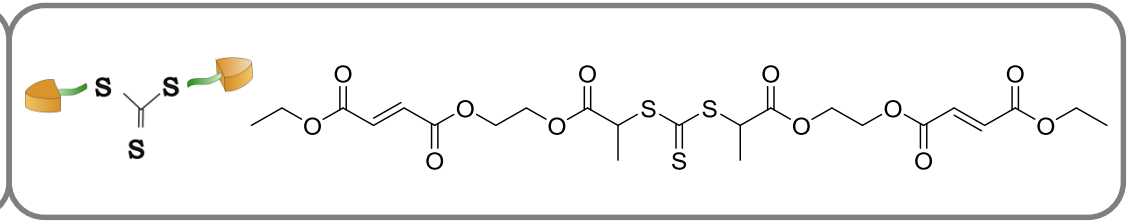
Azirine to Nitrile-ylide

Reaction Pathway and Motivation

- Incorporation of RAFT group within the backbone of a step-growth polymer

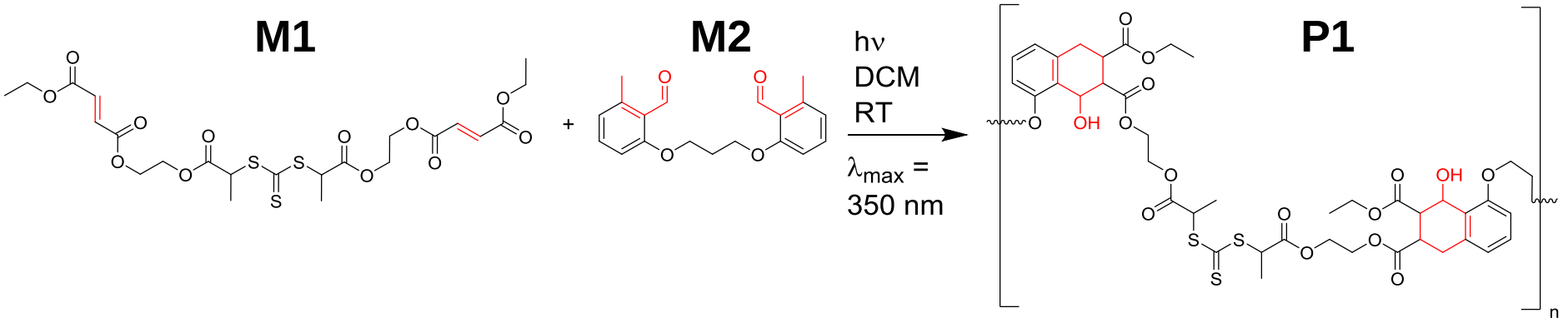




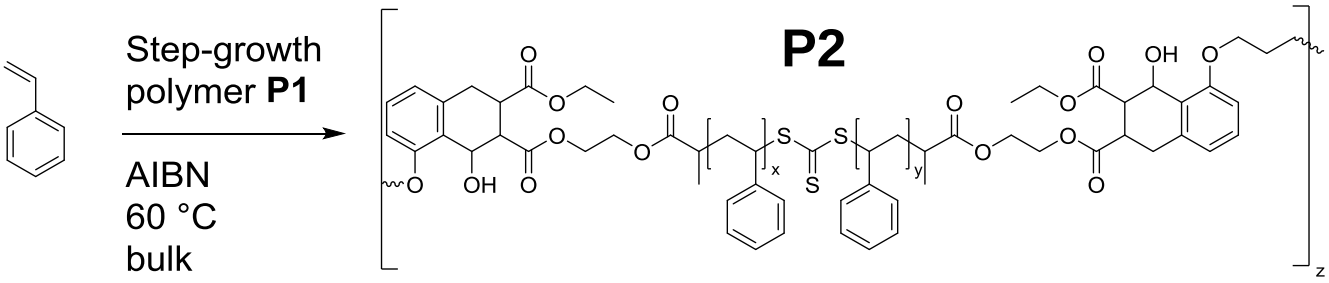


General Polymerization Concept

- Step-growth polymerization using a bifunctional *ortho*-methyl benzaldehyde and a bisfumarate with a trithiocarbonate group

