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Strong influences of polymerization temperature on ethylene/1-hexene copolymerization catalyzed by (2-PhInd)$_2$ZrCl$_2$/methyl aluminoxane[*]

YE Jian-ding (叶坚定)[†], FAN Zhi-qiang (范志强)[†‡], WANG Wei (王 伟)

(*Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China*)

[†]E-mail: stonestone5678@yahoo.com.cn; fanzq@zju.edu.cn

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Abstract: Ethylene/1-hexene was copolymerized by an unbridged zirconocene, (2-PhInd)$_2$ZrCl$_2$/MAO (methyl aluminoxane) at 0 °C and 50 °C respectively. High copolymerization activity and 1-hexene incorporation were observed at 0 °C, with the copolymer formed having random sequence distribution and narrow molecular weight distribution. Ethylene polymerization at 50 °C showed high activity, but copolymerization at 50 °C showed much lower activity, which decreased sharply with increasing 1-hexene concentration in the monomer feed. Copolymer formed at 50 °C showed blocky sequence distribution and broad molecular weight distribution. A mechanism model based on ligand rotation hindered by the propagation chain has been proposed to qualitatively explain the observed phenomena.

Key words: Unbridged metallocene, Ethylene, 1-Hexene, Copolymerization, Temperature effect
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INTRODUCTION

Various metallocene complexes, when activated with methyl aluminoxane (MAO), have been found to be effective catalysts for the copolymerization of ethylene with C_4~C_{20} α-olefins (Brintzinger *et al.*, 1995; Koivumaki and Seppala, 1993; Tsutsui and Kashiwa, 1988; Kaminsky, 1986). In the reported cases of copolymerization of ethylene and α-olefin catalyzed by unbridged metallocenes (Yoon *et al.*, 2000; Reybuck *et al.*, 2002; Hung *et al.*, 2003; Dankova and Waymouth, 2003), only a moderate influence of reaction temperature on the copolymerization behaviors was observed in the temperature range of 0~50 °C. Yoon *et al.*(2000) investigated the copolymerization of ethylene with 1-hexene, 1-dodecene and 1-octadecene by two unbridged zirconocenes, (2-MeInd)$_2$ZrCl$_2$ and (2-BzInd)$_2$ZrCl$_2$. It was reported that raising polymerization temperature from −20 °C to 40 °C caused less than one fold change in activity. Reybuck *et al.*(2002) and Hung *et al.*(2003) and Dankova and Waymouth (2003) reported higher 1-hexene incorporation in ethylene/1-hexene copolymerization by (2-PhInd)$_2$ZrCl$_2$/MAO than severel other unbridged zirconocenes and a bridged *ansa*-zirconocene, *rac*-Et(Ind)$_2$ZrCl$_2$. The copolymerization was carried out at low temperature in medium of 1-hexene, and copolymers containing more than 30 mol% 1-hexene units were obtained.

Regarding the catalysis mechanism of propylene polymerization by unbridged zirconocene (2-PhInd)$_2$ZrCl$_2$/MAO, there are two different models in the literature. Coates and Waymouth (1995) proposed a mechanism based on 'oscillating' conformations of the active species between a '*rac*-like' and a '*meso*-like' conformer (Bruce *et al.*, 1997). On the

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[‡] Corresponding author

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contrary, Busico *et al.*(2002; 2003) proposed that the '*rac*-like' conformer of the active species is relatively more stable and cannot be converted into '*meso*-like' conformer. The high ability of $(2\text{-PhInd})_2ZrCl_2/MAO$ to incorporate 1-hexene in ethylene/1-hexene copolymerization was explained based on steric restriction of the 2-phenyl on the conformations that are unfavorable to the coordination of large comonomer (Reybuck *et al.*, 2002).

In this paper, we report the results of ethylene/1-hexene copolymerization by $(2\text{-PhInd})_2ZrCl_2/$ MAO at 0 °C and 50 °C. A strong effect of temperature on the copolymerization activity and copolymer structure, especially at high 1-hexene concentration, was observed and preliminary explanation is proposed.

EXPERIMENTAL PART

Materials

All manipulations were carried out under an atmosphere of argon using standard Schlenk technique. $(2\text{-PhInd})_2ZrCl_2$ was synthesized according to Bruce *et al.*(1997) and characterized by ^1H NMR. Methyl aluminoxane (10 wt% in toluene) from Albemarle was used without further treatment. Toluene was refluxed over sodium/benzophenone and distilled before use.

