

Study of Ethylene Polymerization Catalyzed by nBu-Cp₂ZrCl₂/MAO Catalytic System and Their Polymerization Kinetics

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Received 19 August 2000; accepted 26 October 2000

ABSTRACT: Polyethylene was prepared by using a nBu-Cp₂ZrCl₂/MAO catalytic system. Considering the reactivation of Zr species, a novel and reasonable mathematical model of kinetics has been developed and the kinetic profiles of ethylene polymerization have been fitted satisfactorily. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3186–3189, 2001

Key words: ethylene polymerization; metallocene catalyst; kinetics

INTRODUCTION

In recent years, many new and highly active titanium-based catalysts and metallocene catalysts suitable for the preparation of polyolefins, particularly for polypropylene, polyethylene, and copolymers of ethylene and propylene, have been discovered and developed.^{1–6} Kinetic studies of olefin polymerization using homogeneous metallocene have become the subject of interest.^{7–9} Based on different experimental results, several mathematical models have been developed and kinetic parameters have been estimated. The development of novel kinetic model is important for further understanding the mechanism of the polymerization.

In this work, a novel mathematical model of the kinetics was developed, and the kinetic profile of ethylene polymerization was fitted satisfactorily.

EXPERIMENTAL

Materials

Zirconocene was obtained commercially. Methylaluminumoxane (MAO) was used as received. Toluene was purified by refluxing over Na–K alloy under nitrogen atmosphere and distilled before use. Polymerization-grade ethylene was further purified by passing over 4-Å activated molecular sieves. All manipulations were performed under nitrogen atmosphere.

Ethylene Polymerization

The ethylene polymerization was carried out in a 100-mL flask equipped with an ethylene inlet, magnetic stirrer, and vacuum line. The flask was filled with 50 mL toluene and the stoichiometric quantities of MAO and was saturated with ethylene. The reaction was initiated by adding the solution of metallocene catalyst in toluene. After 30 min, the polymerization was terminated by addition of acidified ethanol. The resultant polymer was separated by filtration and dried under vacuum to constant weight.

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Contract grant sponsors: National Natural Science Foundation of China; Science and Technology Commission of Zhejiang Province.

Journal of Applied Polymer Science, Vol. 81, 3186–3189 (2001)
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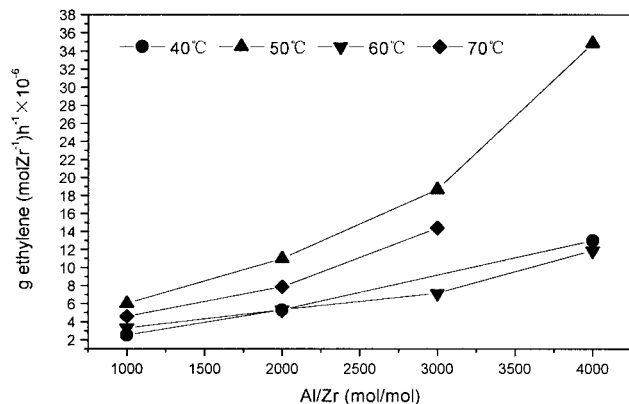


Figure 1 Activities of ethylene polymerization catalyzed by $n\text{Bu-Cp}_2\text{ZrCl}_2/\text{MAO}$.

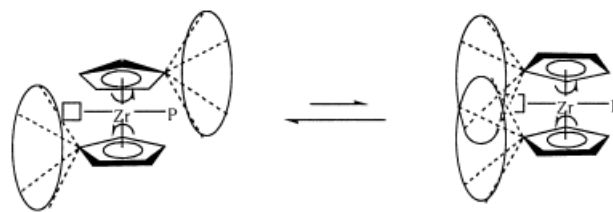
RESULTS AND DISCUSSION

The activities of ethylene polymerization catalyzed by $n\text{Bu-Cp}_2\text{ZrCl}_2/\text{MAO}$ catalytic system are shown in Figure 1, which shows that the activities increase with increasing Al/Zr mol ratios and increase first with increasing polymerization temperatures and then decrease. Possibly, the latter relates to the solubility of ethylene in toluene at different temperatures. However, it is evident that the polymerization activity of $n\text{Bu-Cp}_2\text{ZrCl}_2/\text{MAO}$ catalytic system is higher than $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalytic system under the same polymerization conditions. It has been noted an interconversion of the catalyst occurs between the chiral isospecific rotameric state and the achiral aspecific rotameric state during the course of polymerization.¹⁰ Generally, the distance between two cyclopentadienyl rings is $\sim 5 \text{ \AA}$. If the dimensions of the substituent groups in cyclopentadienyl ring are approximately $< 2.5 \text{ \AA}$, it is believed that an interconversion of the catalyst between chiral isospecific rotameric state and achiral aspecific rotameric state during the course of the polymerization will take place freely, as shown in Scheme 1.

If the dimensions of substituent groups are $> 2.5 \text{ \AA}$, the rotation of cyclopentadienyl ring around the axis between Zr and Cn (the centroids



Scheme 1



Scheme 2

of the cyclopentadienyl ring) will be partially hindered. By contrast, the rotation of substituent groups in the cyclopentadienyl ring makes a monomer more difficult to insert and thus leads to a decrease in polymerization activity, which can be demonstrated conceptually as shown in Scheme 2.

Therefore, considering that the dimension of substituent groups are $> 2.5 \text{ \AA}$, it can be concluded that mainly as a result of the electronic effect of substituent groups, $n\text{Bu-Cp}_2\text{ZrCl}_2/\text{MAO}$ catalytic system yields higher polymerization activity.

