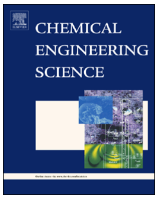
Chemical Engineering Science 110 (2014) 185–199

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces



Improved kinetic Monte Carlo simulation of chemical composition-chain length distributions in polymerization processes

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HIGHLIGHTS

- Kinetic Monte Carlo modeling of radical polymerization processes.
- Introduction of composite binary trees to calculate bivariate distribution.
- Modeling of diffusional limitations on the micro-scale.

ARTICLE INFO

Article history:
Received 30 April 2013
Received in revised form
9 January 2014
Accepted 17 January 2014
Available online 28 January 2014

Keywords:
Chemical composition distribution
Chain length distribution
Diffusion
Modeling
Multivariate

ABSTRACT

Composite binary trees are introduced for an improved kinetic Monte Carlo (kMC) calculation of chemical composition-chain length distributions (CC-CLDs) in polymerization processes, such as the bivariate copolymer composition-CLD (CoC-CLD). For the calculation of the CC-CLD, each leaf node of the main tree, which reflects the number of macromolecules with a given chain length, serves as a root node for a sub-tree containing information on the CC distribution for the macromolecules with the selected chain length. For low maximum chain lengths of 1000, the improvement consists already in a reduction of the kMC operations by a factor between 10^3 and 10^6. The approach is illustrated for the calculation of the CoC-CLD in free and atom transfer radical copolymerization of methyl methacrylate and styrene while accounting for potential diffusional limitations. Main focus is on the capability of the algorithm to ensure an accurate calculation of the average copolymer composition including high chain lengths.

1. Introduction

Polymerization is an important chemical process allowing the production of a wide range of materials used in daily-life and for high-tech applications (Matyjaszewski and Davis, 2002; Wang et al., 2005; Dompazis et al., 2005; Liu et al., 2009). Depending on the polymerization technique (e.g., radical or coordination polymerization), the comonomers (e.g., styrene, (meth)acrylates), the reactor configuration, and the operating conditions (e.g., (semi)batch) a polymer with a given microstructure can be obtained. This polymer microstructure is codetermined by the number of monomer units incorporated per chain, i.e., the chain length distribution (CLD). In particular, the polymer microstructure can be related to the contribution of the different comonomer types and the presence of short/long chain branches (S/LCBs) and functional groups. These microstructural characteristics influence the chemical, rheological, mechanical and physical properties and, hence, determine the application range of the polymer product (Kiparissides, 2006). It is therefore of paramount importance to control the polymer microstructure and to understand its link with the polymerization kinetics.

Typically the polymer microstructure is described by the chemical composition-chain length distribution (CC-CLD) (Asua, 2007; Krallis et al., 2010; Doremaele et al., 1992). This bivariate distribution represents the fraction of macromolecules with a given chain length and given chemical composition, i.e., number of comonomer units of a given type, number of SCBs or LCBs. Frequently "CC-CLD" denotes the copolymer composition-CLD, whereas different acronyms are used to denote other bivariate distributions. For example, Meimaroglou et al. (2007) introduced the SCB-CLD and LCB-CLD to describe the conditional (i.e., per value of the chain length) branching distribution in the production of low density polyethylene (LDPE). Similarly, Konkolewicz et al. (2011) highlighted the importance of the chain branches-CLD (CB-CLD), in which CB is the sum of the number of SCBs and LCBs, in the controlled radical polymerization (CRP) of *n*-butyl acrylate (*n*BuA). These authors showed that careful selection of the mediating agent allows to suppress branch formation compared to conventional free radical polymerization (FRP). In this work, CCD

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0009-2509/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2014.01.019

refers to the general chemical composition distribution, whereas CoCD denotes the copolymer composition distribution in particular.

It should be stressed that control over the CC-CLD during the polymerization is important to attain the targeted polymer microstructure, since both the CCD and CLD codetermine, among others, the strength, toughness and the softening/decomposition temperature of the final polymer product (Sperling, 1986; Young and Lovell, 1991). For example, for polyethylene products, high chain lengths and low branching contents are necessary to ensure a high strength (Aggarwal and Sweeting, 1957). LDPE has a high number of branches and a low crystallinity, whereas high density polyethylene (HDPE) possesses fewer branches and thus results in a stronger polymeric material for a similar CLD (White et al., 1974). Furthermore, a small change in the comonomer (feed) composition in copolymerization processes can already induce compositional drifting and lead to off-spec material properties. For (optical) applications, a copolymer composition drift of 3–5% is undesired (Asua, 2007), since incompatibility issues result in case polymer chains with a different composition are formed leading to phase separation and a change in the refraction index. For instance, Schiers and Priddy (Schiers and Priddy, 2003) indicated that styrene acrylonitrile (SAN) copolymers characterized by a compositional drift cannot be used for the fabrication of an optically transparent product. On the other hand, for gradient index (GRIN) lenses, a controlled dynamic evolution of the CoCD is needed (Asua, 2007) and compositional drift has shown to be beneficial to increase the fracture energy of polymer–polymer interfaces (Benkowski et al., 2001). Hence, depending on the application, it is desired to ensure a constant CC-CLD with conversion or that the CC-CLD follows a pre-fixed path.

