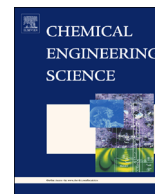




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A model for the structures of impact polypropylene copolymers produced by an atmosphere-switching polymerization process



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HIGHLIGHTS

- A kinetic mechanism for the complex structures of impact polypropylene copolymers.
- A model for a novel atmosphere-switching polymerization process (ASPP).
- Model validation by semibatch ASPP experiments.

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ABSTRACT

This work reports on the development of a model to establish the relationship between the structures of impact polypropylene copolymer (IPC), a high performance polymer material, and the characteristics of an atmosphere-switching polymerization process (ASPP), a new polymerization route. To calculate the complex structures of IPC, a detailed kinetic mechanism was proposed to describe the kinetic behavior of the active centers of Ziegler–Natta catalyst during ASPP. The semibatch ASPP for synthesizing IPC was carried out for the model validation. The model is capable of predicting the evolution of the compositional distributions of IPC as a function of switching frequency (SF), which is the main characteristic parameter of ASPP. ASPP not only allows controlling the contents of ethylene–propylene random copolymers (EPR) and ethylene–propylene segmented copolymers (EPS,) but also tuning the composition of EPS. Other applications of the model are discussed.

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1. Introduction

Impact polypropylene copolymers (IPC) are a class of high performance polymer materials produced from simple olefins (Galli and Vecellio, 2001, 2004). A sequential propylene homopolymerization, followed by a downstream ethylene–propylene copolymerization using the same Ziegler–Natta catalyst, is a convenient way to produce IPC. Interestingly, IPC is not only formed by a matrix of isotactic polypropylene (IPP) and a dispersed phase of ethylene–propylene random copolymer (EPR), but also consists of a series of semi-crystalline ethylene–propylene segmented copolymer (EPS), which is the compatibilizer for the

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system (Fan et al., 2001; Tan et al., 2005; Tian et al., 2011, 2012; Zhu et al., 2008). It is believed that the complex structures of IPC result from the nature of multicenter Ziegler–Natta catalysts. Since the amounts and microstructures of the three components, especially the EPR and EPS, have significant influence on the ultimate mechanical properties of IPC, extensive investigations have been made to explore the relationship among the composition, morphology, and properties of IPC (D’Orazio et al., 1999a, 1999b, 2001; Doshev et al., 2005, 2006; Li et al., 2009; Rungswang et al., 2013).

From an industrial point of view, it is necessary to develop quantitative correlations between process conditions and polymer structures. However, it is particularly challenging to build a model for IPC production. To the best of our knowledge, there are no reports on models that are capable of predicting the structures of IPC. This could be interpreted by three factors. First, the structures of IPC are complex and are therefore difficult to model. Second, EPR and EPS have structural similarities which are not easy to discern experimentally. Third, the mechanisms of the sequential propylene homopolymerization and ethylene–propylene copolymerization

catalyzed by Ti-based Ziegler–Natta catalysts remain poorly understood due to the inherent heterogeneity of multicenter catalysts. However, the fact that these Ti-based Ziegler–Natta catalysts contain several types of active centers exhibiting different regioselectivity, copolymerization capability, and activity profile has long been recognized (Kissin and Rishina, 2008, 2010). It is expected that the EPR and EPS are formed at different types of active centers.

More recently, a novel atmosphere-switching polymerization process (ASPP) was proposed to produce IPC (Tian et al., 2011) and soft polypropylene alloys in a single reactor. Unlike a conventional two stage polymerization process (TSPP), the monomer composition in the reactor was switched periodically with a designated time sequence. The switching frequency denoted as SF is the key parameter of the ASPP that controls the structures of IPC. An increase in SF leads to a better rigidity-toughness balance of IPC. The underlying mechanism was also discussed (Tian et al., 2012). However, no quantitative relationship between the structures of IPC and the characteristics of ASPP was established. Furthermore, since the periodical variation of the gas composition would cause off-specification polymers produced during the transition time, especially under high SF, it is necessary to develop a model that takes into account the effect of the dynamic change in the gas composition.

This work aims at developing a model that is able to predict the structures of IPC produced by ASPP. To that end, first a detailed kinetic mechanism was proposed to describe the kinetic behavior of the different types of active centers of Ziegler–Natta catalysts during the homopolymerization of propylene, copolymerization of ethylene and propylene, and the switching period between them.

Table 1
Elementary reactions of propylene homopolymerization.