Polymerization

Ethylene polymerization and ethylene/1-hexene copolymerization were carried out at atmospheric ethylene pressure in 100 ml glass reactor. After thrice evacuating the reactor ethylene was filled in and toluene, 1-hexene, MAO solution and a solution of $(2\text{-PhInd})_2ZrCl_2$ in toluene were injected into the reactors under stirring. Ethylene of 101325 Pa pressure was continuously supplied to the reactor during the reaction at constant temperature. After 30 min acidified ethanol was injected to terminate the reaction. The polymer was filtered, washed with ethanol and dried in vacuum at 40 °C.

Polymer characterization

Content of 1-hexene in the copolymers was determined by ^{13}C NMR on a Bruker AM 400 spectrometer in *o*-dichlorobenzene-*d4* at 120 °C with 1000 scanning times and a pulse delay time of 5 s. Molecular weights and molecular weight distribution of the polymer were determined using a PL 220 GPC (gel permeation chromatography) instrument at 150 °C in 1,2,4-trichlorobenzene. Universal calibration against narrow standard polystyrene was adopted.

Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 thermal analyzer. The polymer (about 4 mg) was sealed in aluminum pan, which was then sealed in a glass tube at argon atmosphere. The glass tube was immersed in an oil bath and heated to 160 °C, kept at that temperature for 30 min, and then annealed at 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, and 30 °C, respectively, each for 12 h. The treated samples were then scanned in DSC from 0 °C to 160 °C at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Ethylene/1-hexene copolymerization

Using $(2\text{-PhInd})_2ZrCl_2$ as the catalyst and MAO as cocatalyst, a series of ethylene/1-hexene copolymer runs were conducted both at 0 °C and 50 °C, and the results are listed in Table 1.

It can be seen that at 0 °C there is a comonomer synergistic effect, with the copolymerization activity much higher than that of ethylene homopolymerization. However, the comonomer 1-hexene showed a strong deactivation effect on the catalyst when the temperature was raised to 50 °C (Fig.1). Such a strong temperature effect has not been found in other unbridged zirconocene catalyzed ethylene copolymerization.

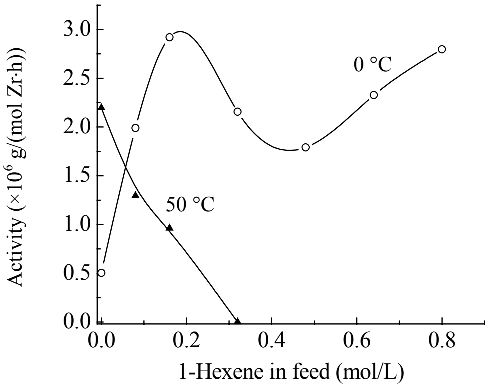

Fig.1 Change of polymerization activity versus 1-hexene in the feed

The 1-hexene content of the copolymer samples was measured by ^{13}C NMR, and a typical spectrum is shown in Fig.2. It is found that in all the copolymerization runs the conversion of 1-hexene is lower than 15%. This means that broadening of inter-molecular composition distribution caused by 1-hexene consumption is negligible. As shown in Table 1, at both 0 °C and 50 °C, the 1-hexene content of the copolymer increases with the increase of 1-hexene concentration in the monomer feed.

Copolymer produced at 50 °C has higher 1-hexene content than the copolymer produced at 0 °C at the same monomer feed. This can be considered as the result of decreasing ethylene concentration in the reaction medium at high temperature. It seems that raising temperature from 0 °C to 50 °C does not influence much the comonomer incorporation.

Table 1 shows that raising temperature from 0 °C to 50 °C greatly lowered the molecular weight of the copolymer, but the molecular weight of ethylene homopolymer is only slightly affected by temperature. At 0 °C, some copolymer samples have molecular weight even higher than the homopolymer, but copolymers produced at 50 °C showed molecular weight values only about one fifth that of the corresponding homopolymer.