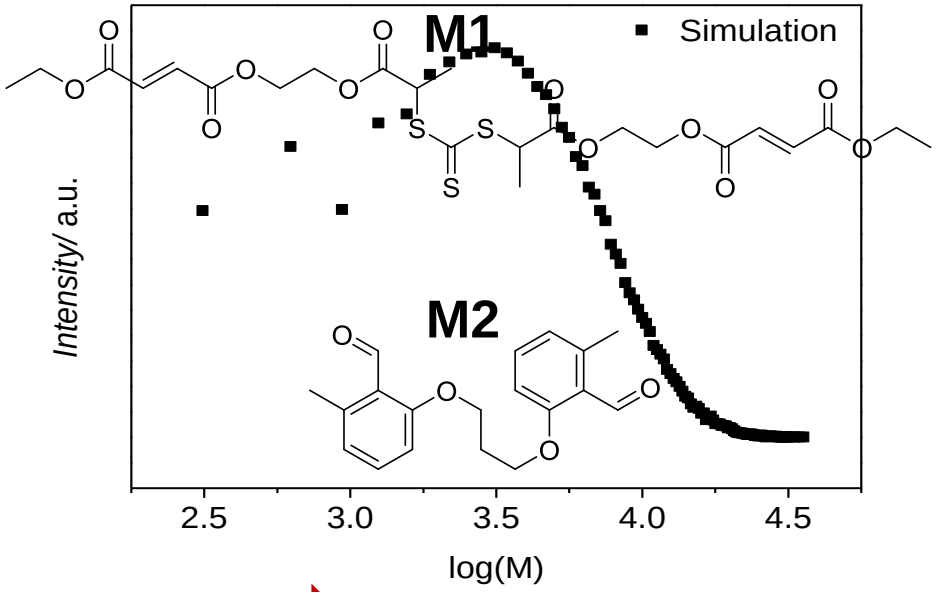


- Chain extension by conventional RAFT polymerization

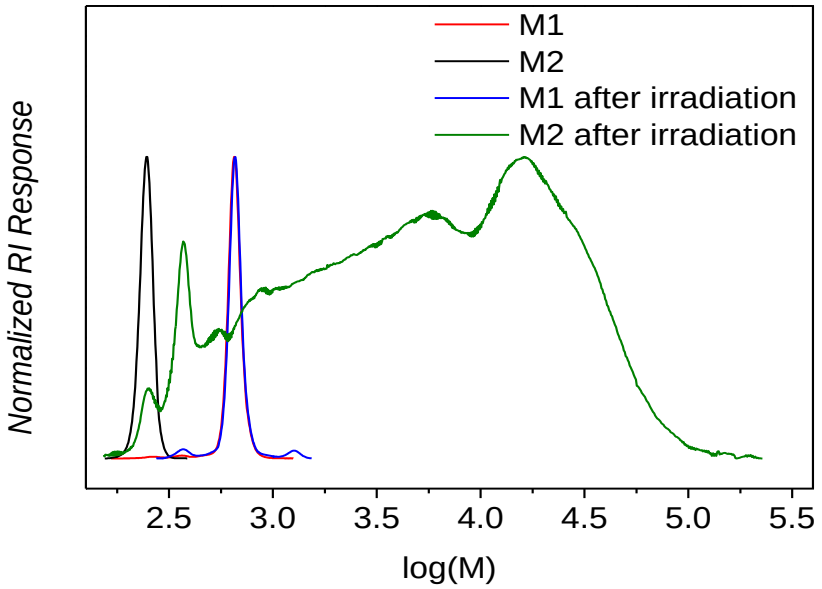


Monomer Stability and Homopolymerization

- Irradiation with conditions for step-growth polymerization of M1 and M2
- Determination of k_{side}



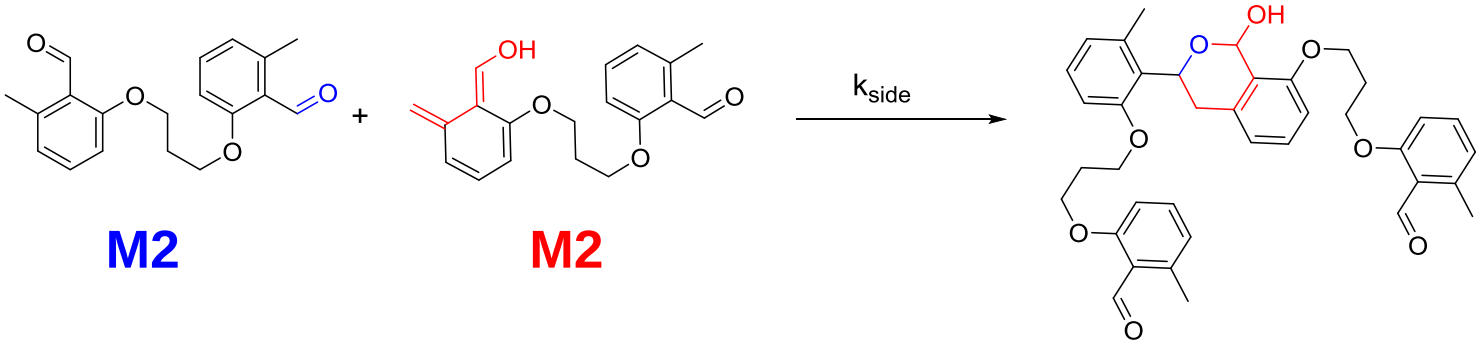
PS calibration



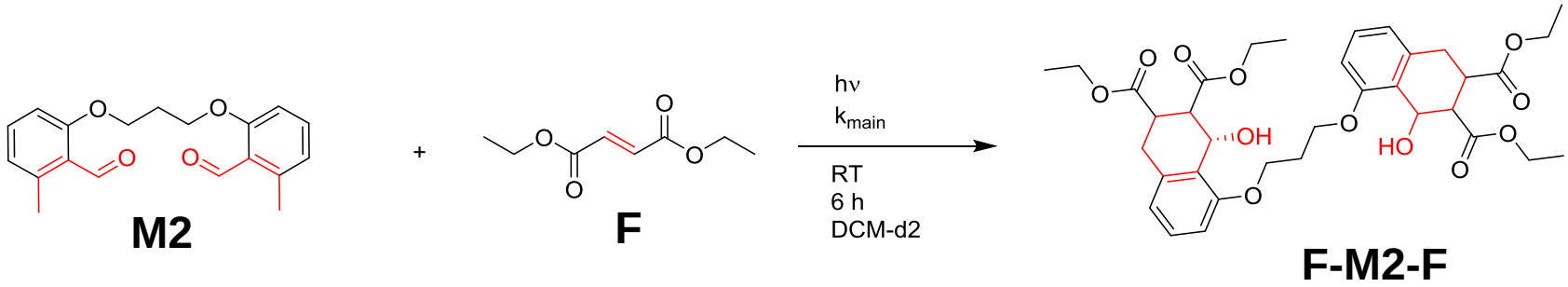
RAFT-fumarate **M1** stable, benzaldehyde **M2** reacts with itself

Side Reactions and k_{side} Determination

- Possible side reactions of activated **M2** *ortho*-quinodimethane and the carbonyl species of the benzaldehyde

