

## SYNTHESIS OF BRANCHED POLYETHYLENE USING ( $\alpha$ -DIIMINE)NICKEL(II) - $\text{TiCl}_4$ COMBINED AND SUPPORTED CATALYST\*

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**Abstract** ( $\alpha$ -Diimine)nickel(II)  $\{[\text{C}_6\text{H}_5 - \text{N} = \text{C}(\text{CH}_3) - \text{C}(\text{CH}_3) = \text{N} - \text{C}_6\text{H}_5]\text{NiBr}_2\} - \text{TiCl}_4$  abbreviated as NiL- $\text{TiCl}_4$  combined catalyst which is supported on  $\text{MgCl}_2 - \text{SiO}_2$  carrier has been prepared, by using alkyl aluminum ( $\text{AlR}_3$ ) as the cocatalyst in place of methylaluminoxane (MAO) to catalyze ethylene oligomerization and copolymerization *in situ*. The influences of procedure for supporting NiL- $\text{TiCl}_4$ , the molar ratio of NiL to  $\text{TiCl}_4$ , cocatalyst type and polymerization temperature on the catalytic performance were studied. The degree of branching and the composition of the branched chain of polymers produced have been investigated by IR and  $^{13}\text{C}$ -NMR spectra. The results show that the combined catalyst can synthesize the branched polyethylene with various banchd chains. The polymerization reaction was monitored by gas chromatography and mass spectrometry (GC-MS). The results show that this catalyst promotes the oligomerization and copolymerization *in situ* for ethylene.

**Keywords** ( $\alpha$ -Diimine)nickel(II)- $\text{TiCl}_4$  combined catalyst, Ethylene oligomerization and copolymerization *in situ*, Branched polyethylene

### INTRODUCTION

In recent years, the study of ethylene polymerization with late-transition-metal catalyst has been rather active<sup>[1–3]</sup> because the late-transition-metal catalysts has some novel properties. For example, ( $\alpha$ -diimine)nickel(II) complexes were used to synthesize branched polyethylene<sup>[4]</sup> and catalyze the copolymerization of ethylene with polar monomers<sup>[5]</sup> resulting in the formation of polyethylene with polar groups. But the majority of the late-transition-metal catalysts used methylaluminoxane (MAO) as the cocatalyst and required an excess amount of MAO. However, MAO is difficult to synthesize and is expensive too. There were only few reports on the late-transition-metal catalyst combined with  $\text{TiCl}_4$ .

The NiL- $\text{TiCl}_4/\text{MgCl}_2 - \text{SiO}_2$  combined and supported catalyst using alkyl aluminum ( $\text{AlR}_3$ ) as the cocatalyst in place of MAO was used to catalyze ethylene polymerization and to synthesize branched polyethylene.

### EXPERIMENTAL

#### Materials

$\text{MgCl}_2$  was provided by the Fushun Aluminium Smelt Factory and  $\text{SiO}_2$  was provided by Davison Co. USA. All reagents were available commercially.  $\text{TiCl}_4$  was distilled before use. Heptane was refluxed with metallic sodium under nitrogen for 12 h and distilled before use. Diethyl aluminum chloride ( $\text{Et}_2\text{AlCl}$ ), triethyl aluminum ( $\text{AlEt}_3$ ) and tri-isobutyl aluminum ( $\text{Al}(i\text{-Bu})_3$ ) were diluted to 30 wt% solution in heptane before use. Ethylene was

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### Preparation of Catalyst

( $\alpha$ -Diimine)nickel(II) complex  $[\text{C}_6\text{H}_5-\text{N}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{N}-\text{C}_6\text{H}_5]\text{NiBr}_2(\text{NiL})$  was synthesized according to the literature<sup>[6-8]</sup>.  $\text{MgCl}_2$  was dissolved with stirring in tetrahydrofuran (THF) and ethanol mixed solvent to form a transparent solution under dry nitrogen. The pretreated  $\text{SiO}_2$  was introduced into the transparent solution to react for 1 h. Under dry nitrogen atmosphere, the product was filtered and dried. The dissolved NiL complex and  $\text{TiCl}_4$  were added to the reactor and reacted for 1 h. The supported reactant was filtered, washed and dried to form catalysts A, B and C as shown in Table 1.

