

Editorial

Special Issue: Modeling and Simulation of Polymerization Processes

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This Special Issue (SI) of Processes on Modeling and Simulation of Polymerization Processes (MSPP), and the associated Special Issue reprint, contain papers that deal with this very important area of scientific investigation in polymer science and engineering, both in academic and particularly industrial environments.

Polymer reaction engineering (PRE), also known as macromolecular reaction engineering (MRE), is the branch of engineering that deals with the technology of large-scale polymer production and the manufacture of polymer products through polymerization processes. PRE is a broad and multidisciplinary area, which combines polymer science, chemistry, and technology with the principles of process engineering. The practical history of PRE started and evolved during the first half of the twentieth century. The 1930s were rich with theoretical findings in polymer science and engineering, and with the commercial production of several new polymers. These investigations would transform our understanding of polymer manufacture and culminate in the development of several continuous polymerization processes and the establishment of PRE as a new area of research in the 1940s. The period from 1950 to 1990 saw the continued growth and evolution of process technologies, largely stimulated by the combination of PRE principles with the fundamental understanding of polymerization kinetics developed in earlier years. These principles include the development of mathematical models for polymerization processes, and their solution using mathematical packages or specialized chemical engineering or polymerization software. MSPP has been fundamental in the development of polymerization technologies since the early stages of PRE to date.

Previous issues of Processes on PRE have focused on recent specialized topics [1–6]. This Special Issue on MSPP aimed to address both new findings on basic topics as well as modeling of emerging aspects of product design and polymerization processes. In spite of rather adverse times for academic paper publishing (the COVID-19 pandemic slowed down academic and all types of activities globally), and the call for special issues on PRE topics in other journals that appeared soon after our call had been released (e.g., [7], where we also contributed), and the fact that potential contributions from emerging countries were indirectly discouraged by Processes (by not providing fee discounts to contributions from these countries), nine interesting papers were published in this SI nonetheless.

A brief description of content and contributions of each of the nine contributed papers from this SI is offered below.

The first contributed paper addresses the reversible deactivation radical polymerization (RDRP) of methyl methacrylate (MMA) using dithiolactone controllers, which in principle should follow a reversible addition-fragmentation chain transfer (RAFT) radical polymerization mechanism [8]. The authors claim that the system can be well represented by reversible addition, thus neglecting fragmentation, a mechanism simplification which



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has been questioned. Although the agreement between calculated and experimental data was only moderate, considering a single set of parameters for a wide window of reaction conditions, there are several interesting ideas and arguments in the discussion: (i) model discrimination in RAFT polymerization is not a straightforward issue and typical experimental data are not enough to discriminate among rival models; (ii) although it should be standard practice, the authors remind us that robust mathematical models should provide adequate description of broad windows of operating conditions with a single set of parameters, and not tuning the parameters for each experimental condition; (iii) full molecular weight distributions (MWD) should be used for model validation purposes; and (iv) as much as possible, independent experimental measurements should be sought (for instance, radical concentration measurements by EPR provided insightful information for the analysis of model completeness).

In the second contribution, Ordaz-Quintero et al. [9] compared the pyrolysis of polystyrene (PS) and a modified PS obtained by adding a nitroxide-end moiety (e.g., TEMPO) (PS-T), hypothesizing that by using PS-T, the initiation process to produce monomer (unzipping) during the pyrolysis process at temperatures above the ceiling temperature of PS (310 °C) would be enhanced due to the tendency of PS-T to activate at the nitroxide end at high temperatures. To test this hypothesis, PS-T was prepared in their lab by nitroxide-mediated polymerization (NMP), and regular PS was synthesized by conventional free-radical polymerization (FRP) and the two types of materials were subjected to their thermal pyrolysis process. They found that the yield of styrene increases from ~33% in the case of dead polymer, to ~38.5% for PS-T (a yield enhancement of 15–16%). Not only did they provide an innovative use of NMP for adding value to plastic waste by pyrolysis of the waste material, but they also presented mathematical models for the pyrolysis of PS and PS-T. They also carried out parameter sensitivity analyses and data fitting, observing adequate agreement with the experimental trends observed.

The third contribution deals with the detailed modeling of the polymerization of non-ionized acrylic acid in aqueous solution [10]. The polymerization process considered is initiated by a persulfate/metabisulfate redox couple and the kinetic scheme considers the possible formation of mid-chain radicals and transfer reactions. The proposed model is validated using experimental data collected in a laboratory-scale discontinuous reactor. The developed kinetic model is then used to intensify the discontinuous process by shifting it to a continuous one based on a tubular reactor with intermediate feeds. One of the experimental runs is selected to show how the proposed model can be used to assess the transition from batch to continuous processes and allows a faster scale-up to industrial scale. This is a nice example of innovative changes in operation of a reasonably well-established polymerization processes. Particularly, the initiating system is non-standard, and the approach adopted to transfer the discontinuous production to a continuous one is relatively new and thus represents an interesting application of the proposed methodology.