Table 1 Results of ethylene/1-hexene copolymerization catalyzed by $(2\text{-PhInd})_2ZrCl_2$/MAO[a]

Run	T (°C)	[1-Hexene][b] (mol/L)	Hexene content[c] (mol%)	Activity ($\times10^6$ g PE/(mol Zr·h))	M_w[d] ($\times10^{-3}$)	PDI[e]
1	0	0.00	0.00	0.50	565	3.84
2	0	0.08	3.70	1.99	646	3.32
3	0	0.16	6.55	2.92	1100	2.90
4	0	0.32	10.18	2.16	631	2.84
5	0	0.48	16.61	1.79	640	2.83
6	0	0.64	20.71	2.33	543	2.75
7	0	0.80	29.83	2.80	540	2.68
8	50	0.00	0.00	2.20	355	3.96
9	50	0.08	8.33	1.29	87	9.27
10	50	0.16	15.24	0.96	78	9.29
11	50	0.32	–	[f]	–	–
12	50	0.48	–	0	–	–
13	50	0.64	–	0	–	–
14	50	0.80	–	0	–	–

[a]: Ethylene pressure=101 325 Pa; [Al]/[Zr]=3000; [Zr]=1×10^5 mol/L; Volume=50 ml; Polymerization time=0.5 h; [b]: Initial concentration of 1-hexene in the reactor (mol/L); [c]: Incorporated 1-hexene; [d]: Average molecular weight determined by GPC; [e]: Polydispersity index determined by GPC; [f]: Trace amount of oily product was collected; PE: Polyethylene

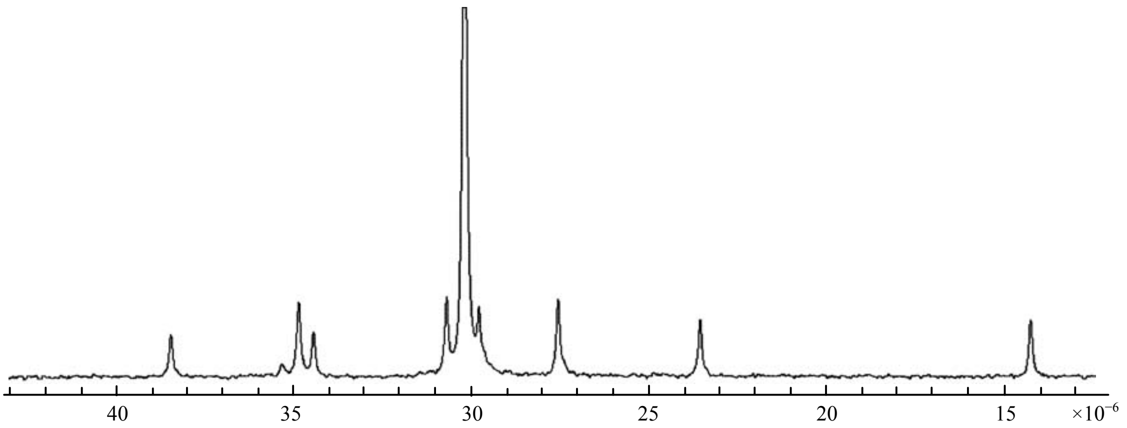

Fig.2 ^{13}C NMR spectra for ethylene/1-hexene copolymer obtained from initial [1-hexene]=0.08 mol/L (0 °C)

On the other hand, copolymers produced at 0 °C have rather narrow and unimodal molecular weight distribution (MWD), while the copolymer samples produced at 50 °C showed very broad MWD. As shown in Fig.3, the copolymer produced at 50 °C has a low molecular weight shoulder in the MWD curve, which accounts for the low M_w and high PDI values. Though the MWD of copolymers determined by GPC is hard to be accurately calibrated, such differences in MWD are clear enough to show the strong effect of temperature on copolymer structure.

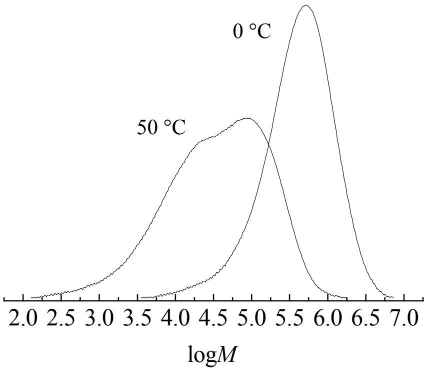

Fig.3 Molecular weight distributions of the copolymer synthesized at different temperatures ([1-hexene]=0.08 mol/L)

Sequence distribution of the copolymer

To characterize the chain structure of the copolymers, crystallization segregation thermal analysis (Adsson *et al.*, 1992; Starck, 1996) of samples was adopted, and the melting scan DSC curves are show in Fig.4 and Fig.5.

