UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Model-based design of homogeneous MADIX/RAFT polymerization of styrene

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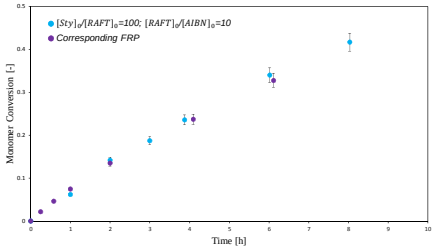
Scope

Stochastic and deterministic modeling tools are applied to allow for a detailed kinetic analysis and design of reversible addition fragmentation chain transfer **(RAFT)** polymerization or macromolecular design by interchange of xanthates **(MADIX)** with O-ethylxanthyl ethylpropionate as RAFT agent and styrene as reference monomer under homogeneous conditions.

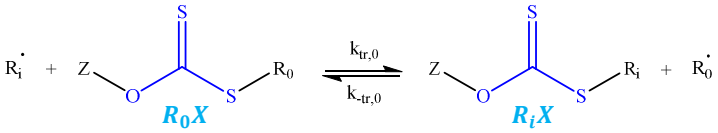
RAFT/MADIX Polymerization Principle

In the class of reversible deactivation radical polymerization techniques, RAFT and MADIX polymerizations have proven to be the most versatile processes in terms of the reaction conditions, the variety of monomers for which microstructural control can be achieved, tolerance to functionalities, and the range of polymeric architectures that can be produced. Excellent **control over chain length and end-group functionality** can often be obtained due to the inherent reversible transfer process of these techniques.

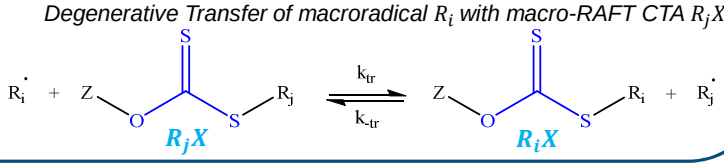


Justification degenerative model

Degenerative Transfer of macroradical R_i with RAFT CTA R_0X



Degenerative Transfer of macroradical R_i with macro-RAFT CTA R_jX



Kinetic Model

Dissociation:

$$I_2 \rightarrow 2I^\bullet$$

Chain Initiation

$$I^\bullet + M \rightarrow R_1^\bullet$$
$$R_0^\bullet + M \rightarrow R_1^\bullet$$

Propagation:

$$R_i^\bullet + M \rightarrow R_{i+1}^\bullet$$

RAFT Exchange:

$$R_i^\bullet + R_0T \rightarrow R_iT + R_0^\bullet$$
$$R_i^\bullet + R_jT \rightarrow R_iT + R_j^\bullet$$

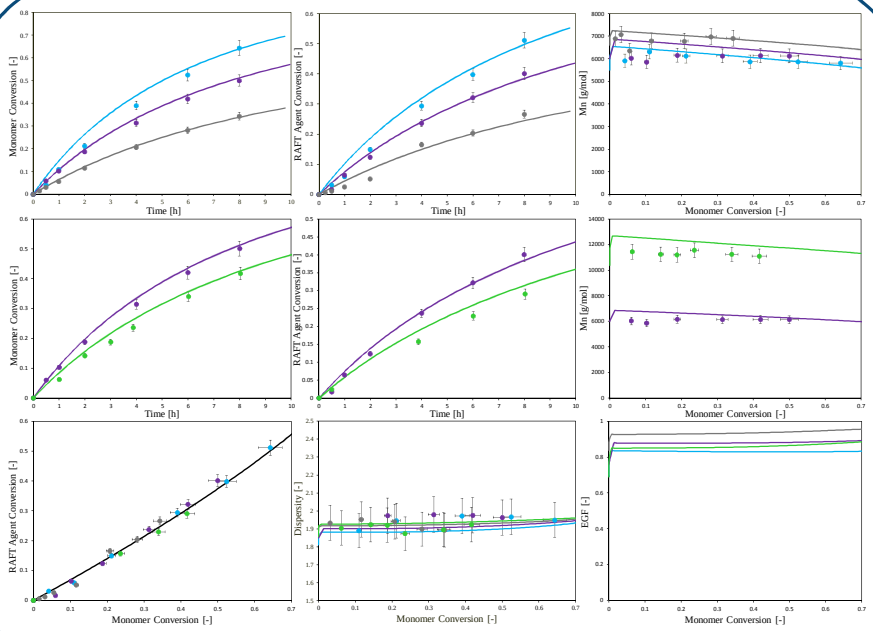
Chain Transfer:

