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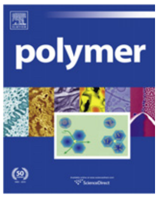

With different structure ligands heterogeneous Ziegler–Natta catalysts for the preparation of copolymer of ethylene and 1-octene with high comonomer incorporation

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ABSTRACT

Comparison with the conventional Ziegler–Natta catalyst $TiCl_4/MgCl_2$ (**I**), the modified supported Ziegler–Natta catalysts (iso-PentylO)$TiCl_3/MgCl_2$ (**II**) and (BzO)$TiCl_3/MgCl_2$ (**III**) were prepared as efficient catalysts for copolymerization of ethylene with 1-octene. The complexes (**II**) and (**III**) were desirable for the production of random ethylene/1-octene copolymers coupled with higher molecular weight, higher comonomer incorporation within copolymer chain and good yield even at high temperature 80 °C and fairly low Al/Ti molar ratio of 100. The effects of catalysts ligands, Al/Ti molar ratio, polymerization temperature, as well as concentration of 1-octene on the catalytic activity, molecular weight and microstructure of the copolymer were investigated in detail. The structure and properties of the copolymers were characterized with ^{13}C NMR, GPC, DSC and WAXD. The kinetic results also indicate that these catalysts (**II**) and (**III**) show higher catalytic activity and the produced polymers feature higher molecular weight, because of lower ratio of K_{trm}/K_p and K_{tra}/K_p, and higher ratio of K_{tra}/K_{trm} which indicates that chain transfer to cocatalyst is predominant.

1. Introduction

The copolymer of ethylene with longer α-olefin has become one of the most widely applied polymers [1]. Many efforts have been done for improving the catalysts' performance for copolymerization of ethylene with longer α-olefins. For decades, the single-site-type catalysts including metallocene and non-metallocene catalysts have opened a new strategy for the synthesis of the ethylene-α-olefin copolymers with high comonomer incorporation, uniform structure and excellent properties. The constrained geometry catalysts (CGC) of *ansa*-monocyclopentadienylamido group 4 metal complexes, a new generation metallocene catalyst, are useful in the copolymerization of ethylene with longer α-olefins, such as 1-hexene and 1-octene, etc. The comonomer incorporation within the copolymer catalyzed by CGC was up to 19 mol% [2]. Xu [3] showed that 2-methybenz[*e*]indenyl-based *ansa*-monocyclopentadienylamido complex, methylaluminoxane(MAO) used as cocatalyst, preferred to the copolymerization of ethylene with 1-octene to form copolymer featured high comonomer incorporation up to 58.5% in mol. Tsutsui [4] reported the synthesis of ethylene/1-octene copolymer with a very low density ($p = 0.853$ g/cm^3), using Ethylenebis(indenyl) diphenyl hafnium and its derivatives as catalysts. Fujita [5] used fluorinated bis(phenoxy-imine) titanium complexes activated by methylalumoxane for producing ethylene/1-hexene copolymer with high comonomer incorporation of 22.6% in mol. Amine bis (phenolate) zirconium complexes for ethylene/1-hexene copolymerization is performed smoothly. The content of the comonomer in the copolymer chain was up to 57.6% in mol [6].

However, the conventional Ziegler–Natta catalysts are less effective in promoting the copolymerization of ethylene with longer α-olefins, and the incorporated comonomer distributions within the copolymers chain aren't uniform. Czaja [7] investigated the copolymerization of ethylene with 1-octene catalyzed by the catalyst system $MgCl_2(THF)_2/TiCl_4/Et_2AlCl$. It was found that the comonomer incorporation in copolymer was only 0.39% in mol. But the heterogeneous Ziegler–Natta catalysts are still dominant in industry. In this work, we report that the modified Ziegler–Natta catalysts whereby the catalyst precursor from one halogen of $TiCl_4$

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replaced by alkyloxy or benzyloxy is supported on $MgCl_2$ dissolved in toluene in the presence of 3-Chloro-1,2-epoxypropane and tributyl phosphate, are for the copolymerization of ethylene with 1-octene. In this procedure 3-Chloro-1,2-epoxypropane and tributyl phosphate improve the solubility of $MgCl_2$ in toluene [8]. The copolymerization behavior and the microstructure of the resultant copolymers are also investigated.

2. Experimental part

2.1. Materials

All operations of air and moisture-sensitive materials were performed using the rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line under a nitrogen atmosphere. Toluene and hexane were refluxed over metallic sodium under nitrogen for 24 h and distilled before use. 3-Chloro-1,2-epoxypropane and tributyl phosphate were treated with activated 5 Å molecule sieves under high-purity nitrogen for one week before use. $MgCl_2$, $AlEt_3$ (2.0 M in n-hexane), 2-methyl-2-butanol (iso-pentylOH) and benzyl alcohol (BzOH) were purchased from Acros and were used without further purification. 1-Octene was purified by distillation over CaH_2 and stored in a Schlenk tube containing 5 Å molecular sieves under high-purity nitrogen. Ethylene (polymerization grade) was purchased from the Institute of Beijing Guangming Chemical and Engineering, and used without further purification.

2.2. Preparation of catalysts

2.2.1. Preparation of $TiCl_4/MgCl_2$(**I**)

The supported titanium magnesium catalyst precursor (**I**) was prepared by the treatment of $MgCl_2$ (solid, 1.0 g) dissolved in toluene (60 mL) in the presence of 3-Chloro-1,2-epoxypropane and tributyl phosphate with $TiCl_4$ (Mg: Ti = 1:2 in mol) at −25 °C for 1 h in a 200 mL Schlenk flask with a magnetic bar. Then the temperature enhanced to 70 °C and kept it constant for 5 h. Cooling the mixture to 50 °C and adding n-hexane 20.0 mL, spherical precipitate was given. The mixture was filtrated and washed with n-hexane (6 × 50 mL), then dried by vacuum. Catalyst spherical particle was obtained in yield 1.07 g with pale purple color. Ti content of the catalyst was 4.1 wt% determined by ICP-AES. About 10 mg of the supported catalyst was dissolved with HF and HNO_3 acid completely. The solution was diluted with distilled water and used for the ICP analysis.