In the DSC curves of the copolymer samples, when the 1-hexene concentration in the feed is lower than 0.2 mol/L, several endothermic peaks appeared, which corresponded to crystalline lamella of different thickness. This distribution of lamellae thickness is caused by interruption of the polyethylene chain by the 1-hexene units, because the hexene units cannot be included in the crystalline phase. Thus the distribution of crystallizable polyethylene segment in the copolymer chain can be estimated from the position and intensity of the peaks. At 0 °C, copolymer with [1-hexene]>0.32 mol/L are completely amorphous, meaning that PE segments in these samples are too short to form crystalline lamella. By comparing the DSC curves of the samples produced at different temperatures, it can be found that the 0 °C samples have more narrow distribution of PE segment than the corresponding 50 °C samples. Let us take the copolymers synthesized at [1-hexene]=0.08 mol/L as example. In the 0 °C product the peak at 90~100 °C is much stronger than the rest of the peaks. Contrarily, in the 50 °C product, the endothermic peaks appear in a much wider temperature range, from 125 °C to 40 °C, and the difference between the area of adjacent peaks is also much smaller. Remembering that the 50 °C product contains more 1-hexene units than the corresponding 0 °C product, the influence of polymerization temperature on the comonomer sequence distribution is rather strong.

The average melting temperature (T_{mAV}) of the copolymer samples was calculated based on the following equation:

$$T_{\mathrm{mAV}} = \sum \Delta H_i T_{mi} / \sum \Delta H_i$$

The crystallinity of the samples (X_c) is calculated based on the experimental $\sum \Delta H_i$ data and the melting

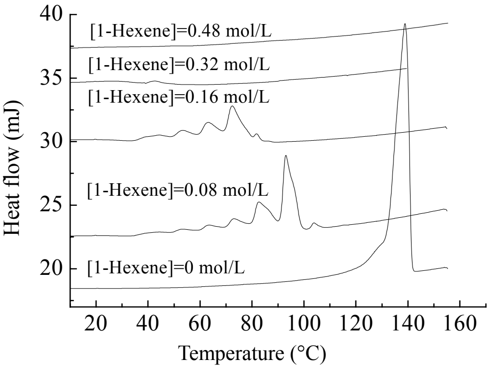

Fig.4 DSC diagrams of the copolymer samples produced at 0 °C with different initial 1-hexene concentration

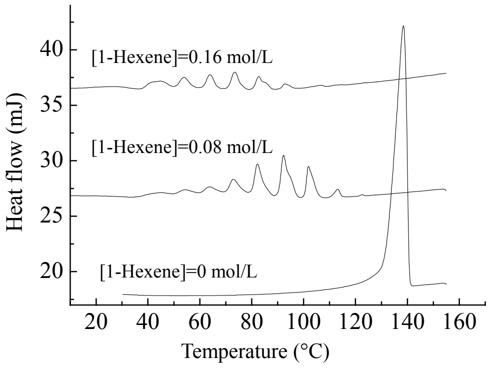

Fig.5 DSC diagrams of the copolymer samples produced at 50 °C with different initial 1-hexene concentration

enthalpy of a 100% defect-free polyethylene (292 J/g) (Wunderlich, 1990). By comparing the changes of T_{mAV} and X_c with 1-hexene content (Table 2), it can also be concluded that the copolymers produced at 50 °C have more inhomogeneous sequence distribution than the 0 °C samples. Such inhomogeneity may either be caused by blocky nature of each copolymer chain in the sample, or by broad chemical composition distribution (CCD) of the sample. In fact, the copolymer samples produced at 50 °C may either be a kind of ethylene/1-hexene 'block' copolymer or a mixture of chains with high and low 1-hexene content, while the samples produced at 0 °C are basically random copolymer with narrow CCD.

Table 2 Average melting temperature and crystallinity of the copolymer

Run	Polymerization temperature (°C)	Hexene content (mol%)	T_{mAV} (°C)	X_c (%)
1	0	0.00	136.10	66.7
2	0	3.70	83.80	24.0
3	0	6.55	65.00	16.0
8	50	0.00	135.10	68.9
9	50	8.33	81.27	24.2
10	50	15.24	63.79	12.5

Polymerization mechanism and model of the active species

To reasonably explain the strong influences of polymerization temperature on the activity and product structure of $(2\text{-PhInd})_2ZrCl_2$/MAO catalyzed ethylene/1-hexene copolymerization, a mechanism model for this catalysis system is proposed.

