

NEW PERSPECTIVES FOR STEP-GROWTH POLYMERIZATION: LIGHT DRIVEN STEP-GROWTH FUSED WITH CHAIN EXTENSION VIA RAFT POLYMERIZATION

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The development of new synthetic strategies in polymer is critical for modern soft matter materials design, with the aim to increase efficiency, complexity and precision control. The design and synthesis of tailor-made polymers requires a variety of synthetic methodologies to fine-tune the polymer microstructure and adjust its final properties. In this field, step-growth polymerization has been rarely explored since it suffers lack of control. Furthermore, the success of a step-growth polymerization is strongly dependent on the stoichiometry of the functional groups.

In the current study, a unique combination of light-induced step-growth and reversible deactivation radical polymerization is presented, aiming at microstructural control of the polymer product. To accomplish the 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 (see Figure 1(a)).

A series of different step growth polymers are synthesized, illustrating the impact of side reactions of the benzaldehyde, justifying the experimental observation of higher molar masses if using an excess of the benzaldehyde. The structure of the polymer product after chain extension is analyzed in detail via size exclusion chromatography (SEC), 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 1(b)). 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.

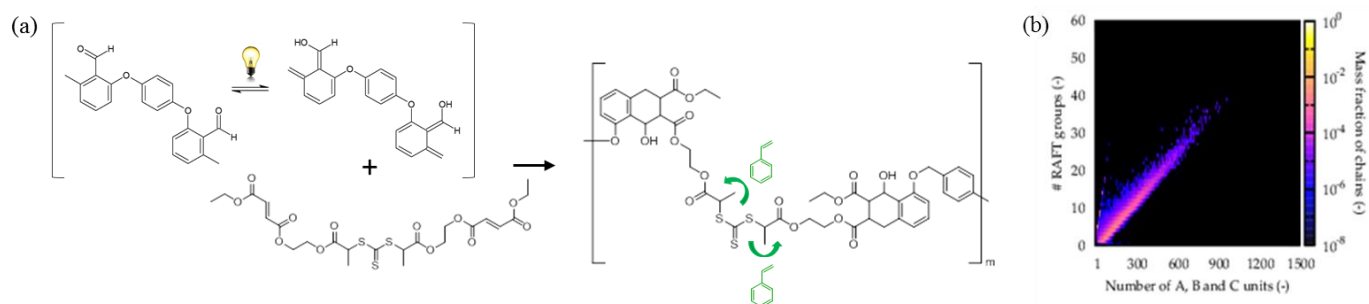


Figure 1. (a) Reaction pathway; (b) Chemical composition chain length distribution