**Table 1.** The results of ethylene polymerization by using NiL- $\text{TiCl}_4$  combined catalysts

| Catalyst | Ni/Ti <sup>a</sup><br>(mol/mol) | Product | Efficiency<br>g PE/g (Ti + Ni) | Degree of branching <sup>b</sup><br>(branches/1000 C) | Density <sup>c</sup><br>(g/cm <sup>3</sup> ) | $M_w$<br>$\times 10^{-5}$ | $T_m$ <sup>d</sup> |
|----------|---------------------------------|---------|--------------------------------|-------------------------------------------------------|----------------------------------------------|---------------------------|--------------------|
| A        | 1.28                            | A7-2    | 1397                           | 9.8                                                   | 0.916                                        | 4.11                      | 122.0              |
| B        | 0.80                            | B3-3    | 3957                           | 8.3                                                   | 0.924                                        | 5.30                      | 123.0              |
| C        | 1.04                            | C3-2    | 5933                           | 8.0                                                   | 0.921                                        | 4.64                      | 123.1              |
| D        | 0                               | D1-1    | 2450                           | 0                                                     | 0.945                                        | 12.29                     | 133.6              |

Polymerization conditions: Al/Ni+Ti (mol/mol) = 200,  $P = 106.7$  kPa,  $T = 40^\circ\text{C}$ ,  $\text{Et}_2\text{AlCl}/\text{AlEt}_3 = 1:1$  (mol/mol),  $\text{Et}_2\text{AlCl}$  was first introduced, and then  $\text{AlEt}_3$  was added to continue the reaction for 0.5 h.

<sup>a</sup> Determined by ICP method; <sup>b</sup> Determined by  $^{13}\text{C}$ -NMR method; <sup>c</sup> Determined by density gradient tube method;

<sup>d</sup> Determined by DSC method

### Polymerization

A three-necked flask was heated and dried in vacuum to remove the air and moisture. Under a dry nitrogen atmosphere, heptane and alkyl aluminum ( $\text{AlR}_3$ ) were added to the reactor with stirring. An appropriate amount of combined catalyst was rapidly added to the reactor and then ethylene was successively introduced into the reactor under 106.7 kPa to polymerize for 1.5 h. The product was filtered and washed with the mixed solvent HCl and  $\text{C}_2\text{H}_5\text{OH}$  as well as distilled water and dried. The catalytic efficiency was calculated by the weight ratio of polyethylene to Ni and Ti in the catalyst.

### Analysis

The melting point ( $T_m$ ) of the polyethylene was obtained from DSC (Perkin-Elmer DSC-7). The molecular weight ( $M_w$ ) was determined by the viscosity method. The density of polyethylene was obtained by the density gradient tube method. The degree of branching was determined by IR spectrometry (Nicolet-205). We used the difference spectrum to detect the absorption band intensity of branched methyl at  $1379\text{ cm}^{-1}$  and calculated the degree of branching  $N$  by the following formula<sup>[9]</sup>:

$$N(\text{branches}/1000\text{C}) = K \times (A/T)/D$$

where  $N$  is the branch concentration;  $A$  is the absorbance value calculated by FTIR,  $T$  is the film thickness in cm,  $D$  is the film density in  $\text{g}/\text{cm}^3$ . The extinction coefficient  $K$  is 0.74 for butyl and hexyl branching chain.

The composition of branched polyethylene was characterized by  $^{13}\text{C}$ -NMR spectra (Varian<sup>Unity</sup> INOVA 500NB), and the oligomer of ethylene was analyzed by GC-MS (VOYAGER GQMS)

The contents of Ti and Ni in the catalysts were measured by Inductively Coupled Plasmas method (ICP) (Perkin Elmer Co.).

## RESULTS AND DISCUSSION

### Influence of Catalysts

Three procedures for the preparation of supported catalysts have been used. For Catalyst A, NiL complex was first added to the polymerization system and then  $\text{TiCl}_4$ . For Catalyst B,  $\text{TiCl}_4$  was first added to the polymerization system and then NiL complex. For Catalyst C, NiL complex and  $\text{TiCl}_4$  were added to the reaction system at the same time. For Catalyst D, only  $\text{TiCl}_4$  was added. The results for four catalysts (A, B, C and D) that catalyze ethylene polymerization are listed in Table 1.