2.2.2. Preparation of (iso-PentylO)$TiCl_3/MgCl_2$(**II**)

To a stirred solution of $TiCl_4$ (5.0 mL, 8.63 g, 0.045 mol) in n-hexane, one equivalent of 2-methyl-2-butanol (iso-PentylOH) (3.96 g, 0.045 mol) and one equivalent of Et_3N in hexane were added drop by drop at −25 °C. The mixture was stirred at 0 °C for 1 h and at 30 °C for 8 h. The mixture was filtrated, and then extracted by n-hexane. The solvent was moved. Brown solid was given with yield 9.48 g (87.8%). (iso-PentylO)$TiCl_3$ compound: mp 82.1 8C, ^1H NMR: d 2.45 (tetra, 2H), d 1.18 (tri, 3H), d1.24 (s, 6H); ELEM.ANAL. Calcd: C, 24.95; H, 4.57. Found: C, 24.86; H, 4.61.

The supported modified titanium magnesium catalyst precursor (**II**) was prepared by a similar procedure as (I). To a mixing solution of solid $MgCl_2$ (solid, 1.0 g) dissolved in toluene (60 mL), 3-Chlogro-1,2-epoxypropane and tributyl phosphate, a solution of (iso-PentylO)$TiCl_3$ (5.1 g) in hexane (Mg:Ti = 1:2 in mol) was added via a syringe at −25 °C over a period of 1 h in a 200 mL Schlenk flask with a magnetic bar. Then the temperature enhanced to 70 °C and kept it constant for 5 h. Cooling the mixture to 50 °C and adding n-hexane 20.0 mL, spherical precipitate was given. The mixture was filtrated and washed with n-hexane(6 × 50 mL), then dried by vacuum. Solid catalyst spherical particle was obtained in yield 1.27 g with brown color. Ti content of the catalyst was 4.0 wt% determined by ICP-AES.

2.2.3. Preparation of (BzO)$TiCl_3/MgCl_2$(***III***)

To a solution of $TiCl_4$ (5.0 mL, 8.63 g, 0.045 mol) in n-hexane, one equivalent of BzOH (4.86 g, 0.045 mol) in hexane and one equivalent of Et_3N was added at −78 °C with a syringe within 1 h. The mixture was slowly warmed to 40 °C and kept constant for 8 h. The mixture was filtrated, and then extracted by hexane. The solvent was moved by vacuum. Yellow solid was given with yield 10.86 g (92.7%). (BzO)$TiCl_3$: mp 93.1 °C, ^1H NMR: d 7.21 (s, 5H, ph), d 4.54 (s, 2H, O−CH_2−); ELEM.ANAL. Calcd: C, 32.25; H, 2.69. Found: C, 32.30; H, 2.71.

The supported modified titanium magnesium catalyst precursor (**III**) was prepared by the treatment of $MgCl_2$ (solid, 1.0 g) dissolved in toluene (60 mL) in the presence of 3-Chloro-1,2-epoxypropane and tributyl phosphate with (BzO)$TiCl_3$ (2.7 g) (Mg:Ti = 1:2 in mol) at −25 °C for 1 h in a 200 mL Schlenk flask with a magnetic bar. Then the temperature enhanced to 70 °C and kept it constant for 5 h. Cooling the mixture to 50 °C and adding n-hexane 20.0 mL, spherical precipitate was given. The mixture was filtrated and washed with n-hexane (6 × 50 mL), then dried by vacuum. Solid catalyst spherical particle was obtained in yield 1.21 g with yellow color. Ti content of the catalyst was 4.0 wt% determined by ICP-AES.

2.3. Copolymerization procedure

All polymerizations were carried out in a 200 mL glass flask equipped with a magnetic stirrer after purging all moisture and oxygen by a high-vacuum pump, the reactor was sealed under a nitrogen atmosphere. Freshly distilled hexane (60 mL), desired amounts of heterogeneous Ziegler–Natta catalyst and $AlEt_3$ were added in the order. The mixture was stirred for 15 min for pre-activation. After that, 1-octene was charged into the reactor and the copolymerization was initiated by the introduction of ethylene. The monomer pressure was kept constant during the polymerization by continuously charging with ethylene. The reaction was stirred for 60 min. Finally, the polymerization was terminated with 10 wt% HCl in alcohol. The obtained polymer was filtered and washed with alcohol and water, then dried overnight in a vacuum oven at 50 °C. Ethylene consumption was automatically recorded by a flowmeter.

2.4. Characterization

^{13}C NMR spectra was recorded on an INOVA500 MHz instrument operating at 125 MHz. The condition used for quantitative ^{13}C NMR was of the copolymer content up to 15 wt% in solution, using *ortho*-dichlorobezene(d_4) as the solvent at 125 °C. Tetramethylsilane was used as internal chemical shifts reference. The 1-octene incorporation is estimated from ^{13}C NMR spectra according to the literature [9]. The average molecular weight and molecular weight distribution were measured by PL-GPC200 instrument using standard polystyrene as reference and 1,2,4-trichlorobenzene as solvent at 150 °C. DSC thermograms were recorded with a PA5000-DSC instrument at a rate of 10 K/min. WAXD was recorded with a Rigaku D/max 3A instrument, using Ni films to sieve wave, using Cu Kα radiation ($\lambda = 1.5405 \times 10^{-10}$ m). WAXD intensities were recorded from 5° to 40° with a continuous scanning speed.

As for catalyst analyses, ^1H spectra was measured on an INOVA500 MHz instrument. All ^1H chemical shifts were reported in ppm relative to proton resonance in chloroform-*d* at δ 7.26 ppm. Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer at the College of Material Science and Technology, Beijing University of Chemical Technology.

