

Modeling and kinetics of tandem polymerization of ethylene catalyzed by bis(2-dodecylsulfanyl-ethyl)amine-CrCl₃ and Et(Ind)₂ZrCl₂

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Abstract

A mathematical model was developed to describe ethylene–1-hexene copolymerization with a tandem catalysis system. A series of semi-batch polymerization runs catalyzed by a trimerization catalyst bis(2-dodecylsulfanyl-ethyl)amine-CrCl₃ and a copolymerization catalyst Et(Ind)₂ZrCl₂ in toluene at 74 °C were carried out to verify the model. Both experimentation and modeling showed that adjusting the Cr/Zr ratio yielded various branching densities and thus melting temperatures, as well as molecular weights and polydispersities. Broad composition distributions and thus broad DSC curves were observed at high Cr/Zr ratios. Modeling results elucidated that this is due to an accumulation of 1-hexene component and to composition drifting during the copolymerization. It was also found that applying a short time period of pre-trimerization improved homogeneity in chain microstructure and minimized broadening in DSC curves.

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Keywords: Ethylene–1-hexene copolymer; Ethylene trimerization; Tandem catalysis system; LLDPE; Modeling

1. Introduction

The conventional route of LLDPE production involves two stages operated at different conditions: one is oligomerization of ethylene to produce α -olefin comonomer, and the other is copolymerization of ethylene with α -olefin. Since both stages use the same monomer, many efforts have been devoted to develop new processes that use tandem catalysis system and integrate two stages into one, i.e. synthesis of LLDPE from ethylene as the sole monomer in one reactor (Wasilke et al., 2005; de Souza and Casagrande, 2001). As shown in Scheme 1, α -olefin is produced in the first cycle by Catalyst 1 and ethylene is copolymerized with the in situ produced α -olefin by Catalyst 2 to synthesize ethylene– α -olefin copolymers. Compared to the commonly used two-stage process, this

single-stage approach has a clear advantage in the costs of plant investment, α -olefin purification, storage, and transport. Many tandem catalytic systems have been developed and studied to examine the influence of both oligomerization and copolymerization catalysts, to establish the relationships between reaction condition and polymer performance, to find out the way to tailor copolymer properties, etc. (Komon and Bazan, 2002; Ye et al., 2004; de Wet-Roos and Dixon, 2004; Bianchini et al., 2005; Zhang et al., 2005). However, kinetic modeling of ethylene polymerization with tandem catalysis system has been lacking.

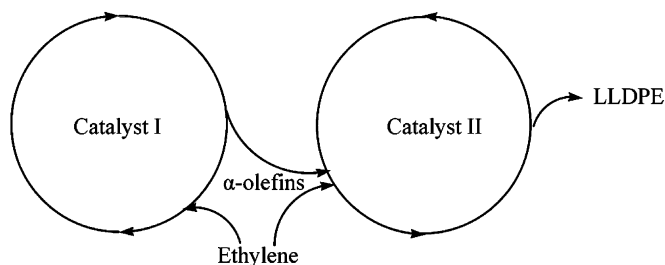
Since the first kinetic model for ethylene polymerization with metallocene catalyst was developed, the interest in the use of models to describe olefin polymerization reaction has been growing (Chien and Wang, 1990). Modeling allows one to better understand experimental observations when a great number of reaction parameters are involved. It can not only explain the important phenomena during polymerization qualitatively, but also predict the relationships between operating conditions and polymer properties quantitatively (Kou et al., 2005). In view of the fact that there exists a big difference between conventional copolymerization of two monomers and tandem

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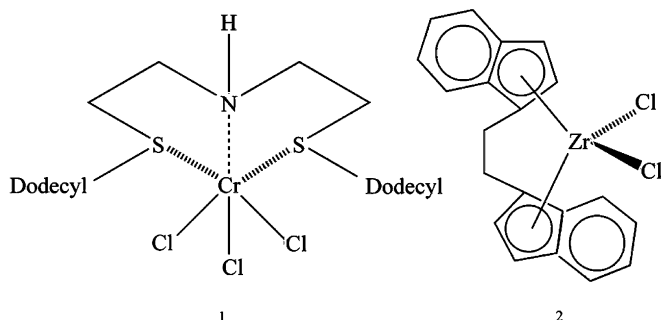
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Scheme 1. Generic LLDPE production by tandem catalysis.



Scheme 2. Structure of the trimerization and copolymerization catalysts.

catalyzed copolymerization of one monomer, it is necessary to develop a kinetic model for thorough analysis of operation of the system, and for design of more efficient and controllable copolymerization process. A good kinetic model is also needed to provide good insight into the relationship of reaction condition and polymer properties. In this article, a mathematical model was developed to simulate a tandem catalysis system that consisted of bis(2-dodecylsulfanyl-ethyl)amine- CrCl_3 which is a new trimerization catalyst and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ at atmosphere pressure (Scheme 2). The ethylene consumption rate (R_p), as well as the number- and weight-average molecular weight (M_n , M_w) and polydispersity index (PDI), short chain branching levels (C_6 mol%), and 1-hexene concentration in liquid phase (f_2), as well as copolymer composition (\bar{F}_2) were predicted and compared with the experimental results.

2. Experimental

Materials: All the manipulations were performed under nitrogen atmosphere using glove box and Schlenk techniques. Toluene was refluxed over metallic potassium with benzophenone as indicator and distilled under nitrogen atmosphere prior to use. Nitrogen and polymerization-grade ethylene (Sinopec China) were purified by passing through CuO catalyst, and 3 Å molecular sieves. The cocatalyst methylaluminoxane (MAO) in toluene from Albemarle Corporation was used as received. The trimerization catalyst precursor **1** was synthesized according to the published procedure (McGuinness et al., 2003). The catalyst $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ from Strem Chemicals was used as received.