Table 1 shows that Catalyst A, B and C can produce branched polyethylene, but not Catalyst D. The results show that  $\text{NiL}$  and  $\text{TiCl}_4$  combined catalyst has different properties from the single supported  $\text{TiCl}_4$  catalytic active center. The  $\text{NiL}$  active center has the function of oligomerization to produce  $\alpha$ -olefin. The  $\text{NiL}$  and  $\text{TiCl}_4$  combined catalyst form a dual-functional active center that induces ethylene oligomerization to obtain  $\alpha$ -olefin and also makes  $\alpha$ -olefin copolymerize with ethylene to obtain the branched polyethylene with low density and low melting point. The catalytic activity is also high.

The polyethylenes prepared from these three catalysts (Catalysts A, B and C) were analyzed by  $^{13}\text{C-NMR}$ <sup>[10]</sup> as shown in Fig. 1. Polyethylenes with different branched chains have been obtained by using  $\text{NiL}$  and  $\text{TiCl}_4$  combined catalysts. The characteristic chemical shifts at 11.19 ( $1\text{B}_2$ ), 39.66 ( $\text{BrB}_2$ ), 14.08 ( $1\text{B}_4$ ), 38.17 ( $\text{BrB}_4$ ), 32.18 ( $3\text{B}_n$ ) and 29.88 ( $4\text{B}_n$ ) for A7-2, B3-3 and C3-2 manifested that these polyethylenes have ethyl, butyl and long branched chains ( $C \geq 6$ ). According to the equation proposed by Usami and Takayama<sup>[9]</sup>

$$N = \frac{1000(I_{\text{Me}}/0.90 + I_{\text{Et}}/0.84 + I_{\text{Pr}}/0.83 + I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80)}{I_{\text{main}} + 5.5(I_{\text{Et}}/0.84) + I_{\text{Pr}}/0.83 + 8.0I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80}$$

where  $N$  is total branches (total branches/1000 C).  $I_{\text{Me}}$ ,  $I_{\text{Et}}$ ,  $I_{\text{Pr}}$ ,  $I_{\text{Bu}}$ ,  $I_{\text{Pe}}$  and  $I_{\text{Lg}}$  are the corresponding integral intensity of  $^{13}\text{C-NMR}$  chemical shift of  $1\text{B}_1$ ,  $1\text{B}_2$ ,  $1\text{B}_3$ ,  $2\text{B}_4$ ,  $3\text{B}_5$  and  $3\text{B}_n$ , respectively. The proportion of various branches content is as follow: methyl:ethyl:propyl:*n*-butyl:*n*-pentyl:longer =  $(I_{\text{Me}}/0.90):(I_{\text{Et}}/0.84):(I_{\text{Pr}}/0.83):(I_{\text{Bu}}/0.90):(I_{\text{Pe}}/0.90):(I_{\text{Lg}}/0.90)$ . Therefore, concentration and distribution of various branched chains of A7-2, B3-3 and C3-2 can be calculated. The results are shown in Table 2.

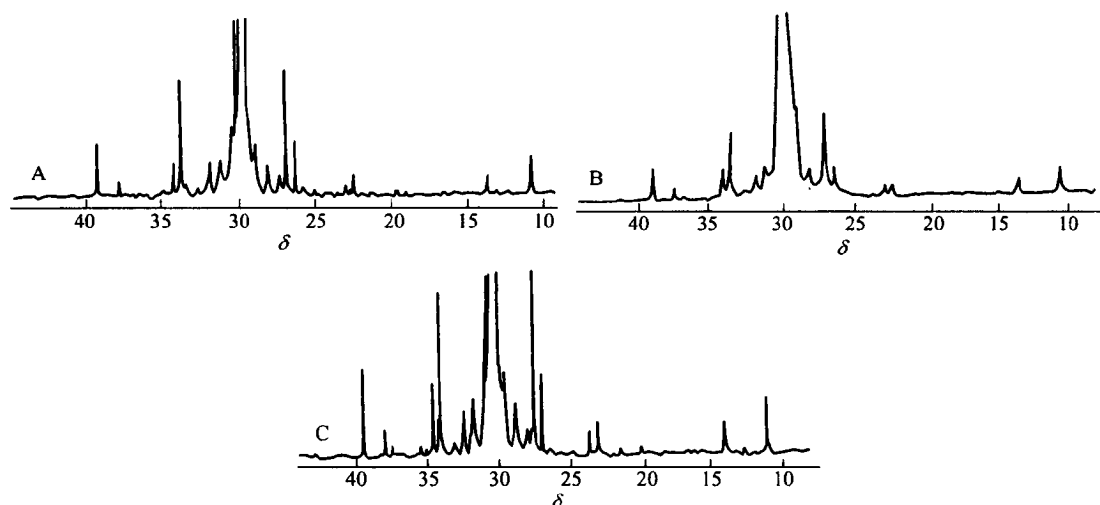


Fig. 1  $^{13}\text{C-NMR}$  spectra of polyethylene obtained by using Catalysts A, B and C

