

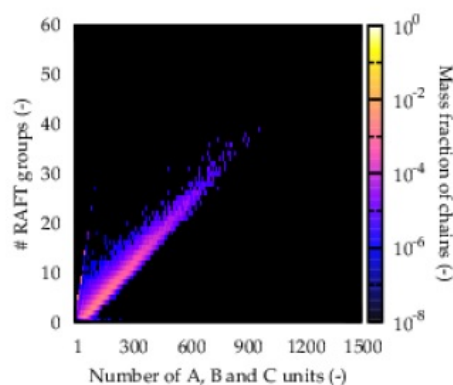
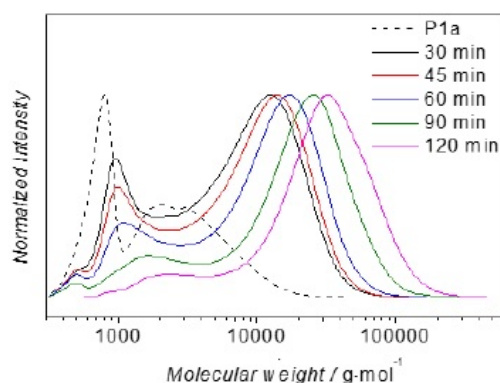
A KINETIC UNDERSTANDING OF THE COMBINATION OF LIGHT-DRIVEN STEP-GROWTH AND RAFT POLYMERIZATION

Lies De Keer (1), Thomas Gegenhuber (2), Paul H.M. Van Steenberge (1), Anja S. Goldmann (2), Marie-Françoise Reyniers (1), Christopher Barner-Kowollik (2,3), Dagmar R. D'hooge (1,4)

- 1) Department of Materials, Textiles and Chemical Engineering, Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Zwijnaarde (Ghent), Belgium
 2) Preparative Macromolecular Chemistry, Institute for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76128 Karlsruhe, Germany
 3) School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD 4000, Australia
 4) Department of Materials, Textiles and Chemical Engineering, Centre for Textile Science and Engineering, Ghent University, Technologiepark 907, B-9052 Zwijnaarde (Ghent), Belgium

Over the last decade, the development of new synthesis strategies in polymer science has expanded with the aim to increase efficiency, complexity and precision control. Combining light-induced chemistry via a step-growth mechanism and reversible deactivation radical polymerization (RDRP) is one promising approach. Step-growth polymerization can however suffer a lack of control since all functional groups can in principle react in an uncontrolled manner. Furthermore, the success of a step-growth polymerization is strongly dependent on the stoichiometry of the functional groups. Therefore, step-growth polymerization has been rarely explored in polymer design.

In this work, a unique combination of light-induced step-growth polymerization and RDRP is presented, aiming at microstructural control of the polymer product. To accomplish the light-induced polymerization Diels-Alder chemistry is used, *i.e.* ortho-methyl benzaldehydes (AA) are combined with electron deficient enes such as fumarates (BB) bearing a trithiocarbonate group. The reactivity of the benzaldehydes is based on the light-triggered isomerization of an o-methyl-substituted aromatic aldehyde into an o-quinodimethane species carrying a highly reactive diene functionality that undergoes a Diels-Alder reaction with a fumarate group [1]. Since a bisfumarate molecule is selected with a trithiocarbonate group, the step-growth polymerization generates macro-RAFT species enabling a subsequent chain extension via RAFT polymerization (monomer: styrene; C) within the polymer chains.



The structure of the polymer product is analyzed in detail via size exclusion chromatography (SEC; see figure: left), nuclear resonance spectroscopy (NMR) and electrospray ionization mass spectroscopy (ESI-MS), evidencing the different polymerization mechanisms. Subsequently, stochastic modeling tools are applied to allow for a detailed kinetic analysis, allowing for the first time the mapping of the evolution of the number of RAFT groups and styrene insertions per chain length (see figure: right). RAFT-specific parameters are determined based on an extensive set of experimental polymerization data on chain extension and a complex reaction scheme consisting of more than 200 reactions. Good agreement between experimental and simulated data is obtained. The modeling results are useful in order to achieve in-depth knowledge of the chain extension possibilities.

References

- 1) Gruendling, T.; Oehlenschlaeger, K. K.; Frick, E.; Glassner, M.; Schmid, C.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2011**, *32*, 807–812.