Ethylene trimerization with 1/MAO: The details of trimerization and polymerization can be found elsewhere (Zhang et al.,

2007). The trimerization was carried out in a 250-mL glass reactor equipped with a magnetic stirrer under atmospheric ethylene pressure. After evacuated and exchanged with pure and dry nitrogen at 100 °C, the reactor was evacuated, pressurized with ethylene, and then placed into an oil bath set at the operating temperature. Toluene 100 mL and desired amount of MAO were introduced to the reactor. After equilibrating for 10 min, a prescribed amount of a toluene stock solution of **1** was injected to start the trimerization. The reaction temperature and ethylene pressure were kept constant throughout the trimerization process. Magnetic stirring was applied. An electromagnetic valve was used to measure the ethylene feed rate. After 30 min, the reactor was cooled down and vented. Heptane of 1 mL was injected as internal standard and the trimerization product was collected for gas chromatography or GC–MS analysis.

Ethylene polymerization with 1/2/MAO: A procedure similar to the trimerization was applied. For the ethylene polymerization with **2/MAO**, only the stock solution of Catalyst **2** was added to the reactor. For the polymerization with **1/2/MAO**, the stock solutions of **1** and **2** were added at the same time. For the polymerization with pre-trimerization, the stock solution of **1** was added firstly, followed by the addition of Catalyst **2** after a preset period of time. After 30 min of polymerization, the reactor was vented and 200 mL of acidified alcohol was added. The polymer materials were collected, washed with alcohol, and dried overnight.

Characterization: The GC analysis was conducted on an Agilent 6890N GC to determine the 1-hexene concentration in the trimerization product. The polymer melting point (T_m) and crystallinity (X_c) were measured using a Perkin Elmer DSC 7 in the standard mode. Polymer molecular weight (MW) and polydispersity index (PDI) were measured at 150 °C in 1,2,4-trichlorobenzene using a PL-GPC220 coupled with an in-line capillary viscometer. The 300 MHz ^{13}C NMR analyses were conducted on a Varian Mercury 300 pulsed NMR spectrometer at 120 °C. The polymer samples were dissolved in a *o*-dichlorobenzene with a concentration of about 5 wt%. The chemical shift assignments and calculation followed the Randall method (Randall, 1989).

3. Model development

In the case of producing ethylene copolymers by a tandem action of two catalysts, one must consider both oligomerization and copolymerization reactions, which consume ethylene simultaneously. Here we used a simplified kinetics developed by Briggs to simulate the operation of trimerization catalyst (Briggs, 1989). It was proposed that the trimerization proceeded via metallacyclopentane and metallacycloheptane intermediates (see Scheme 3). Because of the high selective formation of 1-hexene (> 99%), the insertion of ethylene into metallacyclopentane to yield metallacycloheptane must be faster than the elimination of 1-butene, and the elimination of 1-hexene from metallacycloheptane must be faster than the further insertion of ethylene to yield a larger ring. Meanwhile, the literature works revealed a second order dependence on ethylene for two different chromium-based ethylene trimerization catalyst systems,

suggesting that the rate-determining step is the formation of metallacyclopentane intermediate (Manyik et al., 1977; Yang et al., 2000). Therefore we considered the catalyst activation and deactivation, and the chelation of two ethylene to active site in the trimerization, while ethylene insertion into the metallacyclopentane and 1-hexene elimination were fast reactions which did not affect the 1-hexene production rate.

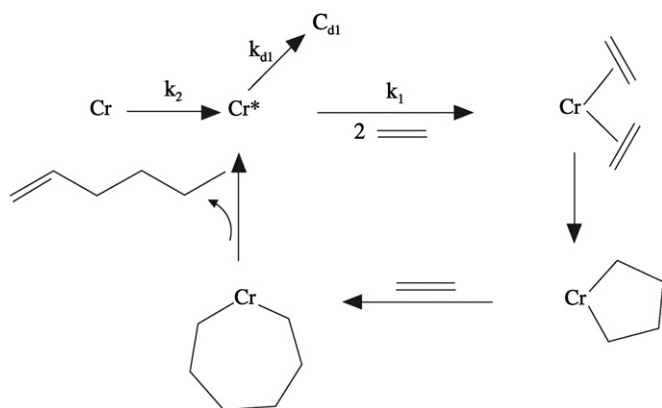
Concerning the copolymerization of ethylene with the in situ generated 1-hexene, a generic model was developed to describe the copolymerization reaction, taking into account activation of active site, chain propagation, β -hydrogen elimination, chain transfer to 1-hexene and spontaneous deactivation of the active sites (Soares, 2001). The trimerization and copolymerization mechanisms were summarized in Table 1. Based on the kinetic model, the equations which describe a set of dynamic mass balances for all the species present in the liquid phase of the reactor where the reactions happened were derived.

