



# Automated reaction generation for polymer networks

Yuliia Orlova\*, Ivan Kryven, Piet D. Iedema

Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, XH Amsterdam, 1098, Netherlands



## ARTICLE INFO

### Article history:

Received 23 October 2017

Revised 22 January 2018

Accepted 29 January 2018

### Keywords:

Rule-based network generation

Polymerization

Reaction network

Kinetic modeling

Macromolecular properties

## ABSTRACT

Most of the theoretical studies on polymer kinetics has been performed by manually reducing the chemical system to a few simple reaction mechanisms having a repeatable nature. Not being constrained by such reducibility, this work considers the polymerization as a product of a complex network of reactions that need not to be known in advance. Combining various ideas from graph theory, combinatorics and random graphs, we introduce a new modeling approach to complex polymerization that automatically constructs a reaction network, solves kinetic model, and retrieves such topological properties of the final polymer network as, for instance, distribution of molecular weight. In this way, the new approach acts as an intermediate layer that propagates the knowledge of the basic chemistry in order to capture and understand the complexity of the real world polymerizing systems.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Many real-life chemical systems consist of a large number of molecular species perpetually reacting with each other. Writing the formal reaction mechanism by hand, even for small molecules, is a labor-intensive task. One molecule can undergo numerous transformations until it reaches its final state. In some special cases, as for instance in polymers consisting of interconnected repeat units, even the notions of a species or the final state are not well defined, as they are rather expressed as probability distributions. This leads to extraordinarily large networks of interdependent reactions, counting thousands of distinct chemical species and much larger numbers of reactions. This proved to be an interesting topic for a wide range of application areas. To name a few, a theory explaining the origin of life as arising from simple organic compounds (Nijemeisland et al., 2016) and a number of plausible prebiotic scenarios (Dmitry Yu Zubarev, 2015) have been developed with the help of reaction networks. Analysis of metabolic networks Jeong et al. (2000), Stelling et al. (2002), Otero-Muras et al. (2017), Kryven et al. (2015) allows to study gene regulation, information transfer, cell-fate decision and many other important processes associated to the cell cycle. Furthermore, reaction networks are applied to the field of drug discovery (Lounkine et al., 2012) and the risk assessment of hazardous byproducts (Palaniappan et al., 2002). Various useful properties of chemical systems can be extracted solely from the underlying reaction network, as for instance, absolute concentration robustness (Shinar and Feinberg, 2010). The

present paper offers a novel methodology to design reaction networks in the context of complex polymerization processes.

In areas other than polymerization kinetics the complexity of real life reaction systems has motivated the development of many software packages to automatize reaction mechanism. For example, MAMOX (Ranzi et al., 1995) software generates detailed kinetic models for pyrolysis, oxidation or combustion mechanisms of large hydrocarbons. EXGAS (Battin-Leclerc, 2002) is developed to model the oxidation of linear and branched alkanes up to C<sub>16</sub>, linear alkenes from C<sub>3</sub> to C<sub>7</sub> and cycloalkanes. NetGen (Broadbelt and Pfaendtner, 2005) reconstructs chemical reaction networks for gas phase pyrolysis, biochemical reactions and nanoparticle synthesis. This package also allows to perform on-the-fly quantum chemistry calculations to estimate the kinetic parameters of the system. Reaction networks of free radical hydrocarbon chemistry are well reconstructed by RMG (Song, 2004). The algorithm generates all possible molecular species and reactions and then estimates whether the reactions are thermodynamically feasible and should be added to the final mechanism. Genesys (Vandewiele et al., 2012) is a rule-based reaction generating software which also allows the estimation of the kinetic parameters. In this package, the reaction rules are defined by the user, which allows a large flexibility for its use in a broad range of chemical systems. RING (Rangarajan et al., 2012) reconstructs reaction networks from a mechanism written in English-like reaction language. The software also offers many graph theory tools for further analysis of the resulting reaction network.