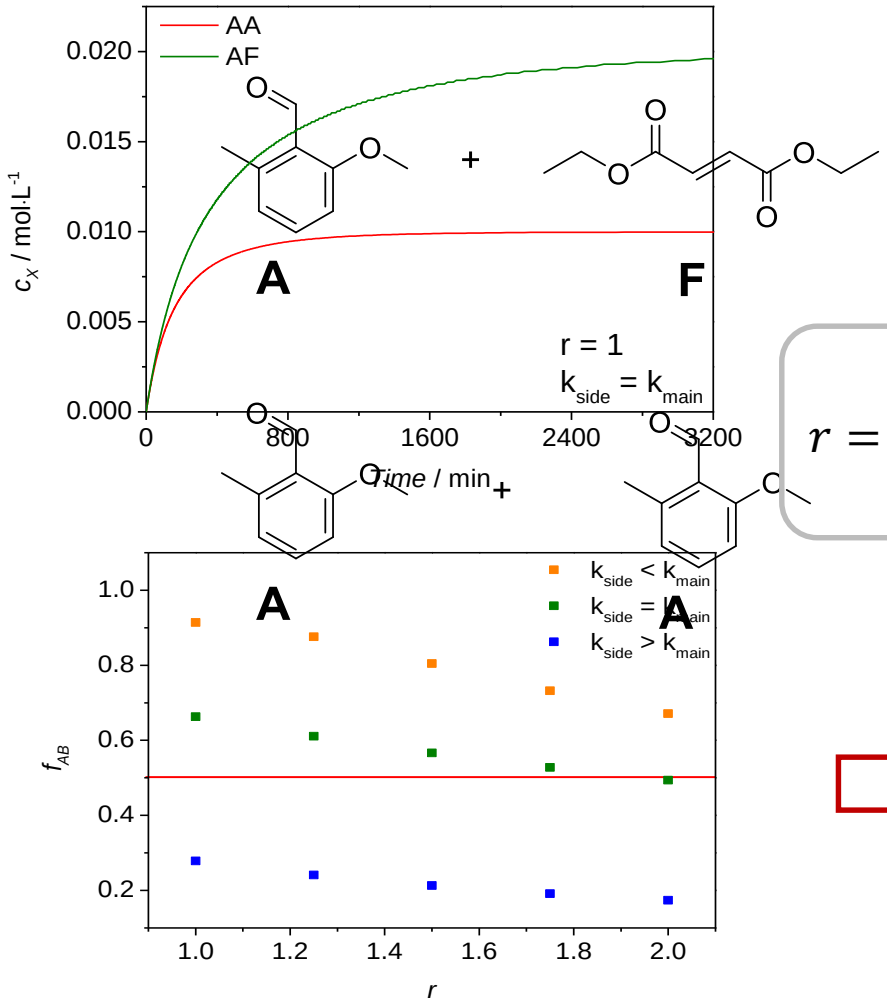


- Determination of k_{main} in relation to k_{side} *via* small molecules

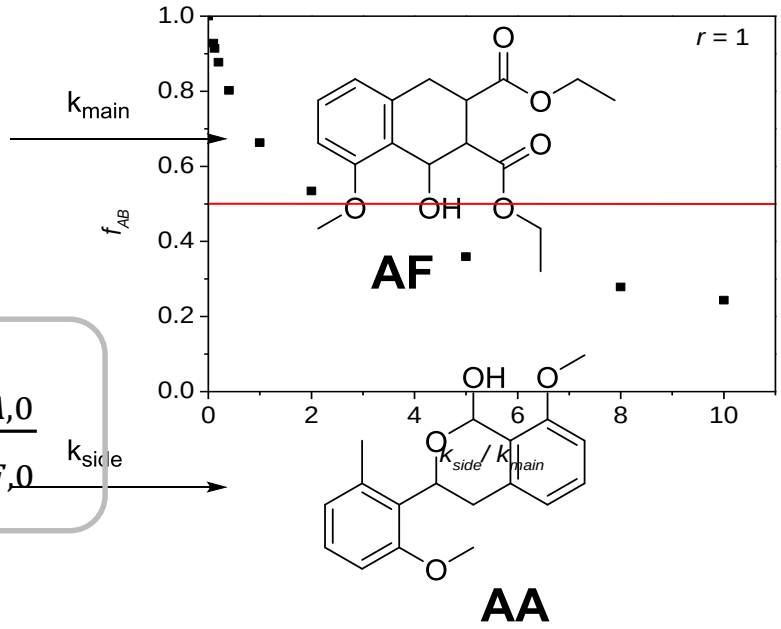


k_{main} vs. k_{side} and Off-Stoichiometry in Simulations

- Side reaction, imbalance and k values