The mass balances in the liquid phase are the following. Catalyst species:

$$\frac{d[C_1]}{dt} = -k_{a1}[C_1], \quad (1)$$

$$\frac{d[C_1^*]}{dt} = k_{a1}[C_1] - k_{d1}[C_1^*], \quad (2)$$

$$\frac{d[C_2]}{dt} = -k_{a2}[C_2], \quad (3)$$



Scheme 3. Generic trimerization kinetic of bis(2-dodecylsulfanyl-ethyl)amine-CrCl₃.

$$\begin{aligned} \frac{d[C_2^*]}{dt} &= k_{a2}[C_2] - k_{iA}[C_2^*][M_A] - k_{iB}[C_2^*][M_B] \\ &\quad + k_{\beta}Y_A^0 + k_{\beta}Y_B^0. \end{aligned} \quad (4)$$

Monomers:

$$\begin{aligned} \frac{d[M_A]}{dt} &= q_{in} - \{k_{iA}[C_2^*] + k_{pAA}Y_A^0 + k_{pBA}Y_B^0\} \\ &\quad \times [M_A] - 3k_1[C_1^*][M_A]^2, \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{d[M_B]}{dt} &= k_1[C_1^*][M_A]^2 - \{k_{iB}[C_2^*] + (k_{pAB} + k_t)Y_A^0 \\ &\quad + (k_{pBB} + k_t)Y_B^0\}[M_B]. \end{aligned} \quad (6)$$

0th-order moments for the living chains and dead chains:

$$\begin{aligned} \frac{dY_A^0}{dt} &= k_{iA}C_2^*[M_A] + k_{pBA}[M_A]Y_B^0 - k_{pAB}[M_B]Y_A^0 \\ &\quad - (k_t[M_B] + k_{\beta} + k_{d2})Y_A^0, \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{dY_B^0}{dt} &= k_{iB}C_2^*[M_B] + k_t[M_B]Y_A^0 + k_{pAB}[M_B]Y_A^0 \\ &\quad - k_{pBA}[M_A]Y_B^0 - (k_{\beta} + k_{d2})Y_B^0, \end{aligned} \quad (8)$$

$$\frac{dX^0}{dt} = (k_t[M_B] + k_{\beta} + k_{d2})Y_A^0 + (k_t[M_B] + k_{\beta} + k_{d2})Y_B^0. \quad (9)$$

1st-order moments for the living chains and dead chains:

$$\begin{aligned} \frac{dY_A^1}{dt} &= k_{iA}C_2^*[M_A] + k_{pAA}[M_A]Y_A^0 + k_{pBA}[M_A]Y_B^1 \\ &\quad - k_{pAB}[M_B]Y_A^1 - (k_t[M_B] + k_{\beta} + k_{d2})Y_A^1, \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{dY_B^1}{dt} &= (k_{iB}C_2^* + k_tY_A^0 + k_tY_B^0)[M_B] + k_{pBB}[M_B]Y_B^0 \\ &\quad + k_{pAB}[M_B]Y_A^1 - k_{pBA}[M_A]Y_B^1 \\ &\quad - (k_t[M_B] + k_{\beta} + k_{d2})Y_B^1, \end{aligned} \quad (11)$$

$$\frac{dX^1}{dt} = (k_t[M_B] + k_{\beta} + k_{d2})Y_A^1 + (k_t[M_B] + k_{\beta} + k_{d2})Y_B^1. \quad (12)$$

Table 1
Reaction mechanisms of tandem catalysis system

Trimerization catalyst		Copolymerization catalyst	
Active-site formation	$C_1 \xrightarrow{k_{a1}} C_1^*$	Active-site formation	$C_2 \xrightarrow{k_{a2}} C_2^*$
Ethylene chelation	$C_1^* + 2M_A \xrightarrow{k_1} C_1M_A M_A^*$	Active-site initiation	$C_2^* + M_j \xrightarrow{k_{ij}} P_{1,j}^*, j = A, B$
Ethylene insertion	$C_1M_A M_A^* + M_A \rightarrow C_1M_A M_A M_A^*$	Propagation	$P_{n,i}^* + M_j \xrightarrow{k_{pij}} P_{n+1,j}^*, i = A, B, j = A, B$
1-Hexene elimination	$C_1M_A M_A M_A^* \rightarrow M_B + C_1^*$	Transfer to monomer	$P_{n,i}^* + M_B \xrightarrow{k_t} D_n + P_{1,B}^*$
Deactivation	$C_1^* \xrightarrow{k_{d1}} C_{d1}$	β -hydrogen elimination	$P_{n,i}^* \xrightarrow{k_{\beta}} D_n + C_2^*$
		Spontaneous deactivation	$P_{n,i}^* \xrightarrow{k_{d2}} D_n + C_{d2}$

2nd-order moments for the living chains and dead chains:

$$\frac{dY_A^2}{dt} = k_{iA}C_2^*[M_A] + k_{pAA}[M_A](2Y_A^1 + Y_A^0) + k_{pBA}[M_A]Y_B^2 - k_{pAB}[M_B]Y_A^2 - (k_t[M_B] + k_\beta + k_{d2})Y_A^2, \quad (13)$$

$$\frac{dY_B^2}{dt} = (k_{iB}C_2^* + k_tY_A^0 + k_tY_B^0)[M_B] + k_{pBB}[M_B](2Y_B^1 + Y_B^0) + k_{pAB}[M_B]Y_A^2 - k_{pBA}[M_A]Y_B^2 - (k_t[M_B] + k_\beta + k_{d2})Y_B^2, \quad (14)$$

$$\frac{dX^2}{dt} = (k_t[M_B] + k_\beta + k_{d2})Y_A^2 + (k_t[M_B] + k_\beta + k_{d2})Y_B^2. \quad (15)$$

The ethylene consumption was composed of two parts, one to produce 1-hexene and the other to copolymerize with 1-hexene. The liquid phase composition was calculated based on the assumption that all the generated 1-hexene was in the liquid phase and a constant ethylene pressure remained throughout the reaction. The instantaneous mole fraction of 1-hexene in the copolymer was evaluated from the Stockmayer equation, and integrating it with the reaction rate resulted in the content of short chain branches. The number- and weight-average molecular weights, as well as PDI, were calculated using the method of moments.