In the polymerization processes, monomers gradually connect to each other forming higher order arrangements: linear chains or networks. Progress was made in modeling of polymer mi-

\* Corresponding author.

E-mail address: [Y.Orlova@uva.nl](mailto:Y.Orlova@uva.nl) (Y. Orlova).

crostructure using advanced Monte Carlo techniques (Dhooge et al., 2015; Lemos et al., 2015; Steenberge et al., 2012; Steenberge et al., 2015). However, from the perspective of currently available network-generation packages, polymer networks are treated as large molecules and thus the repeatability of structural units is being ignored. As the size of a molecule grows, it becomes rather complicated to capture all possible intermediate products and the reaction pathways. Graph theory tools which are the foundation of most reaction generating mechanisms, become computationally prohibitive due to NP-hardness: there are no polynomial time algorithms which can solve some of the graph theory problems (Garey and Johnson, 1979). Moreover, the reaction network of the polymerization process has infinite size, which is the main limiting factor.

Due to such a prohibitive computational complexity, currently available case studies of polymerization regarded only well-defined reaction mechanisms. That is to say, the mechanisms in which both the repeated units and the complete set of reactions are known in advance. In these cases, the numerical computations are of polynomial complexity and are necessary only to perform time integration of the kinetic model in the deterministic or stochastic fashions. Efficient tools have been developed describing macromolecular properties in terms of numbers of monomer units, branches, functional groups, etc. (Dhooge et al., 2016; Iedema and Kolhapure, 2008; Mastan et al., 2015; Mueller et al., 2011; Tobita and Hamielec, 2000). A class of polymerization systems exists, however, with more than usually complex chemistry, for which we nevertheless desire to predict macromolecular properties. An example is the drying of linseed oil (Iedema et al., 2014; Oakley et al., 2015), where a complex radical-based photo-oxidation process leads to the formation of a dense polymer network. Properly dealing with such a system would require combining the best of both worlds of polymer modeling and automated reaction network generation. The present paper introduces a new methodology designed for complex polymer systems, and constitutes a synergy between these two, rarely intersecting, modeling worlds.

The overview of automated reaction network generation shows that many concepts and algorithms have already been developed. These have proved to be valuable in the development of our new methodology. Similarly to the above-described reaction generating packages, we utilize a reaction-rule approach to generate the reaction network. Knowing the reaction families and initial species, our method reconstructs all the intermediate and product molecular structures, while keeping track of the reactions that occur between them. The novelty of our method is - unlike all the previous developments - that we keep the model on the level of repeated units and therefore limit the size of molecular species involved. This means that the resulting polymer network is defined only by its fragments. In the terms of our methodology, we will refer to these fragments as "species". Although in this way the explicit macromolecular topology does not directly become available, the essential features of the topology may be retrieved. For instance, the size distribution of connected components can be reconstructed by using tools from random graph theory (Kryven, 2017a; Kryven, 2017c; Schamboeck et al., 2017). Other topological properties of the polymer networks that can be obtained from the degree distribution are discussed in Kryven et al. (2016).

We illustrate the methodology for a reaction generation mechanism on the example of self-condensing vinyl polymerization with 4-(1-hydroxyl-1-methylethyl) styrene-co-styrene as a macro-initiator and  $\text{TiCl}_4$  as a Lewis acid in a batch reactor, which produces finite macromolecules. More details about chemistry can be found in Puskas and Grasmiller (1998). This reaction mechanism is well studied in the work of Zhao et al. (2016) by means of advanced Monte Carlo modeling. The reaction equations listed in Table 1 are expressed in terms of the reactive groups  $V_i$  and

**Table 1**

Reaction steps for copolymerization of IM with IB, rate coefficients are in  $\text{Lmol}^{-1}\text{s}^{-1}$  (Zhao et al., 2016).