Activation by aluminum alkyl	$C_p(j) + A \xrightarrow{k_{as}(j)} P_0(j)$
Activation by monomer	$C_p(j) + M \xrightarrow{k_{am}(j)} P_0(j)$
Chain initiation	$P_0(j) + M \xrightarrow{k_i(j)} R_1(j)$
Propagation:	$R_n(j) + M \xrightarrow{k_{pp}(j)} R_{n+1}(j)$
	$R_n(j) + M \xrightarrow{k_{ps}(j)} S_{n+1}(j)$
	$S_n(j) + M \xrightarrow{k_{sp}(j)} R_{n+1}(j)$
	$S_n(j) + M \xrightarrow{k_{ss}(j)} S_{n+1}(j)$
Chain transfer by hydrogen	$R_n(j) + H_2 \xrightarrow{k_{RH}(j)} P_0(j) + Q_n(j)$
	$S_n(j) + H_2 \xrightarrow{k_{SH}(j)} P_0(j) + Q_n(j)$
Chain transfer by monomer	$R_n(j) + M \xrightarrow{k_{RM}(j)} P_0(j) + Q_n(j)$
	$S_n(j) + M \xrightarrow{k_{SM}(j)} P_0(j) + Q_n(j)$
Deactivation	$P_0(j) \xrightarrow{k_d(j)} C_d(j)$
	$R_n(j) \xrightarrow{k_d(j)} C_d(j) + Q_n(j)$
	$S_n(j) \xrightarrow{k_d(j)} C_d(j) + Q_n(j)$

The structures of IPC in terms of the EPR, EPS, and IPP can be described mathematically through the proposed mechanism. Second, the method of moments and the instantaneous distributions were adopted to calculate the material balance, molecular weight distribution (MWD) and chemical composition distribution (CCD) of polymers, respectively. Third, the dynamic change in the gas phase monomer composition in the reactor during ASPP was also taken into account in the model. The model predictions of the structures of IPC prepared by TSPP were validated by experimental results. Then the capabilities of the model were demonstrated by the semibatch ASPP for preparing IPC. Potential applications of this model are discussed.

2. Model development

2.1. Polymerization mechanisms and kinetic behavior of active centers

The synthesis of IPC is associated with two different polymerization reactions over the same Ziegler–Natta catalyst system, namely, the homopolymerization of propylene and copolymerization of ethylene and propylene, respectively. Concerning the homopolymerization kinetics, the generally accepted mechanism has been outlined in the literature such as Zacca and Ray (1993) and Soares (2001). In the present model, the elementary reactions involved in the propylene homopolymerization are shown in Table 1. They account for multiple types of active centers. Each type of center (site j) has its own kinetic constants.

It is interesting to note that, unlike common homopolymerization kinetics, there are four different elementary propagation reactions in Table 1. $R_n(j)$ denotes a living polymer chain of length n with a terminal 1, 2 (primary) monomer insertion, whereas $S_n(j)$ is a dormant polymer chain of length n with a terminal 2, 1 (secondary) monomer insertion. To clearly show the formation of dormant sites, the four propagation reactions are illustrated in Fig. 1.

For a living polymer chain, the insertion of propylene monomer includes regular 1, 2 insertion (primary) and irregular 2, 1 insertion (secondary). The primary insertion generates a highly stereospecific center and can grow further by another primary insertion. Whereas after the secondary insertion, the growing chain deactivates to a dormant center with a poor reactivity, due to the β -agostic interaction and high steric hindrance (Kissin et al., 1999). The dormant centers may still grow via the two types of insertion, in spite of the low intrinsic reaction rate. The molar fraction of dormant sites X_D is given by (Busico et al., 2005)

$$X_D = \frac{1}{1 + k_{sp}/k_{ps}} \quad (1)$$

where k_{sp} and k_{ps} are defined in Table 1. Actually, X_D of each type of active center represents its own stereo-selectivity, depending

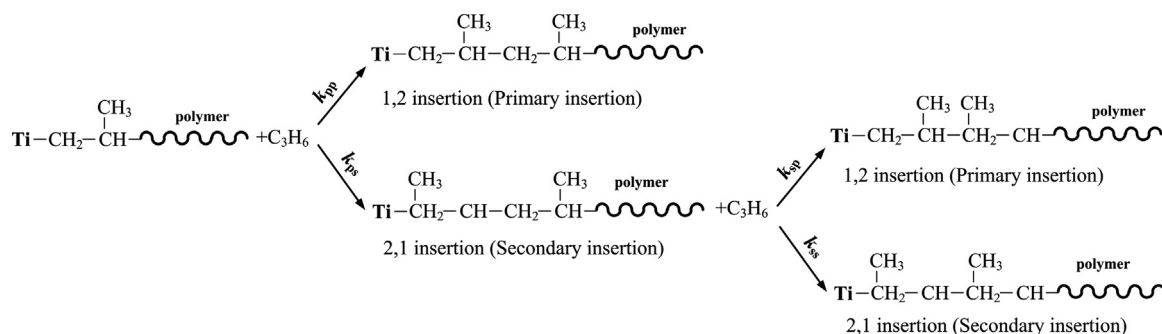


Fig. 1. Schematic of the four different chain propagations.

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