The kinetic curves of ethylene polymerization obtained at 50° , 60° , and 70°C are shown in Figures 2, 3, and 4, respectively. It is obvious that polymerization activity increases with increasing Al/Zr mole ratio at different T_p , which relates to reactivation of the Zr species.

To obtain the kinetic model, several underlying assumptions must be made in the development of the model: (1) instantaneous formation of active site; (2) first-order propagation with monomer and active sites; (3) first-order chain transfer to monomer; (4) first-order deactivation of each active site; and (5) considering the reactivation of the Zr species. Therefore, the polymerization re-

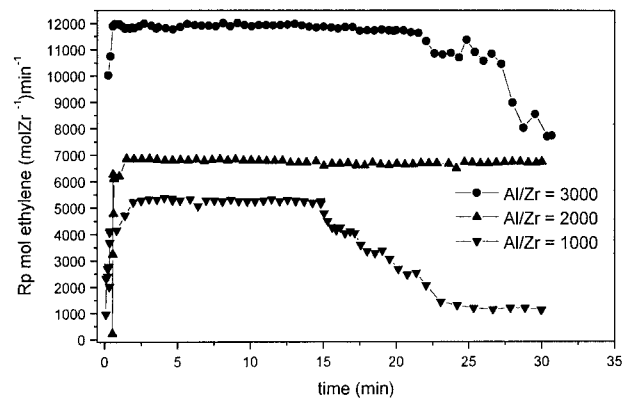


Figure 2 Kinetic curves obtained $[\text{Zr}] = 1 \times 10^{-5} \text{ M}$; $T_p = 50^\circ\text{C}$; 50 mL toluene; $t = 30 \text{ min}$.

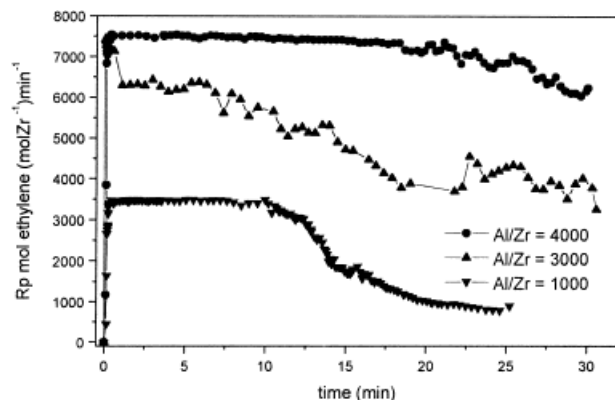


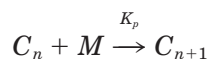
Figure 3 Kinetic curves $[Zr] = 1 \times 10^{-5} M$; $T_p = 60^\circ C$; 50 mL toluene; $t = 30$ min.

actions of a single site system can be described as follows:

1. Instantaneous formation of active species:



2. Propagation of active species:



3. Transfer to monomer:

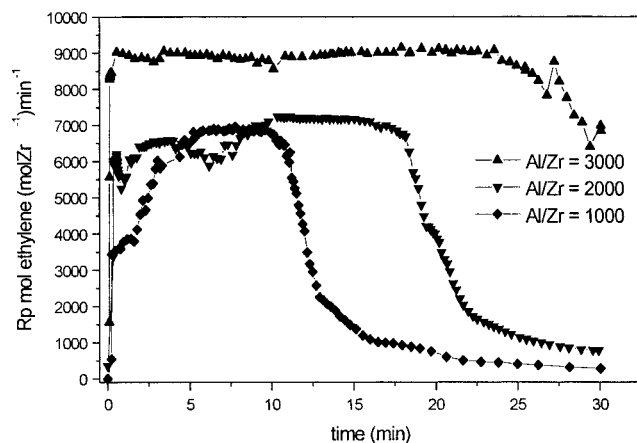
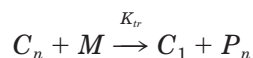


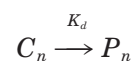
Figure 4 Kinetic curves $[Zr] = 1 \times 10^{-5} M$; $T_p = 70^\circ C$; 50 mL toluene; $t = 30$ min.

Table I Kinetic Parameters of Ethylene Polymerization

Al/Zr (mol/mol)	$k_p = k'_p/M$ [L/(mol · min)]	k_d [(min ⁻¹)]
3000	8.5×10^4	0.00651
2000	8.2×10^4	0.0033
1000	6.0×10^4	0.12216

Conditions: $T_p = 50^\circ C$, $[Zr] = 1 \times 10^{-5} M$, 50 mL toluene, $t = 30$ min.

4. Deactivation of active species:



5. Reactivation of deactivated species:



A kinetic mode was obtained as follows:

$$R_p = k_p \left[\frac{k'_a}{k_d + k'_a} + \frac{k_d}{k_d + k'_a} e^{-(k_d + k_a)(t - t_0)} \right] M C_0$$

Typical experiment results obtained at different T_p are shown in Figures 2, 3, and 4, respectively. The kinetic parameters of ethylene polymerization obtained by simulating kinetic model are summarized in Table I. Simulated results are consistent with experiment results and previous works,⁸ which indicates the model including reactivation of deactivated species is reasonable.

CONCLUSIONS

Polyethylene was prepared using a nBu-Cp₂ZrCl₂/MAO catalytic system. It is believed that mainly as a result of the electronic effect, the nBu-Cp₂ZrCl₂/MAO catalytic system yields higher polymerization activity. Considering the reactivation of the Zr species, a novel and reasonable mathematical model of kinetics is developed, and the kinetic experiment profiles of ethylene polymerization can be fitted satisfactorily using the mathematical model of kinetics. Further research is under way.

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