Cavallo *et al.*(1996) studied the conformation of a model $[(2\text{-PhInd})_2ZrR]^+$ cation by molecular mechanics and found that the most stable conformations are *rac*-like (Fig.6). Further rotation of the ligand leads to a 'T-shaped' conformation. Based on this prediction, we believe that the active species for ethylene/1-hexene copolymerization at 0 °C mainly exist in *rac*-like conformation. Uozumi *et al.*(1997) reported higher 1-octene incorporation rate in ethylene/1-octene copolymerization by *rac*-Me_2Si (2-Me-1-Ind)$_2ZrCl_2$ than the corresponding *meso*-isomer. This suggests that the racemic conformation should be more favorable for ethylene/α-olefin copolymerization. The relatively high α-olefin incorporation in $(2\text{-PhInd})_2ZrCl_2$/MAO catalyzed ethylene/α-olefin copolymerization (Reybuck *et al.*, 2002; Hung *et al.*, 2003; Dankova and Waymouth, 2003) may be understood on this basis. At 0 °C, the *rac*-like conformation becomes stable partly because of the low molecular mobility of the active species and partly because of the steric hindrance between the ligands and the propagation chain which forms highly ordered structure (Fig.6a). Thus the *rac*-like conformer function as the main active center at 0 °C and efficiently copolymerize ethylene and 1-hexene to form copolymer with high 1-hexene content, random sequence distribution and narrow molecular weight distribution. When the temperature is raised to 50 °C, the *rac*-like conformer can still be stabilized when ethylene homopolymerization is carried out, because polyethylene chains have a strong tendency to form ordered structure (Fujiwara and Sato, 2002). This ensures efficient ethylene polymerization at 50 °C and yields high molecular weight product. However, when ethylene/1-hexene copolymerization is conducted at 50 °C, the propagation chain becomes partly or completely soluble (depending on the copolymer composition) in the reaction medium and behaves like a random coil (Fig.6b), and the steric hindrance to ligand rotation or vibration by the propagation chain is lowered. Therefore, at high temperature the active species has high probability of converting from the most active *rac*-like conformer to other less active or even inactive conformers. This will result in decreases in polymerization activity and molecular weight, and broadening of molecular weight distribution as 1-hexene content in copolymer increases, as observed in the experiments. The blocky sequence distribution of the copolymer produced at 50 °C may also be understood based on this model: when the active species change among the *rac*-like and other conformers, because the later can incorporate only lower amount of 1-hexene than the former, copolymer chain with alternating 1-hexene rich random segments and ethylene rich crystallizable segments will be formed. If new polymer chains are started when the active species swing away from the *rac*-like conformer, copolymer chains with low 1-hexene content may be produced, which form the crystallizable polyethylene segments observed in the DSC curve as well as the low molecular weight shoulder in the GPC curve. According to this mechanism model, the propagation chain plays an important role in the conformation interconversion of the active species.

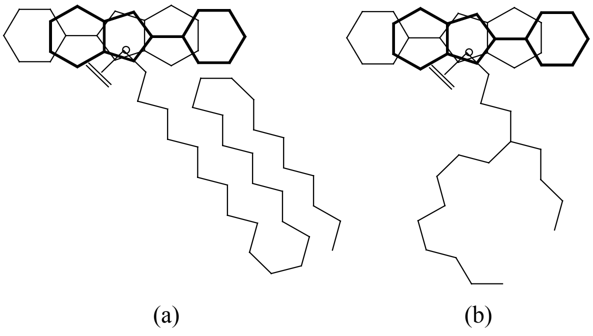

Fig.6 Model of the active species (a) Active rac-like conformer at 0 °C; (b) Less active conformer at 50 °C

CONCLUSION

In conclusion, strong influences of polymerization temperature on $(2\text{-PhInd})_2ZrCl_2/MAO$ catalyzed ethylene/1-hexene copolymerization activity and product structure were observed. At 50 °C the copolymerization activity and polymer structure changed markedly when the 1-hexene content of copolymer increased. A mechanism model based on ligand rotation hindered by the propagation chain has been proposed to qualitatively explain the observed phenomena.

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