Model-based study of 2-oxazolines CROP with special attention to side reactions

Francisco J. Arraez, Paul H. M. Van Steenberge, Xiaowen Xu, Valentin-Victor Jerca, Richard Hoogenboom, Dagmar R. D'hooge, Ghent University, Belgium

Poly(2-oxazolines) (PAOx) are an interesting bioinspired class of polymers whose biocompatibility allows for drug, protein and gene delivery applications. PAOx are available through cationic ring-opening polymerization (CROP) of 2-oxazolines representing an easy and key strategy for the synthesis of well-defined polymers with controlled average polymer composition, narrow size exclusion chromatography (SEC) trace and suitable end-group functionalities. Due to the living nature of CROP and by the incorporation of the correct 2-oxazoline comonomer, a wide variety of linear as well as branched/network (co)polymers can be synthesized with well-tailored structures and less abrupt transitions from one comonomer type to the other. Even so, a key challenge to be dealt with consists of evaluating the PAOx synthesis success at the molecular level, hence, beyond experimentally accessible average CROP characteristics.

In this contribution [1-3], a combination of an advanced kinetic Monte Carlo modeling technique with meticulous experimental analysis is covered, allowing the kinetic analysis of CROP of 2-oxazolines, with specific focus on functionality design per chain length and the effect of side reactions such as chain transfer to monomer (β-elimination) and macropropagation. A novel parameter tuning is introduced with for the first time reliable macropropagation rate coefficients based on complete SEC data. Model-based design is shown to be an effective strategy to identify optimal synthesis conditions that maximize the functionality efficiency for both low and high targeted chain lengths.

1. P.H.M. Van Steenberge, B. Verbraeken, M.F. Reyniers, R. Hoogenboom, D.R. D'hooge Macromolecules 2015, 48, 7765
2. P.H.M. Van Steenberge, J. Hernandez-Ortiz, B. Verbraeken, M.-F. Reyniers, R. Hoogenboom, D.R.D'hooge Nat. Commun. 2019, to be submitted
3. F.J. Arraez, X. Xu, P.H.M. Van Steenberge, V.V. Jerca, R. Hoogenboom, D.R. D'hooge Macromolecules, 2019, submitted