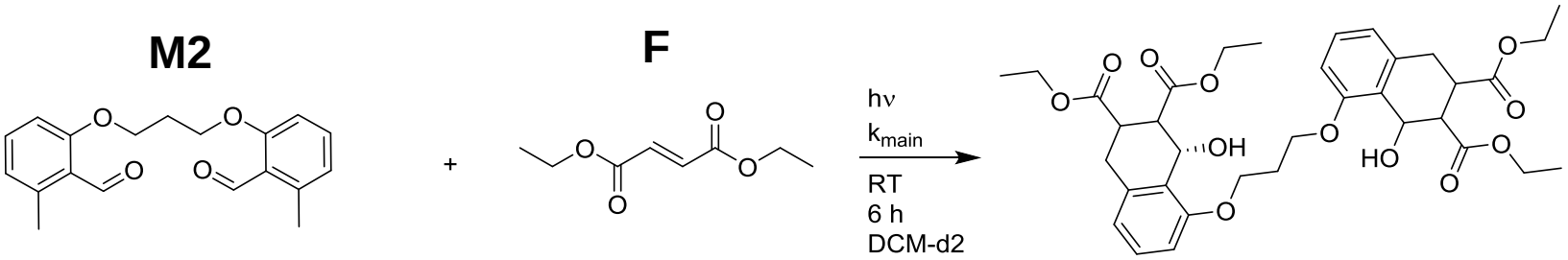


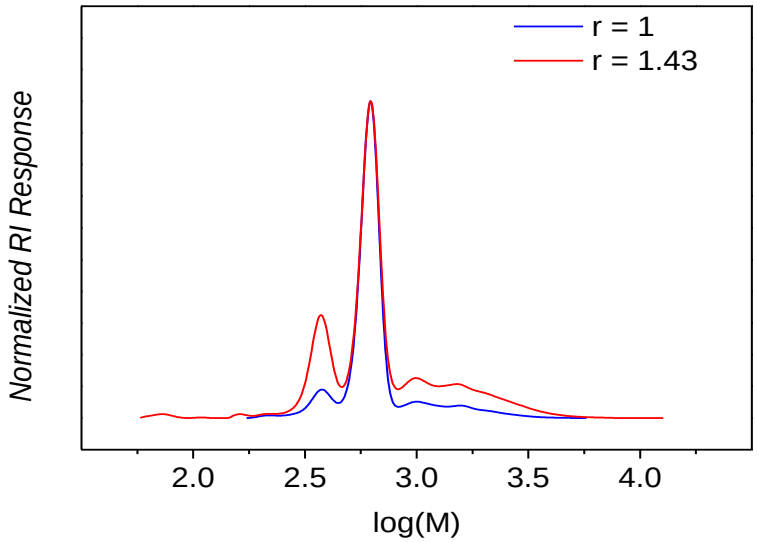
$$r = \frac{N_{A,0}}{N_{F,0}}$$

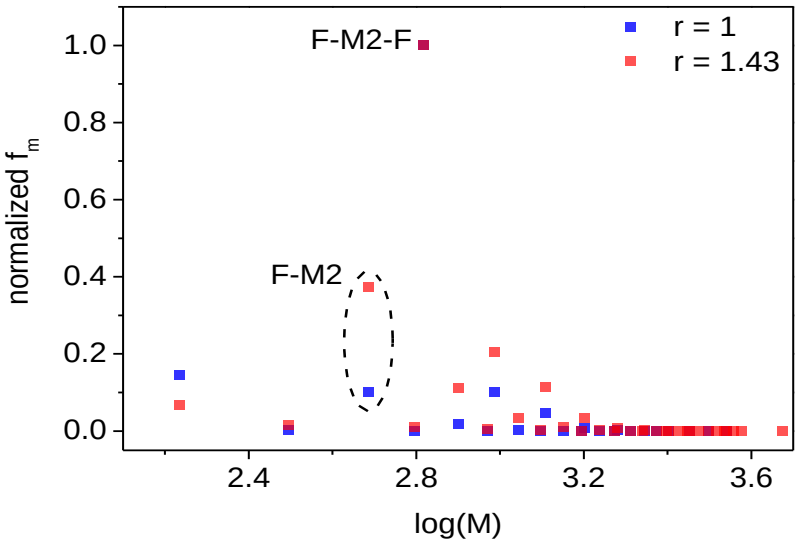


- If k_{side} = k_{main}, still strong suppression of side reaction
- With excess A more side reaction occuring