$$R_p = q_{in} = \{k_{iA}[C_2^*] + k_{pAA}Y_A^0 + k_{pBA}Y_B^0\}[M_A] + 3k_1[C_1^*][M_A]^2, \quad (16)$$

$$f_2 = \frac{[M_B]}{[M_A] + [M_B]}, \quad (17)$$

$$F_2 = \frac{r_B f_2^2 + (1 - f_2)f_2}{r_A(1 - f_2)^2 + 2(1 - f_2)f_2 + r_B f_2^2}, \quad (18)$$

$$\bar{F}_2 = \frac{\int F_2 \int \{k_{iA}[C_2^*] + k_{pAA}Y_A^0 + k_{pBA}Y_B^0\}[M_A]}{\int \{k_{iA}[C_2^*] + k_{pAA}Y_A^0 + k_{pBA}Y_B^0\}[M_A]}, \quad (19)$$

$$M_n = \frac{Y_A^1 + Y_B^1 + X^1}{Y_A^0 + Y_B^0 + X^0} [m_{wA}(1 - \bar{F}_2) + m_{wB}\bar{F}_2], \quad (20)$$

$$M_w = \frac{Y_A^2 + Y_B^2 + X^2}{Y_A^1 + Y_B^1 + X^1} [m_{wA}(1 - \bar{F}_2) + m_{wB}\bar{F}_2], \quad (21)$$

$$PDI = \frac{M_w}{M_n}. \quad (22)$$

The parameters we used were listed in Table 2. In this model, two assumptions were made in sake of the simplicity. Firstly, because the reaction temperature and ethylene pressure were kept constant throughout the process, ethylene concentration in toluene was constant. It was estimated to be $0.0459 \text{ mol L}^{-1}$ at 74°C and 1 atm. Furthermore, we assumed that all the in situ generated 1-hexene stayed in the liquid phase, and it did not affect the ethylene absorption in toluene. For verification, we actually calculated the concentration of all components based

Table 2
Parameters used in the tandem catalysis system

Parameter	Unit	Value
k_{a1}	min^{-1}	0.044
k_1	$\text{mol}^2 \text{L}^{-2} \text{min}^{-1}$	3.73e6
k_{d1}	min^{-1}	2.23
k_a	min^{-1}	2
k_{iA}	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	5e4
k_{iB}	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	1000
k_{pAA}^a	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	2.5e5
k_{pAA}^b	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	6.5e5
k_{pBA}	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	1e5
$r_A(k_{pAA}/k_{pAB})$	–	40
$r_B(k_{pBB}/k_{pBA})$	–	0.01
k_t	$\text{mol}^1 \text{L}^{-1} \text{min}^{-1}$	45
k_β	min^{-1}	12
k_{d2}	min^{-1}	0.01
m_{wA}	g mol^{-1}	28
m_{wB}	g mol^{-1}	84
C_1	mol L^{-1}	$1e-4^c$
C_2	mol L^{-1}	$2e-5^c$
M_A	mol L^{-1}	0.0459

^aHomopolymerization.

^bCopolymerization.

^cDepend on the reaction conditions.

on Holderbaum's work (Holderbaum and Gmehling, 1991), and the results demonstrated that the two assumptions were valid. The parameters concerning the trimerization catalyst were estimated by fitting the ethylene consumption rate in Run 1, and the reaction constants of ethylene polymerization with $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ were cited from the literature with small correction by fitting the data in Run 2, shown in Fig. 1 (Haag et al., 2000; Wu et al., 2005). For ethylene–1-hexene copolymerization, we used different propagation rate constants (k_p). In ethylene–1-hexene copolymerization, both metallocene and Ziegler–Natta catalysts showed significantly higher activities than in ethylene homopolymerization, which is referred to as a comonomer effect. Though a number of kinetic and physical explanations have been suggested in the literature, it is difficult to extend a homopolymerization model to a copolymerization model using the same k_p because of poor prediction of the increase in fast reaction rate (Chakravarti and Ray, 2001).

The above equations were solved by Matlab 7.1 with the parameters given in Table 2. The initial conditions for the ODEs were all set to zero except for the concentrations of monomer and two catalysts.

4. Results and discussion

Detailed investigations of ethylene trimerization with Catalyst 1 and ethylene polymerization with Catalyst 2 have already been reported in our previous works (Zhang et al., 2007). In this work, we report the performance of individual catalysts under our experimental conditions for comparison. The ethylene trimerization and polymerization with 1/2/MAO was carried out under various catalyst ratios, and the recipes are summarized in Table 3. Run 1 and Run 2 were used for the estimate