3. Results and discussion

3.1. Copolymerization of ethylene with 1-octene

The two newly synthesized catalysts (**II** and **III**) were investigated using $AlEt_3$ as cocatalyst for copolymerization of ethylene with 1-octene to demonstrate their catalytic behaviors. Catalytic activities of these catalysts and the properties of the obtained copolymers were compiled in Table 1. From Table 1 we can notice that all of the three catalyst systems (**I**–**III**) exhibit high activity and high stability during the polymerization course even at a fairly high temperature of 80 °C. The activities of catalysts (**II**) and (**III**) maintain nearly constant over 1 h at polymerization temperature of 80 °C even at fairly low Ti concentration, such as 10 mg of the supported catalyst in 60 mL solvent (Fig. 1b and c). But the activity for catalyst (**I**) shows obviously decline after 30 min for the copolymerization of ethylene with 1-octene under the same conditions (Fig. 1a). Thus a low rate of deactivation of these catalysts (**II**) and (**III**) might be attributable to the enhanced steric hindrance of these ligands [10]. The catalysts (**II**) and (**III**) exhibit much higher catalytic activity than that of no ligand substituted catalyst (**I**). The discovery indicates that the presence of ligand moiety meet the electronic coordination requirements for high activity. In addition, due to the charge of active site of catalyst (**III**) could be effectively delocalized overall the phenyl ring, the electron donation and the resonance stabilization increases from phenyl ring substitute would stabilize the active species and make the monomer ethylene or 1-octene access the coordination site easier, which enlarges the polymerization rate. Therefore, the overall activity is enhanced. Comparison with catalyst (**I**), the high molecular weight of polyethylene thus obtained could be mainly due to the electron effect caused by the presence of the electron-releasing iso-pentyl and phenyl ring moiety, resulting in an increase in electron density at the metal center and also at the β-carbon (1-octene). Consequently, the β-hydrogen elimination and chain transfer reactions to monomer would be diminished during the polymerization course [11]. On the other hand, the phenyl ring substitute in the catalyst (**III**) makes that the titanium center might diminish detrimental β-agostic interaction during the propagation [12]. We examined $TiCl_4/MgCl_2$ (**I**), (iso-PentylO)$TiCl_3/MgCl_2$ (**II**) and (BzO)$TiCl_3/MgCl_2$ (**III**) for the copolymerization of ethylene with 1-octene. The comonomer incorporation of the obtained copolymers increases with increasing steric bulk of the ligands of the catalysts. 1-octene incorporation content of the copolymer catalyzed by catalyst (**I**) is 0.34 mol%. However, the comonomer incorporation content of the copolymers catalyzed by catalyst (**II**) and (**III**) are 2.26 mol% and 7.46 mol%, respectively. These results suggest that these steric advantage make comonomer 1-octene insertion easier. It consists that steric and electronic effects in the catalyst systems in a subtle combination are determining the essential properties of catalyst systems and their action [13,14].

The effects of Al/Ti molar ratio on the catalytic activity, 1-octene incorporation and molecular weight of the copolymer were investigated (Table 2). From Table 2 we can notice that the catalytic

Table 1
The effect of the catalysts on the copolymerization of ethylene with 1-octene.

Runs	Catalyst	A^a (kg/g Ti.h)	o-Cont[b] (mol%)	M_n[c] ($\times 10^{-4}$)	MWD	T_m[d] (°C)
1	$TiCl_4/MgCl_2$(**I**)	17.6	0.34	9.40	4.0	130.2
2	(iso-PentylO)$TiCl_3/MgCl_2$(**II**)	22.0	2.26	10.33	4.8	124.1
3	(BzO)$TiCl_3/MgCl_2$(**III**)	26.1	7.46	13.38	3.2	–
4	$(n\text{-}BuCp)_2ZrCl_2$[e]	885[f]	2.33	3.32	2.1	114.5

Polymerization conditions: the catalyst amount adding, 10.0 mg; T, 80 °C; ethylene pressure, 0.12 MPa; solvent, hexane, 60 mL; time, 1 h; 1-octene content in feed, 3.0 mL; cocatalyst, $AlEt_3$; Al/Ti, 100 in mol.

[a] The catalytic activity.

[b] 1-Octene molar content in polymer determined by ^{13}C NMR.

[c] Number average molecular weight of the copolymer determined by GPC.

[d] Melting point of the copolymer determined by DSC.

[e] Homogeneous polymerization conditions: Zr = 10 μmol; Al(MAO)/Zr = 600 (mol/mol); T = 50 °C; t = 30 min; P_{C2H4} = 0.12 MPa; solvent, toluene, 100 mL; 1-octene content in feed, 3.0 mL.

[f] kgPE/molZr.h.

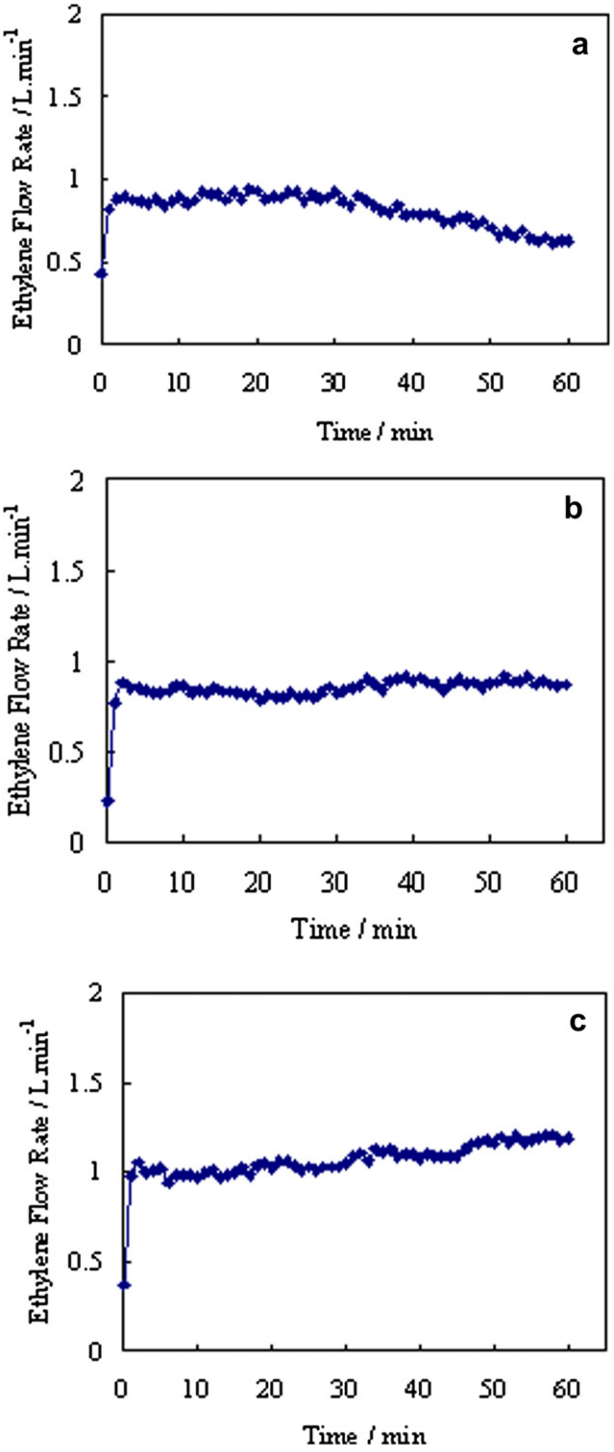

Fig. 1. The kinetic curves of (a) catalyst (**I**), (b) catalyst (**II**) and (c) catalyst (**III**).