Small Molecule Reaction: k_{main} Determination



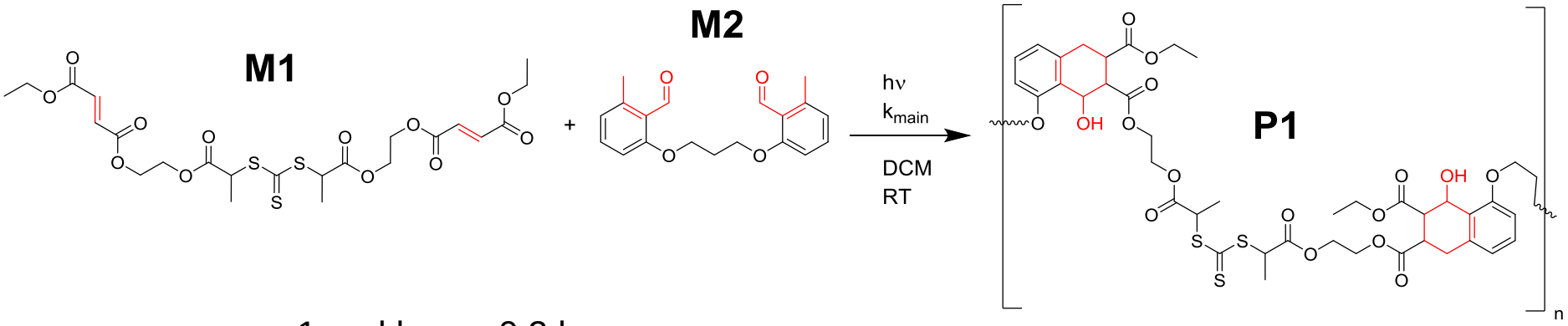


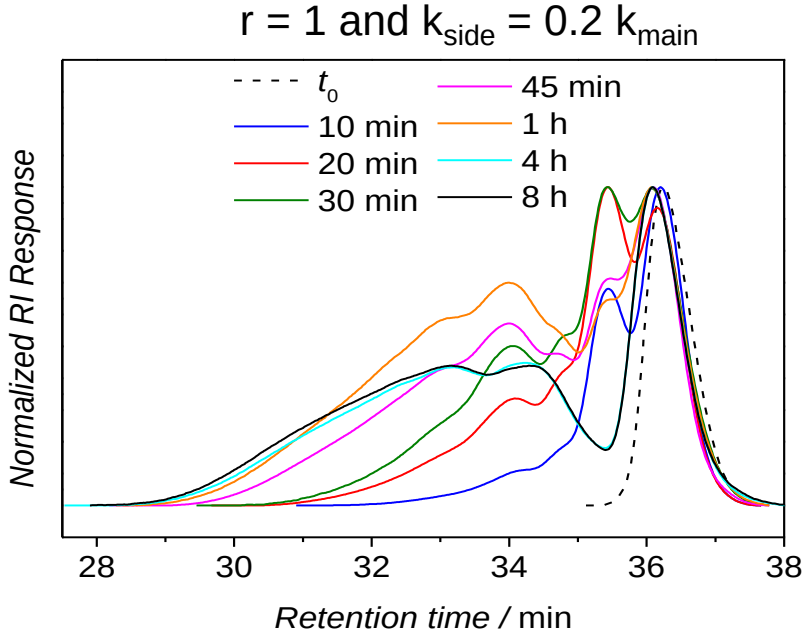


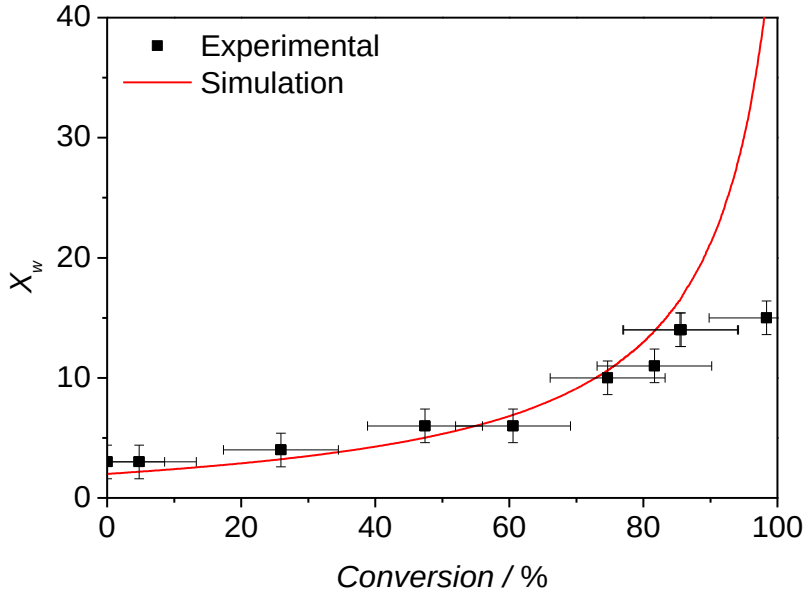
Conversion (NMR): 93 %
Conversion (NMR): 87 %

⇨ **r = 1 with k_{side} = 0.2 k_{main}**

Step-Growth Polymerization Kinetics with Equimolarity

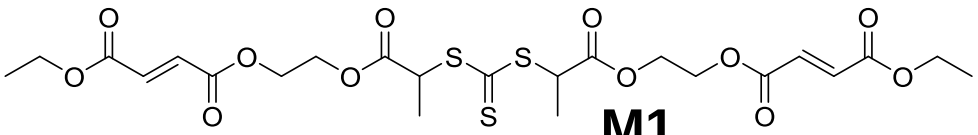




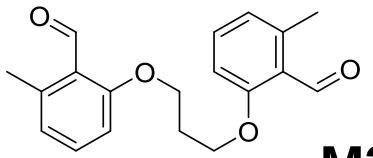


Step-Growth with Imbalance using the Side Reaction

- Increasing the amount of M2 (photoenol)
- Highest M_w for the 1/1.75 ratio of M1/M2 (excess photoenol)
- At ½ ratio decrease of the M_w