Table 2. Branched structure of polyethylenes (A7-2, B3-3 and C3-2)

| Product | Ni/Ti <sup>a</sup> (mol/mol) | Degree of branching <sup>b</sup> (relative to total) |           |                           |
|---------|------------------------------|------------------------------------------------------|-----------|---------------------------|
|         |                              | Ethyl                                                | Butyl     | Long chain ( $n \geq 6$ ) |
| A7-2    | 1.28                         | 4.5 (46%)                                            | 0.9 (9%)  | 4.4 (45%)                 |
| B3-3    | 0.80                         | 5.7 (68%)                                            | 2.6 (32%) |                           |
| C3-2    | 1.04                         | 3.6 (45%)                                            | 1.0 (12%) | 3.4 (43%)                 |

<sup>a</sup> Determined by ICP method; <sup>b</sup> Determined by  $^{13}\text{C-NMR}$  method

Regardless of the supporting sequence of  $\text{NiL}$  and  $\text{TiCl}_4$ , the branched chains of products are composed mostly of ethyl and butyl groups. When the molar ratio of  $\text{NiL}$  to  $\text{TiCl}_4$  in the supported catalyst exceeds unity, the branched chains of products contain not only ethyl and butyl but long branched chain ( $C \geq 6$ ) also. The results show that  $\text{NiL}$  and  $\text{TiCl}_4$  combined catalysts are able to catalyze ethylene polymerization to obtain branched

polyethylene with various branched chains.

### ***Influence of Molar Ratio of NiL to TiCl<sub>4</sub>***

Table 3 shows that the degree of branching increases and the catalytic efficiency decreases with increasing Ni/Ti molar ratio for the three catalysts (A, B and C). Because NiL active center induces ethylene oligomerization to produce  $\alpha$ -olefin, with increasing Ni/Ti molar ratio more  $\alpha$ -olefin is obtained and the degree of branching of the resulting polyethylene increases. When the Ni/Ti molar ratio is nearly equal to one, the polyethylenes with higher degree of branching are obtained by using three catalysts. For example, when the Ni/Ti ratio is equal to 1.04, the efficiency of Catalyst C and the degree of branching of the resulting product reach a high value of 5933 g PE/g (Ni + Ti) and 9.2 branches/1000 C, respectively. However, when Ni/Ti molar ratio exceeds one, the branching degree increases slightly and the catalytic efficiency decreases obviously.

**Table 3** The influence of NiL/TiCl<sub>4</sub> molar ratio on polymerization by using Catalysts A, B and C

| Catalyst | Product | Ni/Ti <sup>a</sup><br>(mol/mol) | Catalyst efficiency<br>[g PE/g (Ni + Ti)] | Degree of branching <sup>b</sup><br>(branches/1000 C) |
|----------|---------|---------------------------------|-------------------------------------------|-------------------------------------------------------|
| A        | A4-1    | 0.20                            | 2961                                      | 3.9                                                   |
| A        | A5-1    | 0.63                            | 2247                                      | 4.9                                                   |
| A        | A7-2    | 1.28                            | 1397                                      | 10.4                                                  |
| B        | B2-1    | 0.29                            | 5610                                      | 2.2                                                   |
| B        | B3-3    | 0.80                            | 3957                                      | 9.3                                                   |
| B        | B4-1    | 3.35                            | 1745                                      | 12.0                                                  |
| C        | C2-1    | 0.35                            | 6170                                      | 2.9                                                   |
| C        | C3-2    | 1.04                            | 5933                                      | 9.2                                                   |
| C        | C4-1    | 2.56                            | 1316                                      | 10.5                                                  |

Polymerization conditions are the same as those listed in Table 1.