activity depends upon the concentration of cocatalyst $AlEt_3$ as associating with the result of MAO for metallocene catalysts [2]. For industrial uses, it is interested in these catalysts (**I**–**III**) because of possessing a high activity at a fairly low Al/Ti ratio to result in lower productive cost. The number average molecular weight of the copolymers thus obtained has changed as increasing Al/Ti molar ratio. The result suggests that $AlEt_3$ acts as a chain transfer agent to some extent. However, 1-octene incorporation within the copolymer has minor change with varying of Al/Ti molar ratio, which implies that comonomer incorporation mainly depends on the catalyst structure, not on the Al/Ti molar ratio.

The copolymerization of ethylene and 1-octene was carried out at 70 °C, 80 °C, and 90 °C to investigate the temperature dependence of the catalytic activity. As shown in Table 3, the catalytic activity increases with the polymerization temperature T_p rising up to 80 °C for these catalysts (**I**–**III**). Further enhancing T_p to 90 °C, considerable reduction of activity is observed for catalysts (**I**–**III**)/$AlEt_3$ system. However, the difference values of the catalytic activities of these catalysts (**I**, **II** and **III**) at 80 °C and 90 °C are dwindled following this order, catalyst **I** > catalyst **II** > catalyst **III**. This result indicates that $TiCl_4$ substituted by alkyloxy or benzyloxy group shows more thermo-stability at high temperature. Comparing to catalyst (**II**), catalyst (**III**) for the copolymerization of ethylene with 1-octene provides higher catalytic activity and can lead to the copolymer with higher number average molecular weight and higher comonomer incorporation, implying that benzyloxy group substituted Ziegler–Natta catalyst (**III**) is preferable to the copolymerization of ethylene with 1-octene. However, 1-octene incorporation within copolymer chain is slightly changed with temperature varying for these catalysts (**I**, **II** and **III**), which confirms that the change of polymerization temperature wouldn't result in considerable varying of 1-octene incorporation. On the other hand, the molecular weight (M_n) of the obtained copolymers decreases with increasing polymerization temperature for all of these catalysts investigated. This is because of the fact that the average molecular weight of copolymers is predominantly decided by the K_p/K_{tr} ratio, where K_p increases with temperature slower than K_{tr}, which results in the decreasing of M_n as increasing temperature. This is very remarkable that these catalysts (**I**, **II** and **III**) can result in high molecular weight polymers even at temperature as high as 90 °C, which indicates that catalysts (**I**, **II** and **III**) are stable at high temperature.

The catalytic activity and the 1-octene incorporation within the copolymer were affected by the concentration of 1-octene in feed. The results were compiled in Table 4. We can notice that the positive "comonomer effective" [15,16] takes place for these catalysts (**I**, **II** and **III**). Compared to ethylene homopolymerization, a significant increase in catalytic activity for the copolymerization upon addition of 1-octene is observed. But over amount of 1-octene in the copolymerization mixture can result in the reduction of the catalytic activity. It is also found that the 1-octene incorporation is affected by the content of 1-octene in feed. With 1-octene amount in feed varying between 0 and 3 mL, the 1-octene incorporation increases obviously. But the amount of 1-octene in feed is up to 6 mL, the content of 1-octene incorporation is slightly increased, which reveals that the content of 1-octene incorporation doesn't depend on the adding amount of 1-octene in feed when the comonomer amount is enough for the copolymerization.

Table 2
The effect of Al/Ti molar ratio on the catalytic activity, 1-octene incorporation and molecular weight of the copolymer.

Catalyst	Al/Ti (mol/mol)	A[a] (kg/g Ti.h)	o-Cont[b] (mol%)	M_n[c] ($\times10^{-4}$)
Catalyst (**I**)	75	9.26	0.21	8.11
	100	17.6	0.34	9.40
	125	12.2	0.27	6.84
Catalyst (**II**)	75	12.8	1.84	8.92
	100	22.0	2.26	10.33
	125	14.3	1.96	8.34
Catalyst (**III**)	75	17.2	6.27	10.21
	100	26.1	7.46	13.38
	125	21.8	6.88	11.92

Polymerization conditions: the catalyst amount adding, 10.0 mg; T, 80 °C; ethylene pressure, 0.12 MPa; solvent, hexane, 60 mL; time, 1 h; 1-octene content in feed, 3.0 mL; cocatalyst, $AlEt_3$.
[a] The catalytic activity.
[b] 1-Octene molar content in polymer determined by ^{13}C NMR.
[c] Number average molecular weight of the copolymer determined by GPC.

Table 3
The effect of polymerization temperature on the catalytic activity and the properties of the copolymers.

Catalyst	T_p(°C)	A[a] (kg/g Ti.h)	o-Cont[b] (mol%)	M_n[c] ($\times10^{-4}$)	MWD	T_m[d] (°C)
Catalyst (**I**)	70	12.7	0.29	9.93	3.5	131.0
	80	17.5	0.34	9.40	4.0	130.2
	90	13.8	0.30	8.56	4.1	130.8
Catalyst (**II**)	70	16.8	2.07	11.12	4.2	123.0
	80	22.0	2.26	10.33	4.8	124.1
	90	19.1	2.11	9.12	4.5	123.9
Catalyst (**III**)	70	21.2	5.52	13.51	3.1	82.1
	80	26.1	7.46	13.38	3.2	–
	90	24.1	6.52	10.35	3.6	–

Polymerization conditions: the catalyst amount adding, 10.0 mg; ethylene pressure, 0.12 MPa; solvent, hexane, 60 mL; time, 1 h; 1-octene content in feed, 3.0 mL; cocatalyst, $AlEt_3$; Al/Ti = 100 in mol.
[a] The catalytic activity.
[b] 1-Octene molar content in polymer determined by ^{13}C NMR.
[c] Number average molecular weight of the copolymer determined by GPC.
[d] Melting point determined by DSC.