Unfortunately, the CC-CLD is difficult to obtain experimentally (Cools et al., 1996; Soares, 2004). For example, the measurement of the branching content by the identification and quantification of quaternary carbon atoms by nuclear magnetic resonance (NMR) involves an intensive experimental procedure (Ahmad et al., 2009) and does not allow to discriminate between identical branches on molecules with different chain lengths. Furthermore, Soares (Soares, 2004) indicated that the CoCD/SCB-CCD in coordination copolymerization of ethylene and α-olefins can only be obtained indirectly. The distribution of crystallization temperatures (CTD) has to be measured and correlated to the CoCD, since it can be expected that higher crystallization temperatures correspond to lower α-olefin contents, i.e., a lower number of SCBs. Additionally, it has been shown that the measurement of the CoC-CLD in FRP is not straightforward (Tacx et al., 1988) and requires the combined use of size exclusion chromatography (SEC) and molecular spectroscopy, e.g., infrared spectroscopy, at high resolution. More recently, more advanced 2D-chromotagraphy methods have been applied (Baumgaertel et al., 2012; Ginzburg et al., 2013; Weidner et al., 2012.) but it remains a tedious task to obtain reliable experimental data.

Hence, taking into account the industrial demand to control the CC-CLD on-line (Richards and Congalidis, 2006), which allows a safe operation and efficient switch to different grades, it is desirable to dispose of a reliable modeling tool which can calculate a variety of bivariate distributions as a function of polymerization time and process conditions in an efficient manner.

The deterministic two dimensional fixed pivot technique (2D-FPT) and the stochastic kinetic Monte Carlo (kMC) technique (Krallis et al., 2008; Narkchamnan et al., 2011; Szymanski and Sosnowski, 2012; Van Steenberge et al., 2012: Van Steenberge et al., 2013) have been widely used to calculate the C(o)C-CLD. In 2D –FPT, the composition domain, representing the number of A and B comonomer units in the copolymer chains, is discretized leading to a reduced number of differential equations. As shown by Krallis et al. (2010) a discretization in a forty by forty grid on a logarithmic scale for each monomer type is necessary to calculate the CoC-CLD in the FRP of styrene and methyl methacrylate (MMA). In the kMC technique, following the algorithm of Gillespie (1977), a large control volume is needed for an accurate calculation of distributions of polymer molecules, i.e., a sufficiently high initial number of molecules has to be considered, in agreement with kMC simulation results of other research groups (Al-Harthi et al., 2009; Vinu et al., 2012; Wang and Broadbelt, 2010; Van Steenberge et al., 2011). Similar conclusions for the 2D-FPT and kMC technique were formulated for the calculation of the LCB-CLD of poly(vinyl acetate) and LPDE via FRP (Tobita and Hatanaka, 1996; Kiparissides et al., 2010).

Recently, Hamzehlou et al. (2012) applied the kMC technique to model the copolymerization of hydroxyethyl methacrylate and *n*BuA and indicated that this technique possesses a higher potential to retrieve microstructural information of the copolymer than deterministic solvers, albeit at a higher computational cost. The latter was shortly afterwards confirmed by Van Steenberge et al. (2012) and Toloza Porras et al. (2013) for the evaluation of respectively the (linear) gradient and block quality of copolymers made by atom transfer radical polymerization (ATRP). Furthermore, Szymanski (2009) highlighted the robustness of stochastic simulations by demonstrating that the shape and evolution of the CoC-CLD in living polymerization depends on the involved intrinsic homopropagation rate coefficients and monomer reactivity ratios.

Importantly, the advent of computer cluster architectures, recent advances in compiler technology and improved implementation of algorithms have led to increases of multiple orders of magnitude in calculation speed for the kMC technique, closing in on simulation times offered by deterministic solvers as for instance included in the software package PREDICI (Wulkow, 2009). For instance, Chaffey-Millar et al. (2007) combined the use of binary trees and the Gillespie algorithm (Gillespie, 1977) to store and retrieve the chain lengths of reacting macroradicals. Such binary trees were shown to be very suitable to describe reactions of chain length distributed species in radical polymerization and, hence, to calculate the CLD. However, for copolymerizations or when branch formation occurs, a similarly fast kMC calculation method is currently lacking, despite the importance of the CC-CLD to optimize polymerization processes.

In this work, a flexible and easy-to-implement kMC method is therefore proposed based on the work of Chaffey-Millar et al. (2007) to efficiently calculate the CoC-CLD, SCB-CLD and LCB-CLD using composite binary trees, i.e., the main tree contains the chain length information and the sub-trees (for each chain length) contain the (conditional) composition information. The proposed approach is illustrated for the calculation of the CoC-CLD in bulk FRP and CRP with styrene and MMA as comonomers, as the reduction in the number of kMC operations is most pronounced in case the CoC is tracked as second variate besides the chain length.

The potential influence of diffusional limitations on the individual chemical reaction steps is accounted for and it is shown that these limitations codetermine the size of the binary trees and thus the efficiency of the proposed method. In particular, for the CRP case for the first time the recently introduced coupled 'parallel' encounter pair model (D'hooge et al., 2013) is implemented in the kMC algorithm to describe the influence of diffusional limitations on the activation/deactivation process. The proposed composite binary tree approach can be extended in a later stage to multivariate calculations, such as the trivariate SCB-LCB-CLD or CB-CoC-CLD.

2. Material and methods

2.1. Reactions and intrinsic rate coefficients

In this work, bulk free radical polymerization (FRP) and controlled radical polymerization (CRP) of styrene (comonomer A; STY) and methyl methacrylate (comonomer B; MMA) are modeled