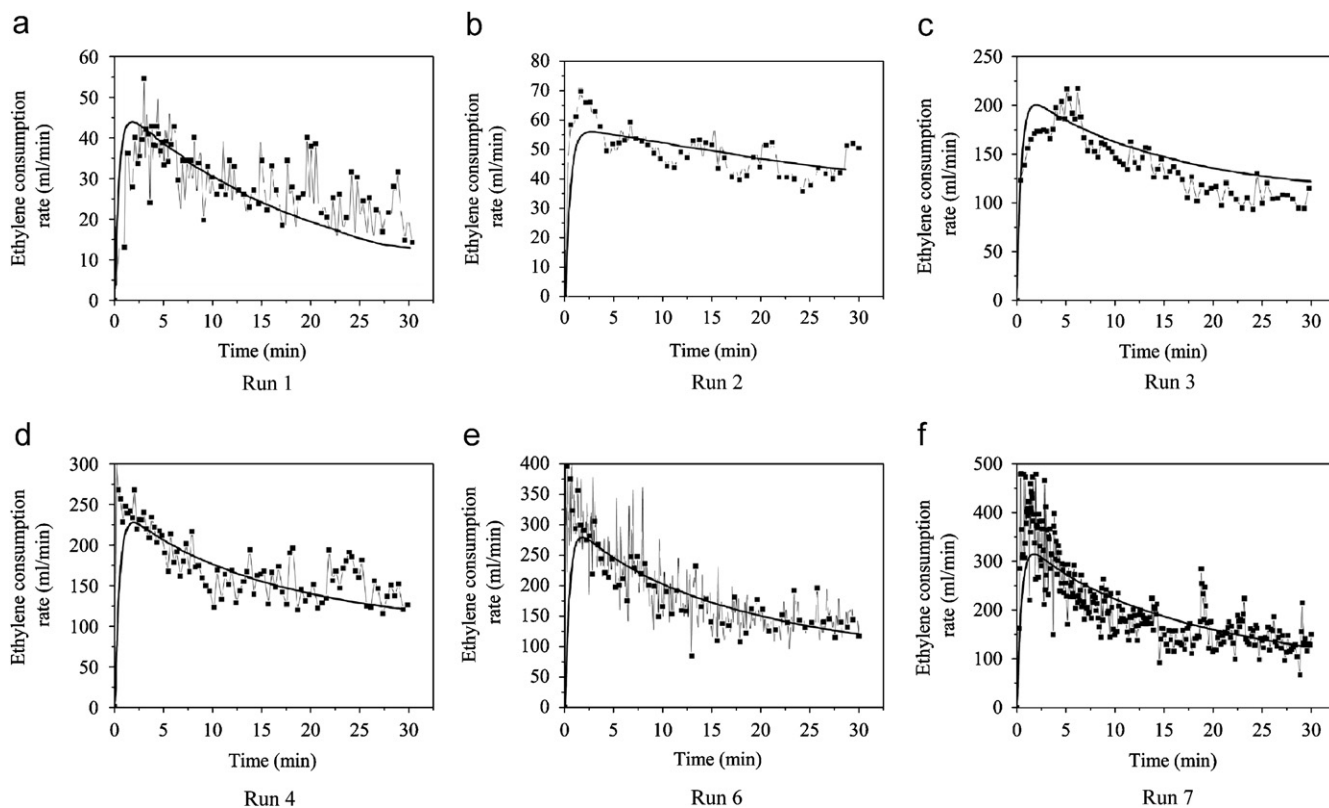


Figure 1. Experimental data and model predictions of ethylene consumption rate in trimerization, homopolymerization, and tandem copolymerization at different Cr/Zr ratios (the thick lines are model predictions, and the solid diamonds are experimental data).

Table 3
Ethylene polymerization with **1**/2/MAO

Run ^a	Cr (μmol)	Zr (μmol)	Cr/Zr	Pre-tri (min) ^b	Act. ^c	C ₆ (%) ^d		M _w (kg mol ⁻¹)		PDI	
						Exp.	Model	Exp.	Model	Exp.	Model
1	5	0	–	0	0.42 ^e	–	–	–	–	–	–
2 ^f	0	0.5	0	0	7.44	0	0	54.7	51	2.4	2.00
3	7	0.2	35	0	39.49	1.9	1.6	82.4	94.1	2.1	2.05
4	10	0.2	50	0	52.01	2.4	2.3	72.9	84.1	2.5	2.09
5 ^g	10	0.2	50	0	43.06	–	–	–	–	–	–
6	16	0.2	80	0	43.13	4.0	3.5	54.6	59.8	2.3	2.19
7	20	0.2	100	0	38.89	4.5	4.4	52.6	54.5	2.2	2.26
8	10	0.2	50	5	27.87	–	–	60.6	64	2.1	2.04
9	10	0.2	50	10	29.31	–	–	56.2	59.4	2.0	2.01
10	10	0.2	50	20	25.38	–	–	52.0	54	2.1	2.00
11 ^g	10	0.2	50	20	24.42	–	–	–	–	–	–

^aReaction conditions: solvent toluene; total volume 100 mL; $n_{\text{Al}}/n_{\text{Cr}} = 600$, $t_{\text{reaction}} = 30$ min, $T = 74$ °C, $P = 1$ atm.

^bThe time copolymerization catalyst was added after trimerization catalyst.

^cIn 10^6 g/(mol Zr h)⁻¹.

^d1-Hexene molar percentage in the copolymer determined by ¹³C NMR.

^eIn 10^6 g/(mol Cr h)⁻¹.

^fAl/Zr = 2500, other reaction conditions is the same as others.

^gReaction medium was sampled every 5 min for gas chromatography analysis.

of ethylene trimerization and ethylene homopolymerization parameters, Run 3 to Run 7 for copolymerization, Run 8 to Run 11 for model validation, and Run 5 and Run 11 were carried out under the same conditions as Run 4 and Run 10, respectively, to obtain the 1-hexene concentrations during reaction by sampling.