From previous work [17], the ligand structure of half-titanocenes showed observable effects on the properties of polymers obtained, especially in polymer molecular weight. It indicates that the ratio of chain propagation rate to chain termination rate or the chain transfer rate determines the polymer molecular weight. In this work we investigate the kinetics of ethylene/1-octene copolymerization catalyzed by conventional and modified Ziegler–Natta catalyst examined (Table 1), it is found that in all cases the relationship between the yield of polymer and monomer concentration around active site follows Eq. (1), which indicates that the chain propagation rate with respect to ethylene concentration is a first-order, which consists with the report in the literature [18,19].

Table 4
The effect of 1-octene concentration on the catalytic activity and the properties of the copolymers.

Catalyst	o-Cont[a] (mL)	A[b] (kg/g Ti.h)	o-Cont[c] (mol%)	M_n[d] ($\times10^{-4}$)	MWD	T_m[e] (°C)
Catalyst (**I**)	0	12.7	0	7.83	3.7	133.4
	3.0	17.5	0.34	9.40	4.0	130.2
	6.0	14.8	0.37	8.92	3.8	129.5
Catalyst (**II**)	0	14.8	0	9.92	4.5	134.6
	3.0	22.0	2.26	10.33	4.8	124.1
	6.0	19.1	2.28	10.55	4.5	124.0
Catalyst (**III**)	0	24.7	0	10.11	3.6	135.7
	3.0	26.1	7.46	13.38	3.2	–
	6.0	24.5	7.52	13.11	3.5	–

Polymerization conditions: the catalyst amount adding, 10 mg; ethylene pressure, 0.12 MPa; solvent, hexane, 60 mL; time, 1 h; cocatalyst, $AlEt_3$; Al/Ti = 100 in mol.
[a] 1-Octene content in feed.
[b] The catalytic activity.
[c] 1-Octene molar content in polymer determined by ^{13}C NMR.
[d] Number average molecular weight of the copolymer determined by GPC.
[e] Melting point determined by DSC.

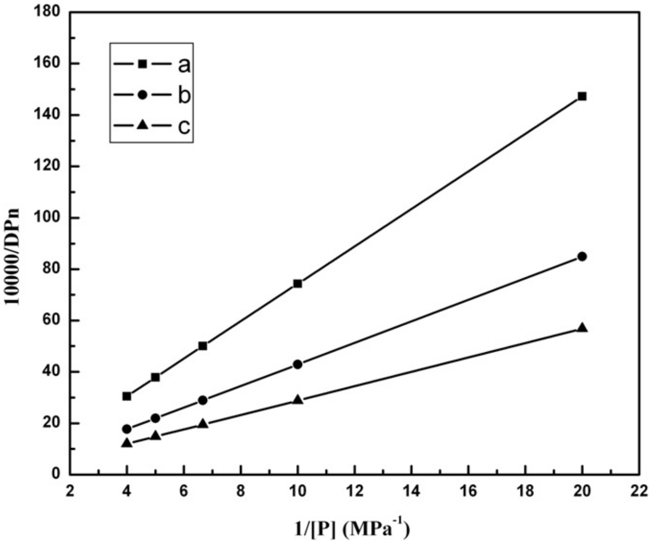

Fig. 2. Curves of 1/DPn v.s. 1/[P] for copolymerization of ethylene and 1-octene catalyzed by (a) catalyst (**I**); (b) catalyst (**II**); (c) catalyst (**III**).

$$R_p = K_p[C^*][M] \tag{1}$$

where R_{pi} is the global chain propagation rate, C^* is active species global molar concentration. $[M]$ is monomer molar concentration around active site, K_p is the specific constant of the propagation reaction. Many works [20,16] have developed the kinetics of olefins polymerization with heterogeneous Ziegler–Natta catalysts, demonstrating that these catalysts have several types of active centers. So in Eq. (1), C^* is the concentration of all polymerization centers around active site. The number average degree of polymerization DP_n ($DP_\text{n} = R_\text{p}/R_\text{tr}$, R_tr is of the global rates of all chain transfer or chain termination) results [21].

$$1/DP_\text{n} = K_\text{trm}/K_\text{p} + \left(K_\text{tra} + K_{\text{tr}\beta}\right)/\left(K_\text{p}[M]\right) \tag{2}$$

where K_p, K_trm, K_tra, and $K_{\text{tr}\beta}$ are the chain propagation rate constant, the chain transfer constant with monomer (ethylene/1-octene), the chain transfer constant with cocatalyst, AlEt_3, and the chain transfer constant with β-H elimination, respectively. On the other hand, the β-H elimination is a weak influence on the molecular weight of the copolymer in this investigation (runs 1, 2 and 3 in Table 1). So Eq. (2) is changed into Eq. (3):

$$1/DP_\text{n} = K_\text{trm}/K_\text{p} + \left(K_\text{tra}/K_\text{p}\right)/(1/[M]) \tag{3}$$

DP_n is given according to Eq.(4):

$$DP_\text{n} = M_\text{n}/(M_\text{m}) \tag{4}$$

Where M_n is the number average molecular weight of the obtained copolymer, M_m is the molecular weight of the monomer ethylene. The content of 1-octene incorporation is less, so 1-octene attributed to M_m is neglected.

Table 5
Kinetics constants of polymerization reaction for ethylene/1-octene polymerization.[a]

Catalyst	$K_\text{trm}/K_\text{p} \times 10^4$	$K_\text{tra}/K_\text{p} \times 10^4$	$K_\text{tra}/K_\text{trm}$
Catalyst (**I**)	1.3	7.3	5.6
Catalyst (**II**)	0.9	4.2	4.7
Catalyst (**III**)	0.8	2.8	3.5

Polymerization conditions: the catalyst amount adding, 15 mg; T, 80 °C; solvent, hexane, 150 mL; time, 10 min; cocatalyst, AlEt_3; Al/Ti = 100 in mol; comonomer, 1-octene, 5.0 mL; ethylene pressure, starting at 0.25 MPa, no ethylene charged again after the starting, so ethylene pressure was decreased with increase of polymerization time.