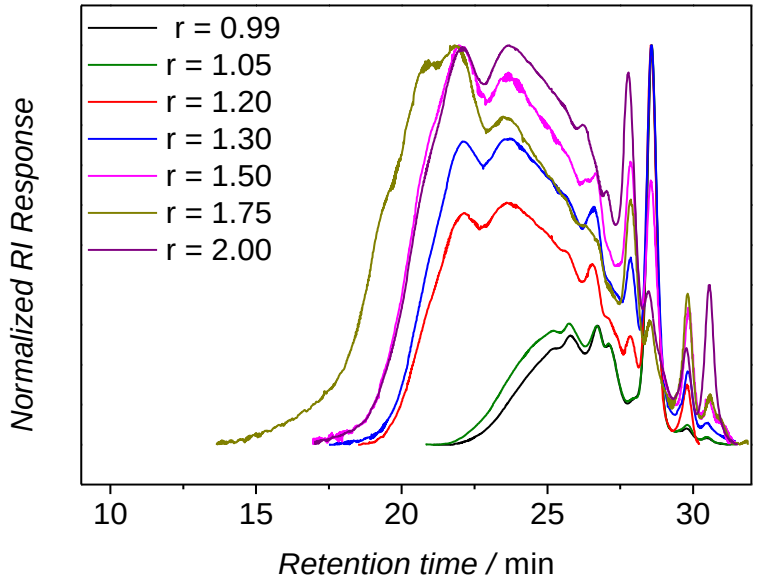


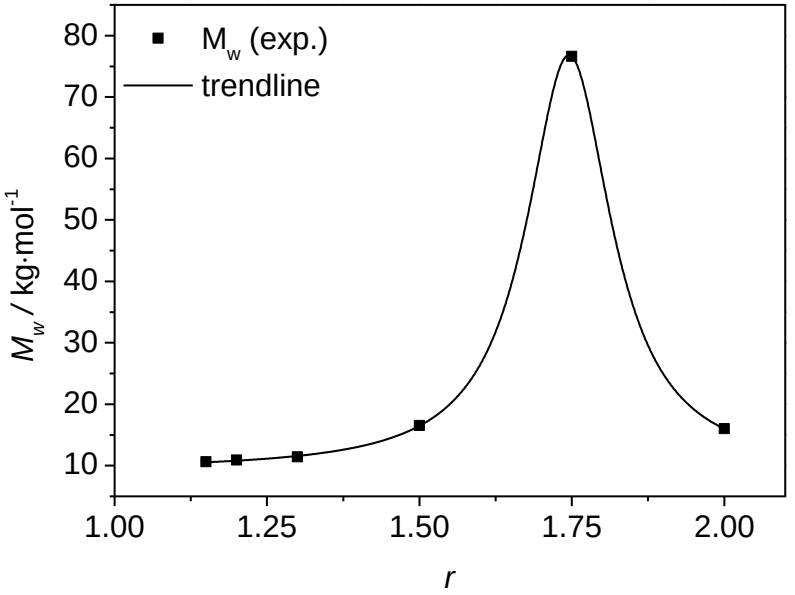
M1



M2

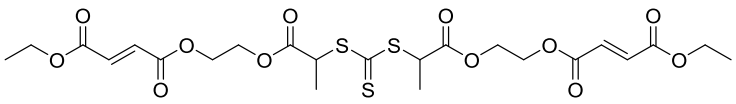
$$r = \frac{N_{M2}}{N_{M1}}$$



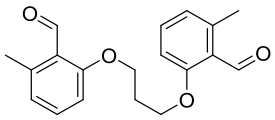


Step-Growth Polymerization with Off-Stoichiometry

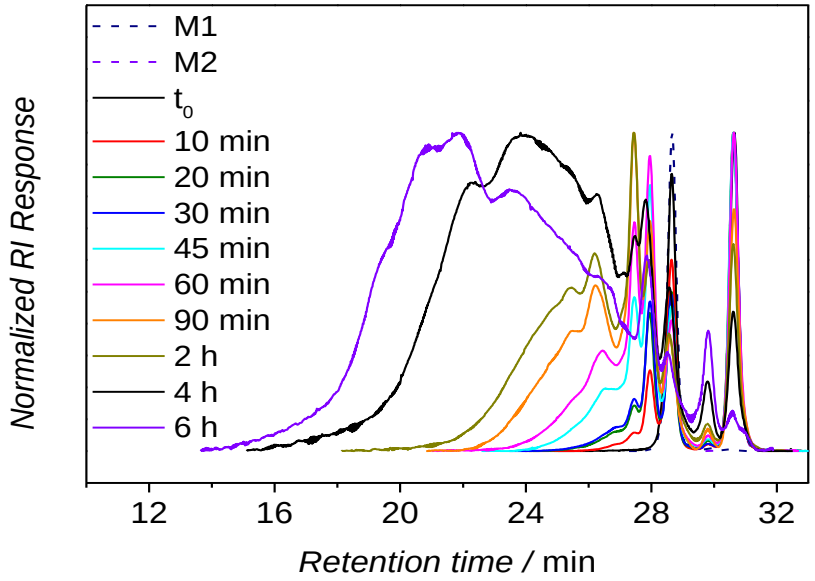
- Excess of M2 (also increased concentration, c(M1) = const.)
- High molecular weight species formed due to coupling of further M2-M2