<sup>a</sup> Determined by ICP method; <sup>b</sup> Determined by IR method

### ***Influence of Cocatalysts***

According to the literature<sup>[2, 3, 5]</sup>, the late-transition-metal catalysts mainly used MAO or boron compounds as cocatalysts, which are difficult to synthesize and are expensive. We only used AlEt<sub>3</sub> or Al(*i*-Bu)<sub>3</sub> and Et<sub>2</sub>AlCl as cocatalysts to carry out ethylene polymerization to synthesize branched polyethylene. The results are shown in Table 4.

**Table 4.** The influence of cocatalysts on polymerization by using NiL-TiCl<sub>4</sub> combined catalysts

| Catalyst | Product | Cocatalyst <sup>b</sup>                  | Reaction temp. (°C) | Catalyst efficiency<br>[g PE/g (Ni + Ti)] | Degree of branching <sup>a</sup><br>(branches/1000 C) |
|----------|---------|------------------------------------------|---------------------|-------------------------------------------|-------------------------------------------------------|
| A        | A6-1    | Al( <i>i</i> -Bu) <sub>3</sub>           | 60                  | 1420                                      | 1.2                                                   |
| A        | A6-2    | Et <sub>2</sub> AlCl                     | 40                  | 209                                       | 40.1                                                  |
| A        | A6-3    | Et <sub>2</sub> AlCl + AlEt <sub>3</sub> | 60                  | 599                                       | 2.3                                                   |
| A        | A6-4    | Et <sub>2</sub> AlCl/AlEt <sub>3</sub>   | 60                  | 797                                       | 6.9                                                   |
| B        | B3-1    | AlEt <sub>3</sub>                        | 40                  | 2220                                      | 1.9                                                   |
| B        | B3-2    | Et <sub>2</sub> AlCl + AlEt <sub>3</sub> | 40                  | 1829                                      | 2.9                                                   |
| B        | B3-3    | Et <sub>2</sub> AlCl/AlEt <sub>3</sub>   | 40                  | 3957                                      | 9.3                                                   |
| C        | C3-1    | AlEt <sub>3</sub>                        | 40                  | 2139                                      | 3.5                                                   |
| C        | C3-2    | Et <sub>2</sub> AlCl/AlEt <sub>3</sub>   | 40                  | 5933                                      | 9.2                                                   |

Polymerization conditions are the same as those listed in Table 1.

<sup>a</sup> Determined by IR method;

<sup>b</sup> Et<sub>2</sub>AlCl + AlEt<sub>3</sub> means that the two cocatalysts are introduced simultaneously; Et<sub>2</sub>AlCl/AlEt<sub>3</sub> means that they are introduced separately.

When AlEt<sub>3</sub> or Al(*i*-Bu)<sub>3</sub> is only used as cocatalysts, the resulting product will have fewer branched chains. When Et<sub>2</sub>AlCl only was used as cocatalysts, the degree of branching of polymerized product attained 40.1 branches/1000 C (see Table 4 A6-2), but its catalytic efficiency was the lowest. When two cocatalysts were simultaneously used, their catalytic efficiency increased, but the degree of branching of the resulting product

decreased. When  $\text{Et}_2\text{AlCl}$  was first introduced to react for 30 min, then  $\text{AlEt}_3$  was added to continue the reaction, both catalytic efficiency and degree of branching of the product were improved. We assume that when two cocatalysts were added consecutively,  $\text{NiL}$  and  $\text{Et}_2\text{AlCl}$  formed an active center which catalyzed mainly ethylene oligomerization and produced a lot of  $\alpha$ -olefin in first 30 min; when  $\text{AlEt}_3$  was added,  $\text{TiCl}_4$  and  $\text{AlEt}_3$  formed active centers which catalyzed ethylene polymerization and copolymerization with  $\alpha$ -olefin to produce higher branched polyethylene. Figure 2 shows the ethylene polymerization kinetic curve for Catalyst B. In the initial 30 min, the kinetic curve rapidly declines and after 30 min. When  $\text{AlEt}_3$  was added, the kinetic curve rose again and afterwards dropped slowly. The order of catalytic efficiency for these three catalysts was  $\text{C} > \text{B} > \text{A}$ . Because the atomic radius of  $\text{Ni}$  (69) is quite close to that of  $\text{Ti}$  (68) and  $\text{Mg}$  (71), they could be easily obtained as mixed crystals in the supported reaction and formed the bridge bond  $\text{Mg}-\text{Cl}-\text{Ti}$ ,  $\text{Mg}-\text{Cl}-\text{Ni}$  or  $\text{Mg}-\text{Cl}-\text{Ni}-\text{Cl}-\text{Ti}$ ,  $\text{Mg}-\text{Cl}-\text{Ti}-\text{Cl}-\text{Ni}$  etc. When the  $\text{NiL}$  complex was added, it improved the coordination environment of the active center and became favorable for the *in situ* oligomerization and copolymerization of ethylene.

