



The evolutionary development of chain microstructure during tandem polymerization of ethylene: A Monte Carlo simulation study



Mohammad Mehdi Khorasani^a, Mohammad Reza Saeb^b, Yousef Mohammadi^{a,*}, Mostafa Ahmadi^c

^a Petrochemical Research and Technology Company (NPC-rt), National Petrochemical Company (NPC), P.O. Box 14358-84711, Tehran, Iran

^b Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran

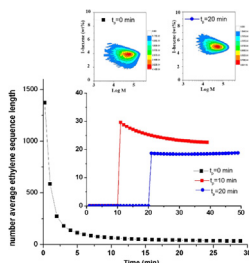
^c Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran

HIGHLIGHTS

- KMC simulation approach was employed to simulate ethylene tandem polymerization.
- Chemical composition distribution (CCD) was monitored in tandem process of ethylene.
- The effect of pre-trimerization time on molecular architecture was investigated.
- The homogeneity was determined in terms of bivariate molecular weight and CCD.
- CRYSTAF model was served to assess crystallization fractionation behavior.

GRAPHICAL ABSTRACT

Tandem polymerization of ethylene is simulated employing Kinetic Monte Carlo approach. Molecular architecture of copolymer chains is thoroughly investigated for simultaneous copolymerization/homopolymerization ($t_p=0$ min) and delayed copolymerization ($t_p=10, 20$ min) schemes.



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ABSTRACT

Employing a Kinetic Monte Carlo (KMC) simulation algorithm, tandem polymerization of ethylene is thoroughly investigated. To do this, the evolution of ethylene copolymerization is evaluated in terms of ethylene consumption and 1-hexene accumulation. The results obtained are in good agreement with the existing experimental kinetic data. It is revealed that the pre-trimerization time is a key factor in controlling the architecture of copolymer chains. Moreover, the precise computation of instantaneous and cumulative comonomer contents along with the chemical composition distribution of simulated copolymers provides a comprehensive image of the growing chains during tandem polymerization. A well-established crystallization fractionation (CRYSTAF) analysis mathematical model is applied to delve into the molecular architecture and the crystallization fractionation behavior of the produced polyolefins.

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1. Introduction

Polyethylene, as the most common member of thermoplastic family of polymers, has very good properties together with reasonable

price for versatile applications. It is well-documented that the ultimate characteristics of polyethylene are significantly dependent on either the extent or the type of branching on the backbone, as well as molecular weight distribution. As a result, in situ control of chain architecture via catalytic coordination polymerization of ethylene has increasingly aroused intensive scientific and industrial interests.

Over the last two decades, a number of investigations were directed towards synthesis of linear low-density polyethylene (LLDPE) copolymers comprising 1-butene, 1-hexene, and 1-octene

* Corresponding author at: HiTech Research Group, Petrochemical Research and Technology Company (NPC-rt), National Petrochemical Company (NPC), P.O. Box 14358-84711, Tehran, Iran. Tel.: +98 2144580504; fax: +98 2144580512.

E-mail address: mohammadi@npc-rt.ir (Y. Mohammadi).

fractions to control the selectivity of the processes through catalytic actions. The idea of using dual-functional catalysts with the potential to produce LLDPE was first conceived by Beach and Kissin (1984) and Kissin and Beach (1986). They examined a series of catalytic systems to assess the reactivity ratios in ethylene/1-butene copolymerization utilizing multifarious homogeneous and heterogeneous Ziegler–Natta catalytic systems. Following this approach, tandem catalysis was proposed on the bedrock of cooperative effects of combined catalytic precursors via a single-step monomer feeding scheme (Komon and Bazan, 2001; Mc Guinness, 2011; Dixon et al., 2004). In a tandem process, the first catalyst oligomerizes ethylene to α -olefins until formation of molecules with specified chain length. At the same time, the second catalyst is responsible for the polymerization of ethylene and incorporation of α -olefins into the growing polymer chains (Quijada et al., 2001; Ye et al., 2004; Yang et al., 2009). Thus, depending on the polymerization conditions and the ratio of the catalytic species, a wide range of ethylenic copolymers with different sequence lengths, microscopic architectures, and final properties could be synthesized from ethylene, as the sole reactant monomer (Alobaidi et al., 2004; Zhang et al., 2007; Bianchini et al., 2008).

Despite the fact that tandem catalysis was indeed so appealing, the titanium derivatives were not compatible enough with reaction species to catalyze both the dimerization and copolymerization reactions (Kissin and Beach, 1986). The incorporation of triethylaluminum (AlEt_3) cocatalyst into the reaction media was also non-utilitarian towards other available oligomerization catalysts. Later, the exploration of metallocene catalysts, which could be activated by methylaluminoxane (MAO), confronted tandem polymerization with a growing interest in virtue of possibility of one-pot combination of different catalytic precursors without the need for preparation of comonomer in a separate reactor (Komon and Bazan, 2001; Quijada et al., 2001).