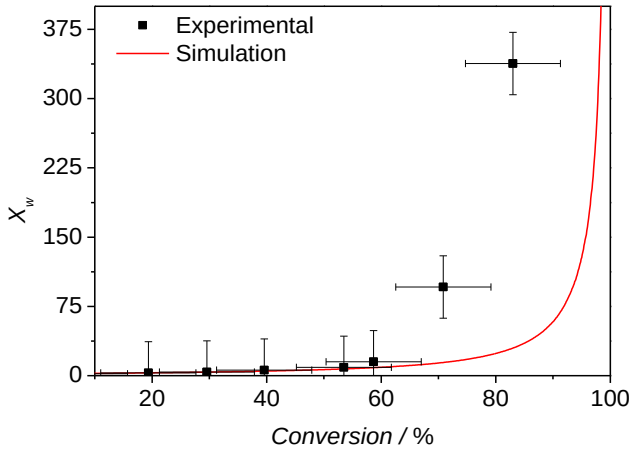


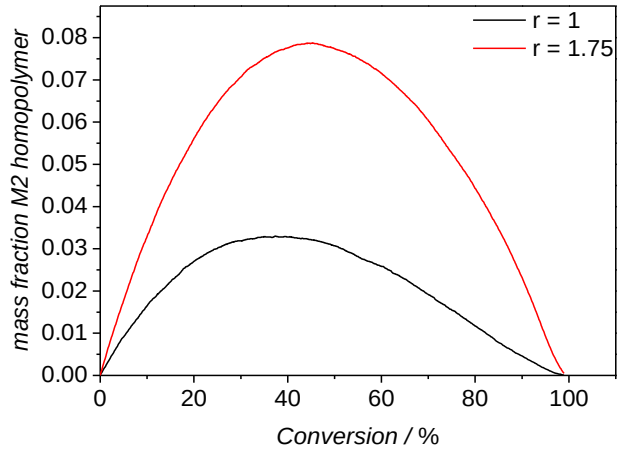
M1



M2



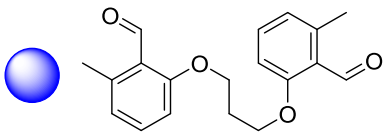




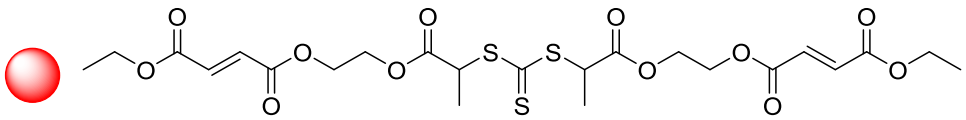
Mechanistic Considerations

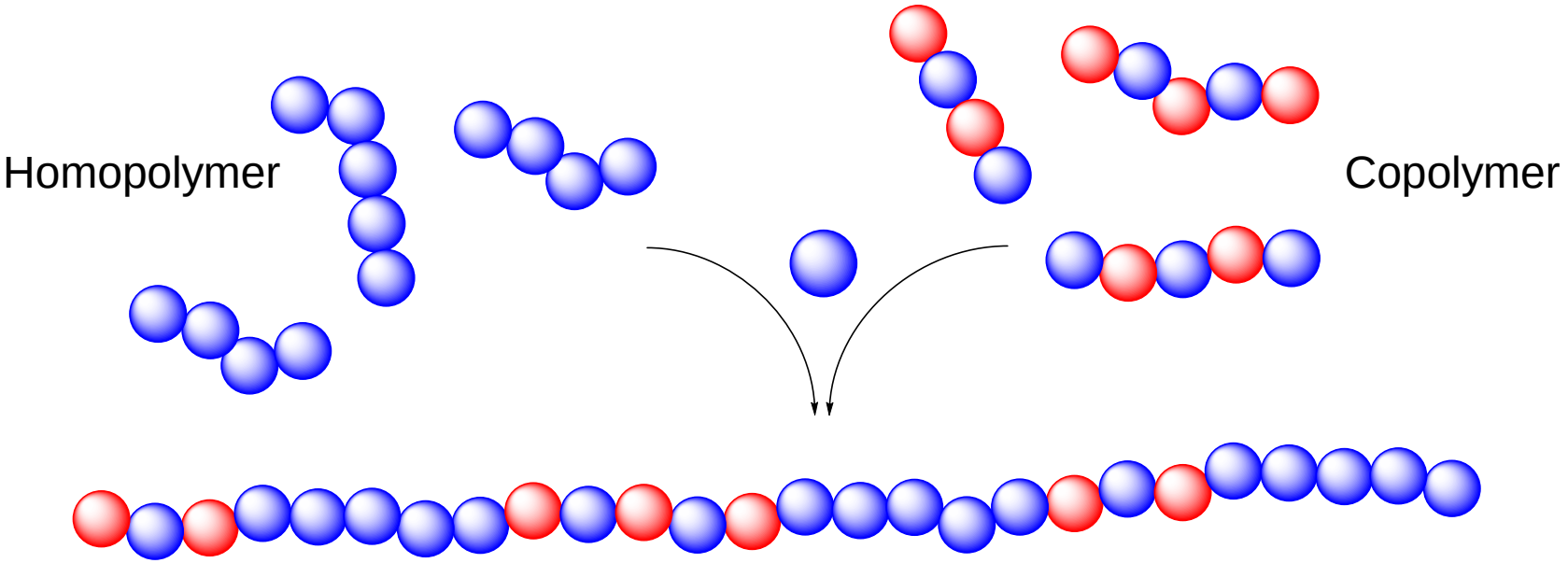
- Insertion of M2M2 homopolymer in M2M1M2M1 (M2+M1) copolymer after exhaustion of M2
- Formation of high molecular species according to Carother