$$R_0^\bullet + M \rightarrow R_1^\bullet + P_0$$
$$I^\bullet + M \rightarrow R_1^\bullet + P_0$$
$$R_i^\bullet + M \rightarrow R_1^\bullet + P_i$$

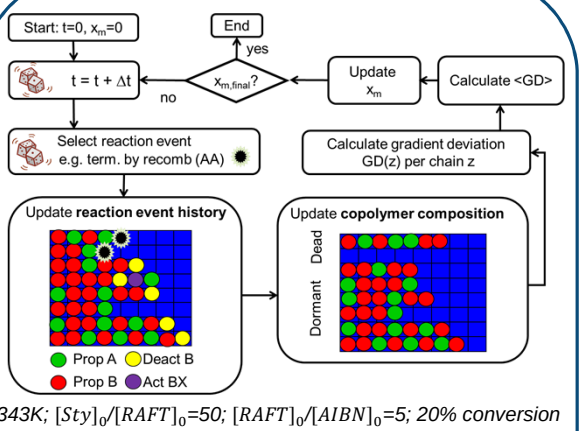
Termination:

$$R_0^\bullet + R_0^\bullet \rightarrow P_0$$
$$R_0^\bullet + R_i^\bullet \rightarrow P_i$$
$$R_i^\bullet + R_j^\bullet \rightarrow P_{i+j}$$

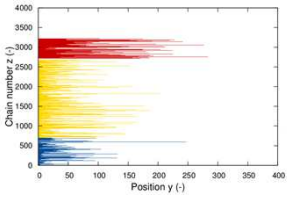
Parameter Tuning via Deterministic Modeling



Microstructural Information via Stochastic Modeling



343K; $[Sty]_0/[RAFT]_0$=50; $[RAFT]_0/[AIBN]_0$=5; 20% conversion



- Chain terminated by recombination
- Dormant chain initiated by $R_0^\bullet$
- Dormant chain initiated by $I^\bullet$

[1] P. H. M. Van Steenberge, D. R. D'hooge, Y. Wang, M. Zhong, M.-F. Reyniers, D. Konkolewicz, K. Matyjaszewski, and G. B. Marin, "Linear Gradient Quality of ATRP Copolymers", Macromolecules, 2012.
[2] D. R. D'hooge, P. H. M. Van Steenberge, M.-F. Reyniers, and G. B. Marin, "The strength of multi-scale modeling to unveil the complexity of radical polymerization", Prog. Polym. Sci., 2016.

Conclusions

Deterministic and stochastic modeling techniques are successfully applied to design homogeneous degenerative RAFT/MADIX polymerization processes, including for the first time visualization of the composition of individual chains. Although **no linear growth of chain length** can be observed, varying the initiator and RAFT/MADIX agent concentrations allows regulation of the polymerization rate and degree. **High end group functionalities** are obtained under the complete range of investigated conditions, that resulted in **high dispersities**, confirmed by stochastic modelling. The obtained modeling results are useful in order to achieve in-depth knowledge of the RAFT/MADIX process, which should allow on a longer term an accelerated transition to RAFT/MADIX emulsion polymerization, permitting in particular the synthesis of better-defined block copolymer structures.

Acknowledgments

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