[a] The experiment was carried out in a 500 mL autoclave reactor equipped with a mechanical stirrer and a cooling and heating jacket. The ethylene pressure value was recorded from a pressure flowmeter.

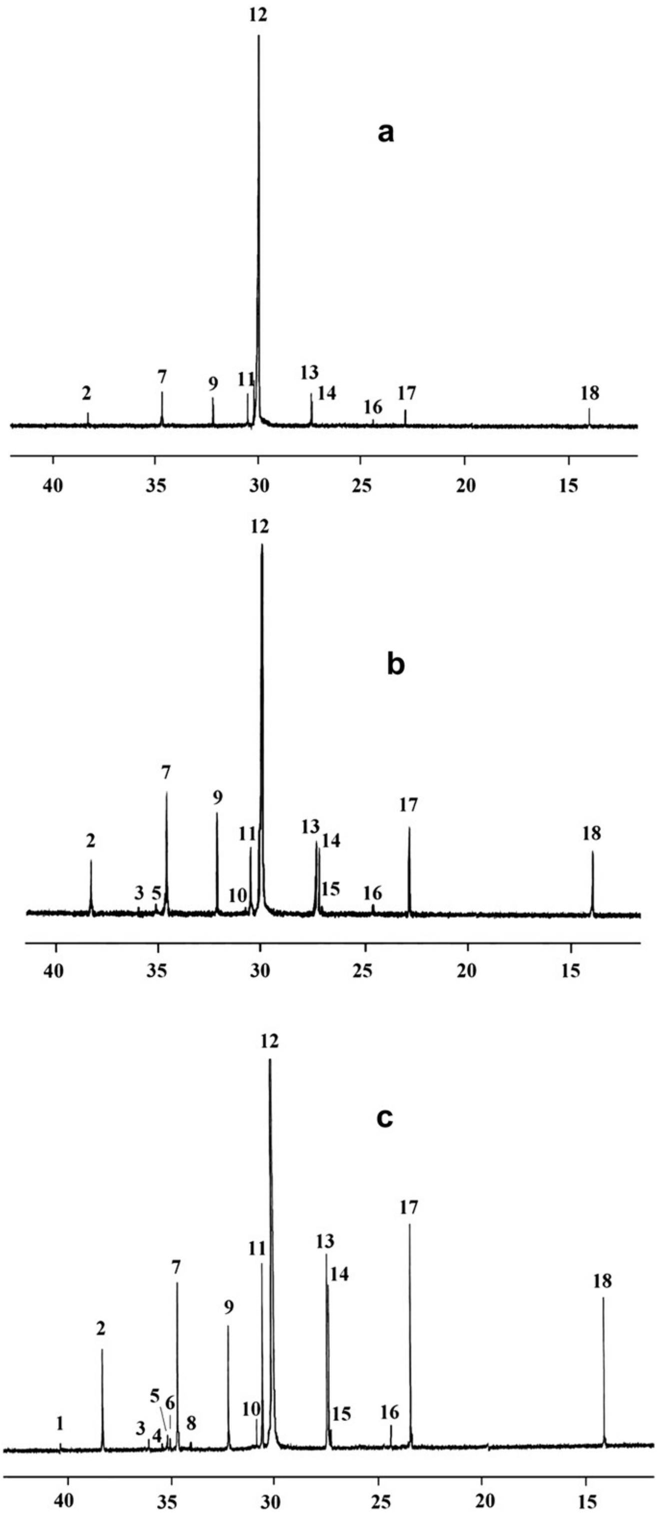

Fig. 3. ^{13}C NMR spectrum of (a) ethylene/1-octene copolymer ([O] = 0.34 mol%) (run 1 in Table 1), (b) ethylene/1-octene copolymer ([O] = 2.26 mol%) (run 2 in Table 1), (c) ethylene/1-octene copolymer ([O] = 7.46 mol%) (run 3 in Table 1).

Table 6
Chemical shift assignments in ^{13}C NMR spectra of ethylene/1-octene copolymers entitled runs 1, 2 and 3 in Table 1.

Peak no.	Carbon type	Monomer sequence	Chemical shift (ppm)		
			Run 1[a]	Run 2[b]	Run 3[c]
1	$\alpha\alpha$	EOOE			40.35
2	CH	EOE	38.31	38.31	38.26
3	CH	OOE		35.97	36.03
4	$\alpha\gamma$	OOEO			35.50
5	$\alpha\delta + CH_2(6)$	EEOO + EOO		35.25	35.14
6	$\alpha\gamma$	EOEO			35.04
7	$\alpha\delta + CH_2(6)$	EOEE + EOE	34.67	34.65	34.65
8	CH	OOO			34.03
9	$CH_2(3)$	EOE + OOE + OOO	32.21	32.20	32.17
10	$\gamma\gamma$	OEEO		30.83	30.87
11	$\gamma\delta^+$	OEEE	30.51	30.51	30.50
12	$\delta^+\delta + +CH_2(4)$	(EEE)n	29.99	30.00	30.00
13	$\beta\delta$	OEE	27.36	27.37	27.36
14	$CH_2(5)$	EOE + OOE + OOO	27.31	27.31	27.17
15	$\beta\delta^+$	OOEE		27.11	27.02
16	$\beta\beta$	OEO	24.40	24.40	24.39
17	$CH_2(2)$	EOE + OOE + OOO	22.87	22.87	22.84
18	CH_3	EOE + OOE + OOO	14.01	14.02	14.06

[a] [O] = 0.34 mol% (in Table 1).
[b] [O] = 2.26 mol% (in Table 1).
[c] [O] = 7.46 mol% (in Table 1).