M2



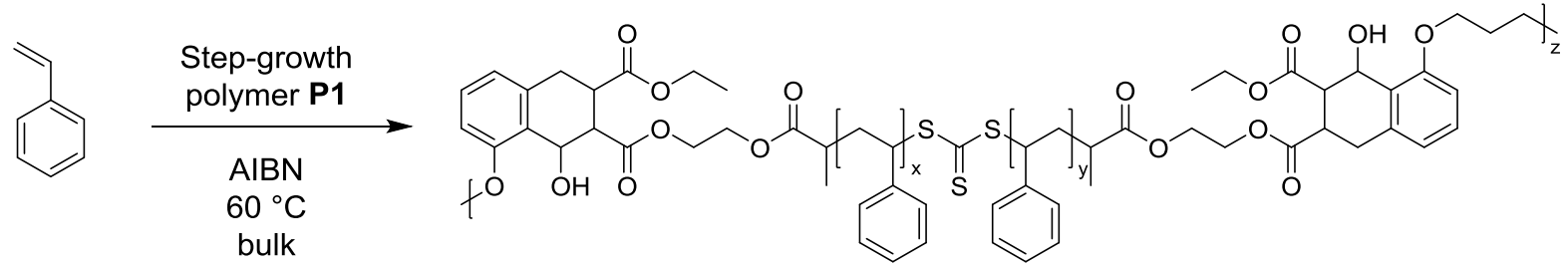
M1

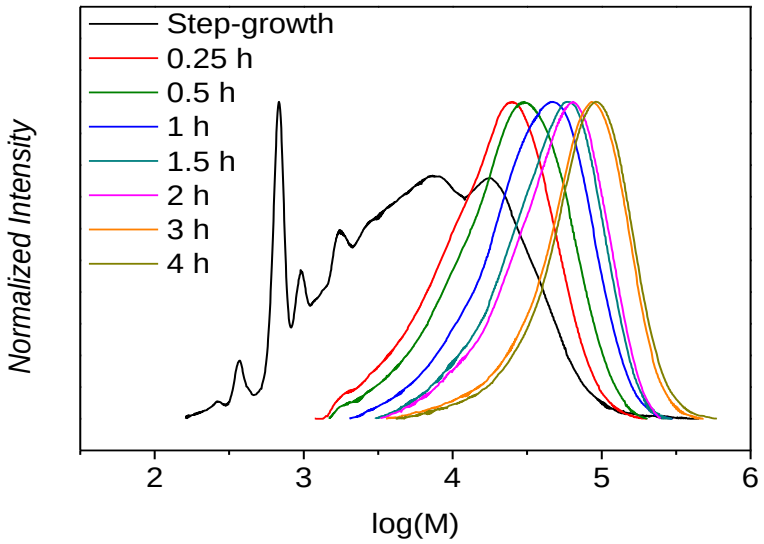


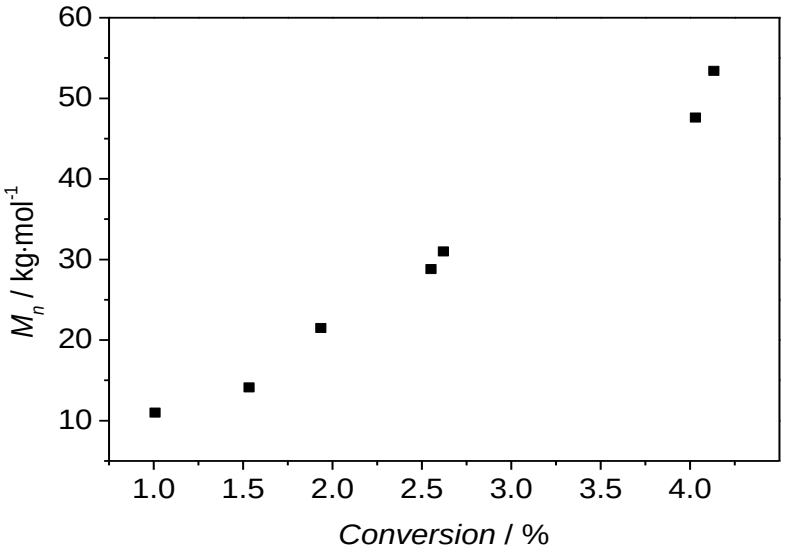


Chain Extension by RAFT Polymerization

- Conventional RAFT polymerization using step-growth polymer with ratio of 1/1.5 M1/M2 (1/1.75 polymer with solubility issues)

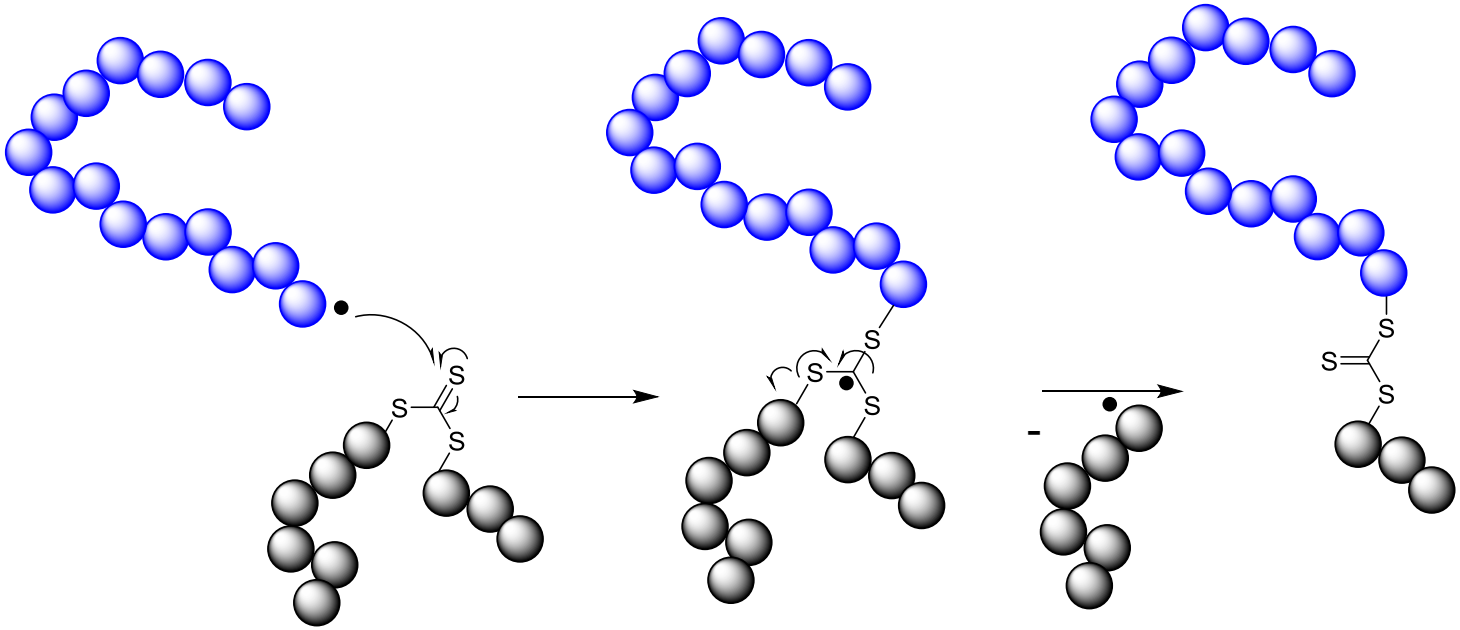






Mechanistic Considerations

- Symmetric trithiocarbonate fragmentation in a random fashion
  - Up to 200 different reactions theoretical taken in account
  - Statistical balancing of chain length by mixing long and short chains during the addition and fragmentation



Summary

- Step-growth polymerization by light-induced reactions
  - Use of *ortho*-quinodimethanes and fumarates
  - Side reaction and theoretical description of k_{side}/k_{main}
  - Off-stoichiometry to obtain high molecular species

- Chain extension by RAFT polymerization
  - Controlled reactio
  - Calculations and simulations currently under investigation
  - High molecular species obtained

Acknowledgements – Barner-Kowollik Team

Baden-Württemberg Stiftung
WIR STIFTEN ZUKUNFT

Prof. Dagmar D´hooge and colleagues

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