Using the parameters estimated in Table 2, the model provided a good fit to most of the data from Run 3 to Run 7. Comparison between experimental data and model predictions shows that the model predicted most ethylene consumption rate data well, especially when low Cr/Zr ratio was applied. We can see that the maximum of R_p was achieved in a few minutes

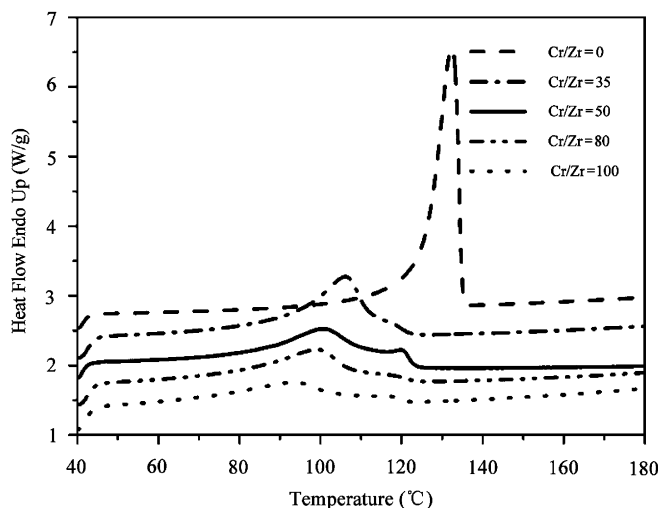


Figure 2. DSC curves of ethylene–1-hexene copolymers obtained with the tandem catalysis system at different Cr/Zr ratios (Runs 2, 3, 4, 6, and 7).

of the reaction time and followed by a subsequently decrease which can be attributed to the deactivation of both catalysts. When a high Cr/Zr ratio was applied, the initial activity was so high that the electromagnetic valve cannot control the feed of ethylene gas which made it difficult to manipulate a well-matched ethylene consumption rate curve at the early stage. As the reaction proceeded, the reaction rate decreased and the model fit well with the experimental data.

As shown in Table 3, both the experimental data and modeling result of M_w decreased with increasing Cr/Zr ratio. This can be contributed to the higher chain transfer rate to 1-hexene at high 1-hexene concentration, which is one of the most important reactions that influence the molecular weight. Unlike the prediction of M_w , the modeling result of PDI did not fit well with the experimental result. The model used in this paper was a simplified model, and we paid our major attention to R_p , comonomer production and consumption rates, and copolymer composition. Chain transfer to ethylene and MAO, deactivation of active chain to contaminant, and chain-end isomerization were not included in this model, which would underestimate the PDI value. It is therefore expected that the modeling result showed PDI around 2.0 while the experiment gave a larger number.

As can be seen from Fig. 2, T_m and X_c decreased with increasing Cr/Zr ratio. The melting transition also became broader, suggesting that higher 1-hexene contents were produced and incorporated. Both the experiment data and modeling results shown in Table 3 illustrated that the C_6 mol% in the produced copolymers increased linearly with increasing Cr/Zr ratio. Very similar results were obtained by others using the same $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system to produce comparable ethylene–1-hexene copolymers (Quijada et al., 1997). It seems that increasing the amount of trimerization catalyst while keeping the copolymerization catalyst content unchanged resulted in a linear increase in 1-hexene concentration in the liquid phase in which the copolymerization

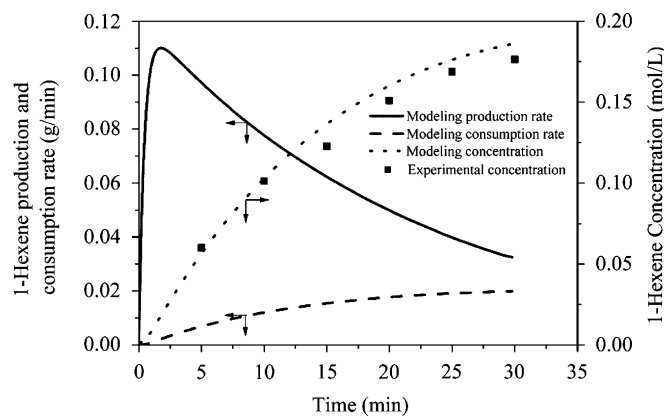


Figure 3. Experimental data and model predictions of 1-hexene production and consumption rate and concentration evolution during reaction (Run 4).

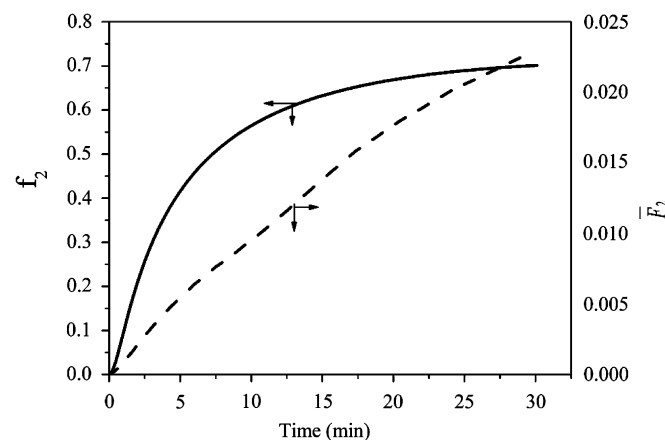


Figure 4. Model prediction of composition evolution in comonomer and copolymer (Run 4).

occurred. That also means that the trimerization catalyst did not interfere with the copolymerization catalyst and the trimerization activity was maintained even at high catalyst concentrations.