The intercept and the slope of a curve of $1/DP_n$ v.s. $1/[M]$ are the K_{trm}/K_p, K_{tra}/K_p ratio, respectively. Herein, the special claim about $[M]$ should be described. $[M]$ is defined as ethylene concentration in order to simplify the calculation of monomer concentration. $[M]$ depends on ethylene pressure, and ethylene pressure is changed up to the desired pressure at the starting of the polymerization course. The curves of $1/DP_n$ v.s. $1/[P]$ for copolymerization of ethylene and 1-octene catalyzed by catalysts (**I**), (**II**) and (**III**) are shown in Fig. 2. The Kinetics constants are compiled in Table 5.

From Table 5 one can notice that, comparison with $TiCl_4/MgCl_2$ catalyst system, these modified Ziegler–Natta catalysts (**II**) and (**III**), especially in catalyst (**III**), have fairly low tendency of chain transfer to monomer or cocatalyst $AlEt_3$, and higher tendency of chain propagation, which results in high molecular weight polymers for olefins copolymerization. On the other hand, the ratio of K_{tra}/K_{trm} for catalyst (**II**) and catalyst (**III**) system is smaller, comparing to catalyst (**I**), which suggest that the ratio of the chain transfer to cocatalyst, $AlEt_3$, is smaller. But the ratio of K_{tra}/K_{trm} for catalysts (**I**), (**II**) and (**III**) is larger than one, which indicates that the chain transfer to cocatalyst is main manner.

3.2. *Microstructure analyses of the copolymer*

The ^{13}C NMR spectrums of the samples in Table 1 were presented in Fig. 3. The nomenclature suggested by Kimura [9] is employed. The chemical shift assignments for the peaks are listed in Table 6.

As revealed by Table 6, the ethylene/1-octene copolymer catalyzed by $TiCl_4/MgCl_2$(**I**) only contains the sequences of EOE, EEE, OEE, EOEE and OEEE, which is characteristic of the 1-octene units existing as isolated sequences. However, the ^{13}C NMR spectrums of ethylene/1-octene copolymers obtained via (iso-PenylO)$TiCl_3/MgCl_2$(**II**) and (BzO)$TiCl_3/MgCl_2$(**III**) differ from those of the copolymers prepared by $TiCl_4/MgCl_2$(**I**). The signal at δ 30.0 ppm, which is assigned to the $S_{\delta\delta}$ carbon in ethylene sequence of polyethylene, decreases with increasing 1-octene incorporation; But these signals at δ 27.17 and 34.65 ppm, which are near to assign to $CH_2(5)$ and $CH_2(6)$, are obviously increased with increasing 1-octene incorporation, confirming the trend of the ethylene momomer to form long sequence. These sequences (OEO, OEEO) in which 1-octene unit separated by one or two ethylene units are appeared at δ 24.40 (peak No. 16 in Table 6) and δ 30.83 (peak No. 10 in Table 6), respectively. The resonances ranging from δ 35 to 41 ppm can confirm the possibility of OO dyad, these signals increase with increasing 1-octene incorporation (Fig. 3b and c). The signal at δ 34.03 ppm assigned to OOO triad sequences is only appeared in Fig. 3c (peak No. 8), indicating the trend of 1-octene toward forming relative long sequences in the ethylene/1-octene copolymer. But these signals of long 1-octene sequences are weak, which unlike ethylene/1-octene copolymers obtained by metallocene catalyst in which the copolymers with high 1-octene content contained abundance of signals of OO dyad and OOO triad sequences besides the alternating and isolating O units [2,3]. The Ethylene/1-octene copolymers obtained by modified Z–N catalyst (II) and (III) have not only improved the incorporation of 1-octene into the polyethylene main chain, but also optimized the uniformity for the whole copolymer molecular chain because of the copolymers mainly containing the isolated and uniform O units.

Based on the ^{13}C NMR result, the microstructures of the obtained copolymers are determined. Additionally, to determine more precisely the microstructures of the analyzed copolymers, the structural parameters such as comonomer mole fractions and the reactivity ratios of the comonomers are calculated using the Randall method [9]. The results are presented in Table 7. For the products catalyzed by (iso-PentylO)$TiCl_3/MgCl_2$(**II**) and (BzO)$TiCl_3/MgCl_2$(**III**), the comonomers reactivity ratios are calculated, respectively, $r_E = 55.00$ for ethylene and $r_O = 0.023$ for 1-octene with $r_E \cdot r_O = 1.27$ for catalyst(**II**); $r_E = 17.15$ for ethylene and $r_O = 0.055$ for 1-octene with $r_E \cdot r_O = 0.93$ for catalyst(**III**). The value of $r_E \cdot r_O$ is close to 1, reflecting a pronounced tendency for the random distribution of the comonomers in the copolymer chain.

Additionally, although the concentrations of the comonomer in the feed are the same for these investigated catalysts (**I, II and III**), the results from Table 7 show that the copolymers obtained with modified Z–N catalysts (**II and III**) have higher contribution of the comonomer in the products than that obtained with the conventional Z–N catalyst (**I**). Also, it can be noticed that in comparing to the conventional Z–N catalyst (**I**), the concentrations of EOE, OEE, OEO, EOO, OOO triad sequences of the copolymer catalyzed by the

Table 7
Observed triad distributions, comonomer mole fractions and copolymerization parameters for runs 1, 2 and 3 in Table 1.

Sample	Copolymerization parameters		Mole fractions				Triad distributions			
	r_E	r_O	[E]	[O]	[EOE]	[EOO]	[OOO]	[OEO]	[OEE]	[EEE]
Run 1[a]	374.6	–	99.66	0.34	0.344	0.00	0.00	0.00	0.672	99.152
Run 2[b]	55	0.023	97.74	2.26	2.15	0.10	0.00	0.04	4.34	93.37
Run 3[c]	17.15	0.055	92.54	7.46	6.17	0.33	0.18	0.34	12.19	79.33

[a] From Table 1.
[b] From Table 1.
[c] From Table 1.