To provide the reader with directions to follow the progress in tandem catalysis, a brief review based upon the available literature needs to be drawn. The dual action of a single catalytic precursor toward formation of α -olefins, as the main product, and polyethylene, namely side product, was examined in a $\text{CpTiCl}_3/\text{MAO}$ system and butyl-branched polyethylene was synthesized from ethylene (Pellecchia et al., 1999, 2000). Tandem action of Cr/SiO_2 Phillips catalysts bearing triazacyclohexane (TAC) groups was also evaluated elsewhere (Nenu and Weckhuysen, 2005; Nenu et al., 2006, 2007). A number of researchers attempted to provoke dual nature of a metallocene catalyst with the aim of simultaneous oligomerization and polymerization of ethylene, where a mixture of AlEt_2Cl and MAO cocatalysts was used (Yang et al., 2009).

In a different way, the second generation was introduced based upon combined effects of dual precursors, in which an oligomerization catalyst was in tandem with polymerization species. Besides, the discovery of late-metallocene catalysts elucidated that compounds having alkyl substituents on ortho position of their bis(imino)pyridyl ligands can deliver α -olefins with Flory distribution of chain length (Small and Brookhart, 1998; Britovsek et al., 1998). Since application of oligomerization catalysts in tandem catalytic systems ends in creation of various side chain lengths on the backbone of a single polymer molecule, this strategy has remained somehow unfavorable (Gorl and Alt, 2007; Zhang et al., 2005a; F.W. Yan et al., 2009; W. Yan et al., 2009; Lu et al., 2006; Zhang et al., 2005b; Schwerdtfeger et al., 2010).

Recently developed catalytic systems with very high selectivity toward 1-hexene, namely tridentate aminodithiol ligand (SNS-Cr) and aminodiphosphine ligand (PNP-Cr) Chromium catalysts, exhibit superior tandem action on formation of purely butyl-branched LLDPEs (De Wet-Roos et al., 2006; De Wet-Roos and Dixon, 2004). In this regard, a desired distribution of incorporated comonomer was achieved by matching the catalytic activities with reaction

conditions (Zhang et al., 2007, 2008a). Noticeably, the polydispersity of the produced copolymer was changed when tandem catalyst was supported on silica particles (Zhang et al., 2008b).

In spite of the significant advantages of one-pot LLDPE production via the tandem process, precise control of the chain microstructure, in particular comonomer content and chemical composition distribution, brings challenges for the experimentalists. Therefore, a systematic study on reaction kinetics and chain microstructure evolutions utilizing fundamental approaches on a molecular level was deemed lacking. Through theoretical and experimental analyses, Zhang and coworkers made a profound sense of copolymerization of ethylene/1-hexene on the principle of tandem catalysis (Ye et al., 2004; Alobaidi et al., 2004; Zhang et al., 2007, 2008a). By varying the catalysts ratios, they traced the rate of ethylene consumption in trimerization, homopolymerization, and tandem copolymerization reactions. They also imposed a short time of pre-trimerization on the reaction to enhance composition homogeneity. Although the model of moments they utilized was an efficient way of anticipating the copolymerization kinetics, the evolution of chain microstructure in the tandem process was reported neither experimentally nor theoretically.

The present study aims to theoretically establish the effect of polymerization scheme on the microstructure of polymer chains based upon evolutionary computations on molecular scale. Applying different pre-trimerization times (t_p) on reaction scheme, tandem polymerization of ethylene was precisely monitored by the Kinetic Monte Carlo (KMC) simulation method. The authors believe that simultaneous modeling of reaction kinetics, instantaneous and cumulative comonomer content, and chemical composition distribution of simulated copolymer chains provides a comprehensive image of the growing chains for the experimentalists willing to keep the LLDPE tandem polymerization under control. Moreover, to give the opportunity of better understanding of the molecular architecture, the ethylene sequence length distribution and the crystallization fractionation behavior of growing copolymer chains was examined applying a well-established mathematical crystallization fractionation (CRYSTAF) analysis model.

2. Theory and simulation

2.1. Monte Carlo algorithm

Monte Carlo simulation methods are based on the use of random numbers to sample the variable space using a probability distribution followed by the selection of an event (Fluendly, 1970). These statistical simulation methods are proved to be powerful enough in the field of polymer science and technology and have precisely given greater insights into macromolecular architecture (Mohammadi et al., 2005; Mohammadi and Jabbari, 2006). In the present study, the principle for the simulation of tandem polymerization of ethylene was constructed on the basis of Gillespie's algorithm. Accordingly, the simulation volume, V , was supposed to be divided homogeneously between the reactants. Microscopic elementary oligomerization and copolymerization reactions occurred discretely and stochastically through M reaction channels and an event was selected in a given time interval ($t, t+dt$) from uniformly distributed random numbers in a unit interval, according to the following relationships:

$$\sum_{v=1}^{\mu-1} P_v < r_1 \leq \sum_{v=1}^{\mu} P_v \quad (1)$$

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