The biggest difference between conventional route and tandem catalysis system to produce ethylene–1-hexene copolymers is the comonomer concentration evolution during reaction (Zhang et al., 2007). In conventional copolymerization, the comonomer was added at the beginning of the reaction, and the comonomer concentration was the highest at the beginning followed by a subsequent decrease due to consumption. In tandem catalysis system, the comonomer concentration was zero at the beginning, accumulated during reaction, reached its highest, and then decreased. The whole process depended on the kinetic nature of oligomerization catalyst which produced the oligomer, the nature of copolymerization catalyst which consumed the produced oligomer, and the reaction time which affected the deactivation of both catalysts. As shown in Fig. 1 (Run 1), the trimerization catalyst showed a typical rapid decrease in rate after reaching its maximum. The 1-hexene concentration in Run 4 as shown in Fig. 3 built up

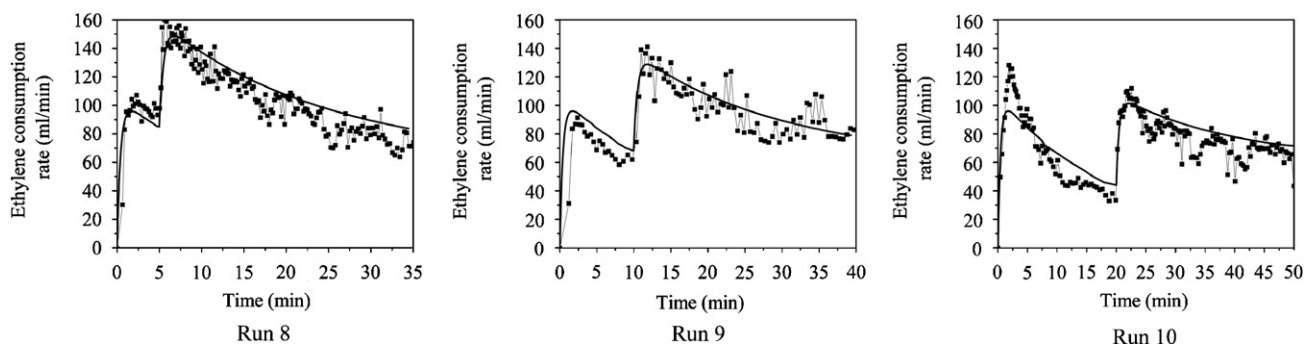


Figure 5. Experiment data and model predictions of ethylene consumption rate in the tandem copolymerization at different pre-trimerization times (the thick lines are model predictions, and the solid diamonds are experimental data).

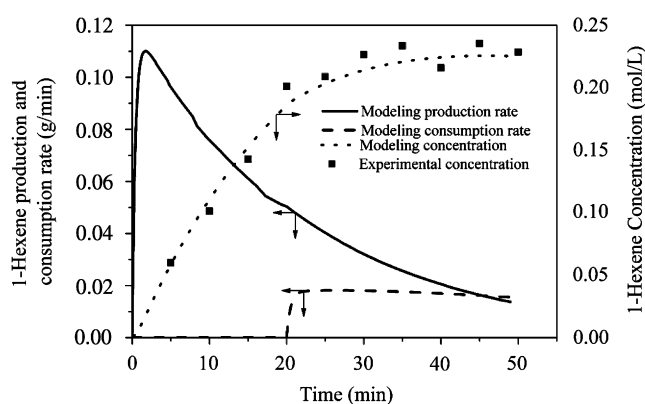


Figure 6. Experimental data and model predictions of 1-hexene production and consumption rate and concentration evolution during reaction (Run 10).

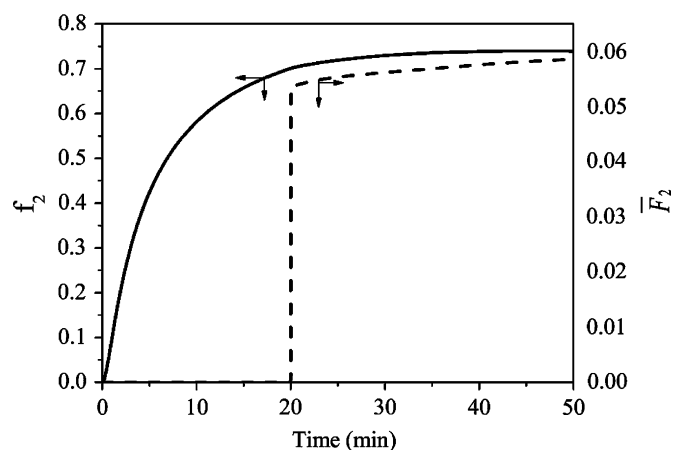


Figure 7. Model prediction of composition evolution in both liquid phase and copolymer (Run 10).

gradually because of unmatched production and consumption rates. The crescent 1-hexene concentration along reaction resulted in a continuous change in liquid phase composition (f_2) and thus influenced the copolymer composition (F_2) according to Stockmayer equation as shown in Fig. 4 by modeling. The sample collected at the end of each run was a blend of copolymers produced along reaction at different compositions. Because of the wide copolymer composition, especially at high Cr/Zr ratios, the DSC curves shown in Fig. 2 were varied and complicated with multiple peaks appeared. This phenomenon was previously observed and reported in literature (Zhang et al., 2005; Zhang et al., 2007). Here we provided an explanation from a kinetic aspect assisted by modeling.