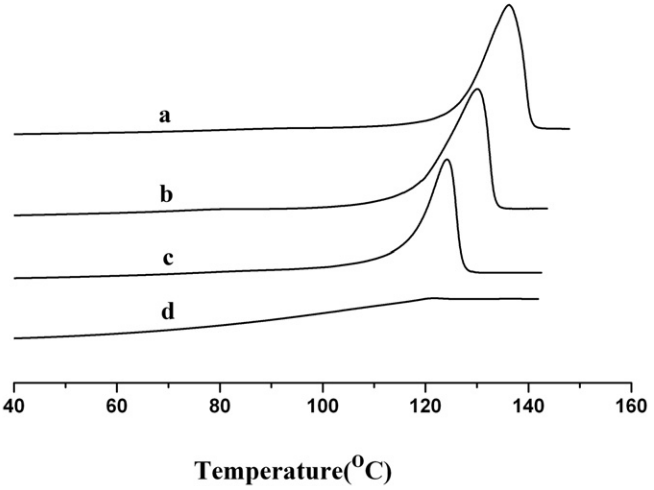

Fig. 4. DSC curves of (a) polyethylene catalyzed by catalyst (**III**) from Table 4, (b) ethylene/1-octene copolymer ([O] = 0.34 mol%) (run 1 in Table 1), (c) ethylene/1-octene copolymer ([O] = 2.26 mol%) (run 2 in Table 1), (d) ethylene/1-octene copolymer ([O] = 7.46 mol%) (run 3 in Table 1).

modified Z–N catalyst (**II** and **III**) are higher and EEE concentration decreases moderately, confirming the tendency of the 1-octene monomer to form relatively longer sequences. Therefore, the incorporations of α-olefins into the polyethylene chain are more effective in case of the modified Z–N catalysts (**II** and **III**) compared to the conventional Z–N catalyst (**I**).

3.3. DSC analyses

Generally, the melting temperature and crystallinity of the ethylene/1-octene copolymers are lower than those of homopolyethylene and decrease with the increase of 1-octene content in the copolymer. The effect of the copolymer compositions prepared with the modified Z–N catalysts (**II** and **III**) and the conventional Z–N catalyst (**I**) on thermal behavior was shown in Fig. 4. Inspection of the DSC profile of the sample (Fig. 4b) with 1-octene incorporated content of 0.34 mol% (run 1 in Table 1) reveals the presence of only one endothermic peak at 130.2 °C which is considerably lower than the homopolyethylene at 136.0 °C (Fig. 4a).

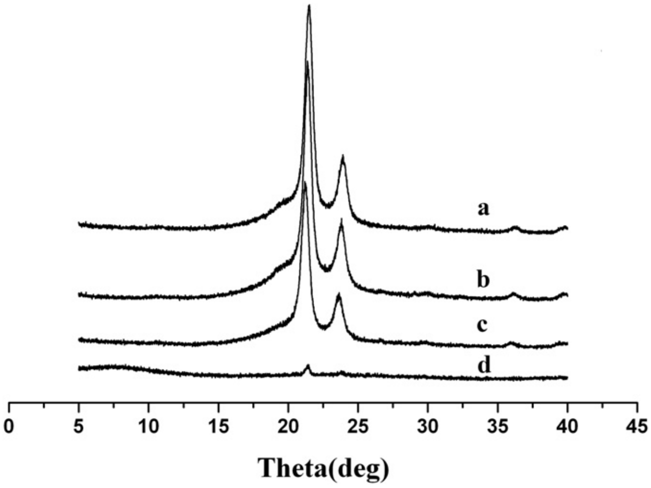

Fig. 5. WAXD diagrams of (a) polyethylene catalyzed by catalyst (**III**) from Table 4, (b) ethylene/1-octene copolymer ([O] = 0.34 mol%) (run 1 in Table 1), (c) ethylene/1-octene copolymer ([O] = 2.26 mol%) (run 2 in Table 1), (d) ethylene/1-octene copolymer ([O] = 7.46 mol%) (run 3 in Table 1).

We can notice that the copolymer with 2.26 mol% 1-octene incorporation catalyzed by modified Z–N catalyst (**II**) significantly decreases its melting temperature to 124.1 °C (Fig. 4c). At high 1-octene contents, the copolymers should be amorphous and usually not show any evidence of melting endotherm. As shown in (Fig. 4d), the copolymer with the content of 1-octene incorporation up to 7.46 mol% catalyzed by modified Z–N catalyst (**III**), becomes amorphous, without a detectable melting point. The copolymer promoted by $(n\text{-BuCp})_2ZrCl_2$/MAO has 1-octene incorporation content of 2.32 mol%, and shows a melting point at 114.5 °C (run 4 in Table 1).

3.4. WAXD analyses

Fig. 5 showed WAXD diffractograms of the copolymers with different contents of 1-octene incorporated. For the copolymer with 1-octene content of 0.34 mol% catalyzed by catalyst (**I**) (Fig. 5b), two sharp peaks appear at $2\theta = 21$ and 24 which are characterized as PE crystal, indicating the existence of long ethylene sequences within the copolymer chain. With the increase of 1-octene content in the copolymers (Fig. 5c and d) catalyzed by modified Z–N catalyst (**II** and **III**), the two peaks become weak. Especially, when the 1-octene content increases to 7.46 mol% (Fig. 5d), the two peaks are almost undetectable, which indicates that the copolymer becomes amorphous.

4. Conclusions

In summary, the effective supported modified Ziegler–Natta catalysts, (iso-PentylO)$TiCl_3/MgCl_2$ (**II**) and (BzO)$TiCl_3/MgCl_2$ (**III**) for copolymerization of ethylene with 1-octene were performed smoothly. Comparing to $TiCl_4/MgCl_2$ (**I**), (iso-PentylO)$TiCl_3/MgCl_2$ (**II**) and (BzO)$TiCl_3/MgCl_2$ (**III**) provide an improved copolymerization activity and stability, a good incorporation of 1-octene into the polyethylene main chain and produce random copolymer with high molecular weight. The kinetic results also indicate that these catalysts (**II**) and (**III**) show higher propagation rate and lower chain transfer termination rate. ^{13}C NMR analysis showed the copolymer catalyzed by $TiCl_4/MgCl_2$ (**I**) contains predominantly alternated and isolated 1-octene units. Dyad and triad sequences of 1-octene unit could be detected in the copolymers with high incorporated 1-octene content which are catalyzed by (iso-PentylO)$TiCl_3/MgCl_2$ (**II**) and (BzO)$TiCl_3/MgCl_2$ (**III**). The melting temperature and crystallinity of the ethylene/1-octene copolymers decrease with the increase of 1-octene content in the copolymer chain.

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