**Influence of Temperature**

The influence of temperature on ethylene polymerization using Catalysts A7 and B3 have been studied. The results are shown in Table 5.

**Table 5.** The influence of temperature on ethylene polymerization using Catalysts A7 and B3

| Catalyst. | Product | Reaction temp.<br>(°C) | Catalyst efficiency<br>[g PE/g (Ni + Ti)] | Degree of branching <sup>a</sup><br>(branches/1000 C) |
|-----------|---------|------------------------|-------------------------------------------|-------------------------------------------------------|
| A7        | A7-2    | 40                     | 1397                                      | 10.4                                                  |
| A7        | A7-4    | 50                     | 1164                                      | 8.0                                                   |
| A7        | A7-5    | 60                     | 907                                       | 5.2                                                   |
| B3        | B3-6    | 30                     | 3507                                      | 8.4                                                   |
| B3        | B3-3    | 40                     | 3957                                      | 9.3                                                   |
| B3        | B3-7    | 50                     | 4617                                      | 6.3                                                   |
| B3        | B3-8    | 60                     | 2364                                      | 8.4                                                   |

Polymerization conditions are the same as those listed in Table 1. <sup>a</sup> Determined by IR method

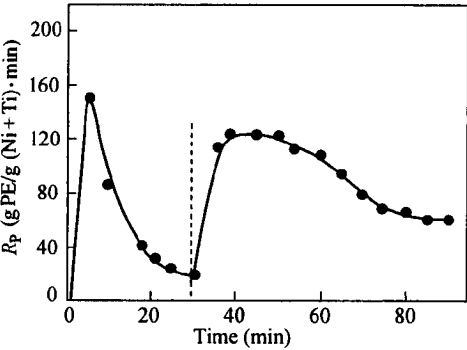


**Fig. 2** Kinetic curve of ethylene polymerization using Catalyst B  
Polymerization conditions are the same as those listed in Table 1.

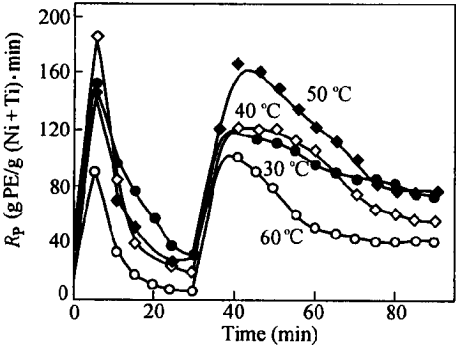


**Fig. 3** Kinetic curves of ethylene polymerization using Catalyst B3 at different temperatures  
Polymerization conditions are the same as those listed in Table 1.

When the polymerization temperature increased from 40°C to 60°C, the catalytic efficiency and degree of branching of the polyethylene obtained on using Catalyst A7 decreased. When the polymerization temperature increased from 30°C to 60°C, the catalytic efficiency of Catalyst B3 first increased, and then decreased. The polyethylene obtained on using two catalysts had the highest degree of branching at the polymerization temperature of 40°C. Figure 3 was the kinetic curves of ethylene polymerization using Catalyst B3 at different temperatures. It shows that the kinetic curves belong to decaying type. With increasing temperature, the rate of

polymerization ( $R_p$ ) quickly decreases. The experimental result shows that polymerization is best at 40°C.

### Polymerization Mechanism

Polymerization with the Catalyst A5— $\text{Et}_2\text{AlCl}$  catalytic system was intentionally stopped at 5 min or 30 min. The products (liquid) were analyzed by GC-MS to monitor the change of the oligomerization. The GC spectra are shown in Fig. 4. As seen, more oligomers were obtained when the polymerization time was 30 min. The kinetic curve shows that catalytic activity is distinctly decreased to a minimum after the polymerization has proceeded for 30 min. The oligomers were analyzed by GC-MS to determine the chemical components. The results are listed in Table 6.