To improve the microstructural homogeneity and to eliminate the bimodality in the DSC curves of copolymers produced at high Cr/Zr ratios, the 1-hexene accumulation time must be shortened or the 1-hexene concentration must reach a high level at an early stage of copolymerization so that the composition drift can be minimized. The broad composition distribution and transition in the DSC curve can be eliminated by conducting pre-trimerization for a short period of time. Run 8 to Run 11 were carried out to verify the efficiency of pre-trimerization on improving homogeneity and the accuracy of the model to predict the rates of ethylene consumption, 1-hexene production

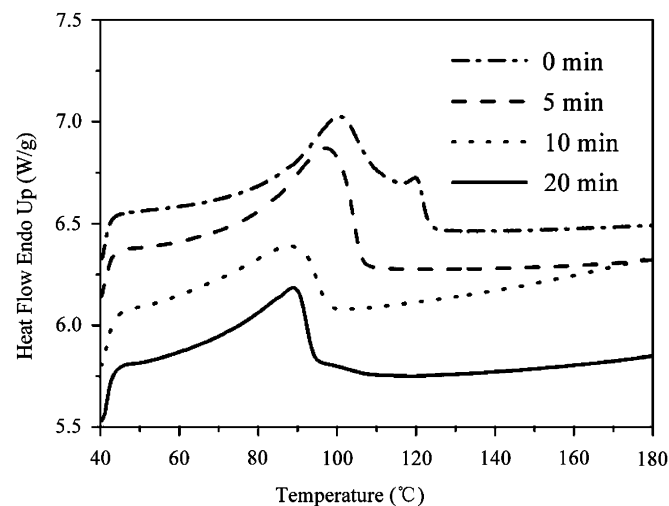


Figure 8. DSC curves of ethylene–1-hexene copolymers obtained with the tandem catalysis system at different pre-trimerization times (Runs 4, 8, 9, and 10).

and consumption, 1-hexene concentration in the liquid phase, and M_w and PDI of the final copolymer.

The model prediction shown in Fig. 5 gives good agreement with experimental ethylene consumption rate, using the same

parameters in Table 2. As we can see from both experiment and modeling results, the reaction could be divided into two parts: In the first a few minutes when only the trimerization catalyst was injected, R_p was relatively low. After the copolymerization catalyst was added, R_p increased dramatically because both trimerization and copolymerization consumed ethylene. The good fit of the model to the experimental data in both parts provided a strong support to the validity of the model.

The experimental data and modeling result of M_w and PDI were listed in Table 3. The M_w decreased with increasing pre-trimerization time, because the longer the pre-trimerization time, the higher the 1-hexene concentration accumulated at the early stage, which decreased the M_w by chain transfer to 1-hexene. When pre-trimerization was applied, the PDI prediction became accurate. The higher 1-hexene concentration made the whole system more homogeneous.

The main purpose of the pre-trimerization was to accumulate 1-hexene to a certain level before the copolymerization started so that little low comonomer content copolymer was produced at the early stage. Fig. 6 gives the 1-hexene production and consumption rates as well as 1-hexene concentration evolution in Run 10. Both experiment and modeling results showed that the 1-hexene concentration increased dramatically in the pre-trimerization period without consumption. After the copolymerization catalyst was added, the concentration increased only a little. The production of 1-hexene by the trimerization catalyst and the consumption of 1-hexene by the copolymerization catalyst reached equilibrium and matched each other. The stable 1-hexene concentration resulted in a stable f_2 , and as a consequence, the copolymer chains having the same composition distribution \bar{F}_2 were generated, as shown in Fig. 7. The final copolymer product had a uniform DSC curve. Fig. 8 shows the DSC curves with different pre-trimerization times. After a few minutes of pre-trimerization, the bimodal distribution became unimodal.

5. Conclusion

Assisted by the proposed model, we studied the influence of different polymerization conditions on the preparation of ethylene–1-hexene copolymers from the tandem action of bis(2-ethylsulfanyldodecyl)amine–CrCl₃ and Et(Ind)₂ZrCl₂ from ethylene stock in a single reactor. The general feature of the model simulation agreed well not only with our experimental data, but also with the other results reported in the literatures. Concerning the ethylene consumption rate, the model fitted the experimental data very well, illustrating that the behavior of the polymerization system depended on both trimerization and copolymerization catalysts. Because of the accumulation of 1-hexene content and the composition drifting in the copolymerization, broad composition distributions and DSC curves were observed especially when the high Cr/Zr ratios were employed. Applying a short time period of pre-trimerization improved the homogeneity in chain microstructure and minimized the broadening in DSC curves.

Notation

C_{di}	dead catalyst of type i
C_i	concentration of catalyst precursor i , mol L ⁻¹
C_i^*	concentration of activated catalyst i , mol L ⁻¹
f_2	mole fraction of 1-hexene in reaction medium
F_2	spontaneous mole fraction of 1-hexene in copolymer
\bar{F}_2	short chain branch mole content
k_1	rate constant for ethylene insertion, L ² mol ⁻² min ⁻¹
k_{ai}	rate constant for activation of catalyst i , min ⁻¹
k_{di}	rate constant for spontaneous deactivation of catalyst i , min ⁻¹
k_{ij}	rate constant for chain initiation by monomer j , L mol ⁻¹ min ⁻¹
k_{pij}	rate constant for chain propagation from i end to j end, L mol ⁻¹ min ⁻¹
k_t	rate constant for chain transfer end to monomer B , L mol ⁻¹ min ⁻¹
k_β	rate constant for β -hydrogen elimination, min ⁻¹
m_{wi}	molecular weight of monomer i
M_i	monomer concentration of type i in the reaction phase, mol L ⁻¹
M_n	number average molecular weight of polymer
M_w	weight average molecular weight of polymer
PDI	polydispersity index
q_{in}	ethylene flow rate, mol L ⁻¹ min ⁻¹
R_p	total reaction rate, mol L ⁻¹ min ⁻¹
T	time, min
X^x	x th-order moment for dead chains
Y_i^x	x th-order moment for living chains terminated with monomer i

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