In the fourth contribution, Seyedi et al. present a comprehensive study on the effect of initiator feeding policies on polymerization rate and molecular weight development in the semibatch homopolymerizations of styrene and MMA using a highly effective and flexible Monte Carlo algorithm developed in their work [11]. This is also a nice example of gaining deeper understanding and new knowledge about apparently fully understood processes, using novel mathematical approaches. The approach is general and can easily be applied to a variety of polymerizations.

The radical homopolymerization kinetics of 3-(methacryloylaminopropyl) trimethylammonium chloride (MAPTAC) and its batch copolymerization with nonionized acrylic acid (AA) in aqueous solution are extensively investigated and modeled in the fifth contribution of this issue [12]. This contribution is part of a series of papers on the copolymerization kinetics of cationic monomers published by the authors in different journals to broaden and generalize the knowledge of these systems. The novelty in this case is the use of a different cationic monomer (MAPTAC), compared to the earlier studies from the same group. One of the unique aspects of this contribution is the way in which an

otherwise conventional free radical copolymerization kinetics modeling framework is soundly adapted to the presence of cationic monomers and their ion-related features.

The sixth contribution of this issue deals with the mathematical modeling of the production of elastomers by emulsion polymerization in trains of continuous reactors [13]. A single mechanistic model was built and used to describe the production of both SBR and NBR elastomers in trains of emulsion polymerization CSTRs. Some novel aspects of this model compared to previous models are the following: (i) radical compartmentalization was considered in more detail, both in the particle kinetics description and in the calculation of the moments of the MWD, and for the first time, a 0-1-2 model was used to describe these two important aspects in these processes; (ii) the monomer partitioning model was as simple as possible, and its parameters could be estimated a priori based on published physicochemical data; and (iii) a single modeling framework was presented in a unified form for the SBR and NBR systems. This is another nice example of how detailed knowledge and experience about an important industrial emulsion polymerization processes significantly benefit from deeper analysis and model improvements of systems considered “well-understood”.

In the seventh contribution, Valencia et al. addressed the analysis of the polymerization of ethylene via zirconocene catalysts and organoboron activators, using experimental and mathematical modeling tools [14]. The novel aspects of this contribution include the proposal of a mathematical model for this type of catalytic system. Highlights include: (i) a systematic investigation of the effect of the different types of catalyst, activators, solvents, and operating conditions on ethylene polymerization rate and catalyst activity; (ii) estimations of ethylene concentrations in the liquid solvent based on Duhem’s theorem in a VLE system; (iii) estimation of kinetic rate constants by optimization protocols and the method of moments; and (iv) description of the kinetic behavior of different species during the polymerizations. This is an example on the use of PRE tools for new systems, or for systems not previously described with these tools.

In the eighth contribution, Vega-Hernández et al. presented a critical review on the synthesis, characterization, and modeling of polymer grafting [15]. Although the motivation behind this review stemmed from grafting synthetic polymers onto lignocellulosic biopolymers, a comprehensive overview is also provided on the chemical grafting, characterization, and processing of grafted materials of different types, including synthetic backbones. Although polymer grafting has been studied for many decades, so has the modeling of polymer branching and crosslinking for that matter, thereby reaching a good level of understanding to describe existing branching/crosslinking systems, polymer grafting has remained behind in modeling efforts. Areas of opportunity for further study are suggested within this review.

Zhang et al. presented a study on the improvement of mechanical properties and thermal stability of a composite material made of cellulose reinforced with clusters of silane coupling agents grafted onto nano-SiO₂ [16]. Mechanical property-related indicators of the composite material, such as tensile modulus (E), shear modulus (G), bulk modulus (K) and Poisson’s ratio (V), are calculated using molecular dynamics simulations. This contribution complements the types of mathematical approaches used in PRE for product or process modeling. This special issue manages to provide a nice view of the state-of-the-art on modeling and simulation of polymerization processes. The use of well-established methods (e.g., the method of moments) and relatively more recent modeling approaches (e.g., Monte Carlo stochastic modeling) to describe polymerization processes of long-standing interest in industry (e.g., rubber emulsion polymerization) to polymerization systems of more modern interest (e.g., RDRP and plastic pyrolysis processes) are comprehensively covered in this issue.

One can locate and read these papers via the following link: https://www.mdpi.com/journal/processes/special_issues/polymerization_processes (accessed on 1 May 2021).

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