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

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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