#	Reaction	Rate coefficient
1	$C_I + V_I \rightarrow C_S$	$3.32 \times 10^{-2}$
2	$C_I + V_M \rightarrow C_M$	$4.46 \times 10^{-4}$
3	$C_M + V_I \rightarrow C_S$	$5.19 \times 10^{-1}$
4	$C_M + V_M \rightarrow C_M$	$2.27 \times 10^0$
5	$C_S + V_I \rightarrow C_S$	$6.45 \times 10^{-3}$
6	$C_S + V_M \rightarrow C_M$	$4.11 \times 10^{-5}$

$C_j$ , which denote the functional groups as shown in Fig. 1. This figure shows a fragment of the polymer network, which can be formed due to copolymerization of inimer (IM) and isobutylene (IB). Since the IM/IB copolymerization has a relatively simple kinetics, it serves as a good context to introduce our new methodology. The rate parameters are known from the literature, so we do not deal with parameter estimation in this methodology. In the same time, the methodology itself is not bound by the scope of this chemical system and constitutes a general framework for complex polymerization.

This paper is organized as follows. After this Introduction, in Section 2 we introduce the definitions and tools necessary for the description of the reaction generating mechanism. In Section 3 we describe the general idea of the algorithm, from which the complete reaction network is obtained. Main steps of the methodology are illustrated in Section 4 by its application to copolymerization of inimer and isobutylene in a batch reactor.

## 2. Tools to describe the reaction system

In this section we will introduce various concepts, definitions and tools required to describe the reaction generating mechanism for the case of polymerization.

### 2.1. Graph theoretical background

A graph  $G = (V, E)$  is an abstract data structure, which consists of a set of  $n$  nodes (or vertices)  $V = \{v_1 \dots v_n\}$  and a set of edges  $E \subseteq V \times V$ , which determines the connections between nodes. The size of a graph  $G$  is  $n$  - the number of nodes in a graph. A graph  $G$  is undirected if  $(v_i, v_j) \in E$  implies  $(v_j, v_i) \in E$ , otherwise a graph is directed. A graph is labeled if each node has a corresponding label  $l(v_i)$ . If a graph is labeled, then it is defined by a triplet  $G = (l, V, E)$ . The edges can be labeled as well.

A graph  $G$  is also described by its adjacency matrix  $A \in \mathbb{R}^{n \times n}$ . In the case of an undirected graph,  $a_{ij}$  has a value of 1 if there exists an edge between nodes  $v_i$  and  $v_j$ , otherwise  $a_{ij}$  has a value of 0. In the case of a directed graph,  $a_{ij}$  has a value of 1 if an edge points from node  $v_i$  to node  $v_j$ , otherwise  $a_{ij}$  has a value of 0.

Nodes  $v_i$  and  $v_j$  are adjacent, if there exists an edge between them:  $(v_i, v_j) \in E$ . The neighborhood  $N(v)$  of a node  $v$  is the set of all nodes which are adjacent to  $v$ :  $N(v) = \{v_i | (v, v_i) \in E\}$ . The degree  $deg(v)$  of a node  $v$  is the number of its neighbors, or nodes  $v$  is adjacent to. If a graph  $G$  is directed, the degree of a node  $v$  can also be classified according to the type of edges connected to  $v$ .  $deg_{in}(v)$  is the incoming degree: number of neighbors which are connected by incoming edges to  $v$  and  $deg_{out}(v)$  is the outgoing degree: number of neighbors which are connected by outgoing edges to  $v$ .

The first order neighbors  $N_I(v)$  of a node  $v$  coincide with the definition of node neighborhood. In other words, the first order neighbors of  $v$  are nodes, which lie at a distance of one edge from  $v$ . The second order neighbors  $N_{II}(v) = N(N_I(v))$  of a node  $v$  are "neighbors of neighbors": nodes, which lie at a distance of two

Download English Version:

<https://daneshyari.com/en/article/6594855>

Download Persian Version:

<https://daneshyari.com/article/6594855>

[Daneshyari.com](https://daneshyari.com)