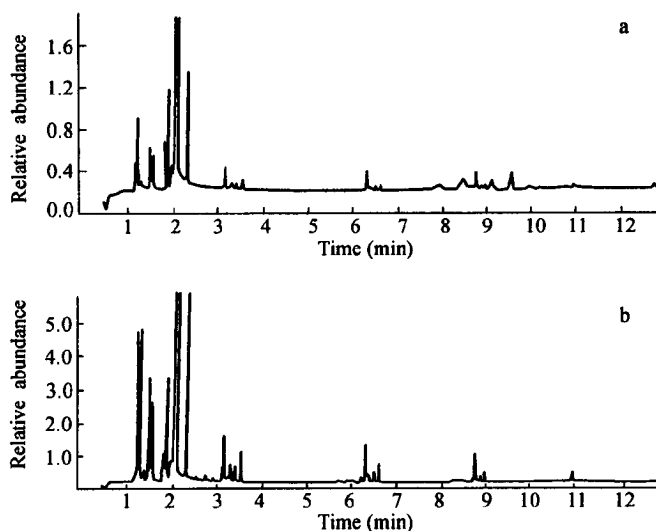
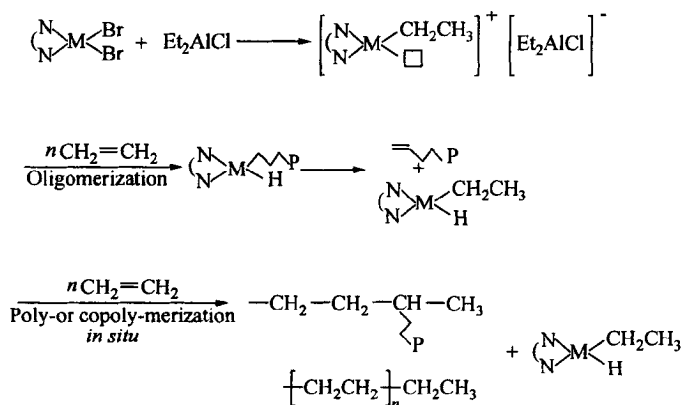


**Fig. 4** GC chromatograms of ethylene oligomerization products  
a) 5 min; b) 30 min  
Polymerization conditions are the same as those listed in Table 1.

**Table 6.** The results of analysis of ethylene oligomers by GC-MS

| Retention time (min) | Compound               | Retention time (min) | Compound           |
|----------------------|------------------------|----------------------|--------------------|
| 1.25                 | 2-Butene               | 3.24                 | 5-Methyl-2-heptene |
| 1.67                 | 3-Methyl-1-pentene     | 3.47                 | 2-Octene           |
| 1.56                 | 1-Hexene               | 3.53                 | 1-Octene           |
| 1.65                 | 3-Hexene               | 3.74                 | 4-Octene           |
| 2.13                 | 3,4-Dimethyl-1-pentene | 3.92                 | 2-Heptene          |
| 3.04                 | 5-Methyl-1-heptene     | 4.06                 | 4-Octene           |

The result shows that ethylene oligomerization produces  $\alpha$ -olefins, such as butene, hexene, heptene and octene *etc.*, which copolymerize with ethylene to form different branched chain polyethylenes. According to the experimental result and the oligomerization and copolymerization *in situ* theory proposed by Brookhart<sup>[11]</sup>, we infer the polymerized process as follows: first,  $\text{NiL}$  and  $\text{Et}_2\text{AlCl}$  form oligomerization active centers which mainly initiate ethylene oligomerize to form  $\alpha$ -olefin; secondly,  $\text{TiCl}_4$  and  $\text{AlEt}_3$  form active centers which mainly initiate the ethylene polymerize and copolymerize *in situ* to synthesize branched polyethylene. The polymerization processes are illustrated as follows:



The experimental results show that  $\text{NiI-TiCl}_4$  combined and supported catalyst using alkyl aluminum as the cocatalyst can catalyze single ethylene polymerization to synthesize branched polyethylene which contains ethyl, butyl and long branched chains ( $C \geq 6$ ).

## CONCLUSION

Novel  $\text{NiI-TiCl}_4$  combined and supported catalysts have been prepared. They can catalyze single ethylene polymerization to synthesize branched polyethylene by using alkyl aluminum as the cocatalyst in place of MAO. Monitoring the polymerization reaction by GC-MS indicates that these catalysts promote oligomerization and copolymerization *in situ* for ethylene.

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