**On the modeling of the kinetics of high-functionality biopolymers. Application to the polycondensation of sugars**

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**Highlights**

* Industrial polycondensation process of sugar syrups of various compositions.
* Kinetic/topological Monte Carlo modeling framework.
* Dynamic evolution of the exact position and type of each bond of all species.
* Generalized framework, not limited to low-degree oligosaccharides.

**1. Introduction**

Polycondensation reactions of oligosaccharides are important in several application fields, such as fuel synthesis or food processing. They are generally carried out in the presence of acid catalysts, in temperatures varying roughly within the range of 100 oC – 200 oC. Nevertheless, despite their industrial importance, only few kinetic modeling studies are found in the literature [1]. In fact, the primary monomer unit of these reactions is glucose, dominantly found in the form of glucopyranose, which is a cyclic molecule containing five –OH groups, all susceptible to react. Hence, the –OH group in the position 1 of the molecule (i.e., with respect to the anomeric carbon atom) is prone to receive a proton from the –OH group of another glucose molecule, thus eventually forming a glucosidic bond with the parallel release of a water molecule. Such bonds can be formed between the C1 atom of the first glucose and any other C atom of the second glucose, found in positions 1, 2, 3, 4 or 6. In addition, the stereochemistry of the formed bond can be either in α- or β- position, resulting in two kinds of stereoisomer products from each type of bond. This means that nothing but the simple reaction between two single glucopyranose units may result in as much as 11 different disaccharides. At the same time, a series of internal ring-closure reactions of the glucose units that result in structurally different, inert anhydrosugars, further complicate the landscape of this reaction system, before even attempting to extend the study to the reactions of disaccharides, trisaccharides, etc. In the present work, a novel modeling framework is proposed for the simulation of the polycondensation reactive systems of sugars, capable of taking into account the above-described complexity.

**2. Methods**

The complexity of the system relies primarily on the fact that the each type of glucosidic bond that is formed during the reaction (i.e., α-1-1, β-1-1, α-1-2, etc.), is dictated by a different formation and hydrolysis rate (i.e., mainly due to steric factors). In this respect, in order to be able to accurately follow the dynamic kinetic developments in the reactor, with respect to the operating conditions and the initial syrup composition, it is crucial to follow all the relevant information concerning the different species concentrations as well as their specific structural characteristics. The first of the above is relatively trivial to achieve via the implementation of any modeling framework that defines the problem through a population-balance perspective. On the contrary, the tracking of the structural information requires an approach capable of treating, in addition to the species concentrations, the associated multi-dimensionality (i.e., expressed in terms of the different bonding positions and stereochemistry of the glucose units). Such a modeling approach has been previously developed and applied on the industrial polymerization paradigm of low-density polyethylene (LDPE) [2]. The developed kinetic/topology Monte Carlo (MC) algorithm, which was implemented in this case to follow the branching architectural developments of LDPE, is adapted in this work to the specificities of the sugars polymerization system.

**3. Results and discussion**

The modeling predictions were compared against a series of experimental data produced in an industrial pilot-scale reactor, under varying conditions. Some preliminary results on the evolution of the average molecular weight and the molecular weight distribution are given in Figure 1.

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**Figure 1.** Evolution of the a) number-average molecular weight and a) molecular weight distributions of the formed oligosaccharides. Comparison between experimental data and MC simulations.

**4. Conclusions**

In the present work, a novel modeling framework is proposed for the kinetic developments of the polycondensation of sugars. This modeling framework relies on the implementation of a powerful kinetic/topological Monte Carlo technique, previously applied for the description of the molecular architecture of industrially-produced highly-branched LDPE. The preliminary results of the study show that, for the first time, an accurate description of the system can be achieved and the compositional and molecular weight evolution can be accurately tracked even for oligosaccharides of relatively high degree of polymerization.

**References [Calibri 10]**

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