Chinese Chemical Letters Vol. 14, No. 9, pp 911 – 913, 2003 911
http://www.imm.ac.cn/journal/ccl.html

Copolymerization of Ethylene/1-Butene with Heterogeneous $TiCl_4$/(α-Diimine)nickel(II) Complex Combined Catalyst

Shao Quan LIN, Qi Xing ZHANG, Hai Hua WANG*

Institute of Polymer Science, Zhongshan University, Guangzhou 510275

Abstract: The new type heterogeneous combined catalyst system $TiCl_4$-(α-diimine)nickel(II) complexes/$MgCl_2$-SiO_2/AlR_3 was prepared. Ethylene and 1-butene were copolymerized with the catalysts in slurry phase. It was found that with combined catalyst, the copolymers with lower density and higher branched degree were obtained. ^{13}CNMR results showed that in the obtained copolymers existed not only ethyl but also some other kinds of branches due to the fact that ethylene exhibits the behavior of oligomerization and copolymerization *in-situ* with combined catalysts.

Keywords: Combined catalyst, oligomerization and copolymerization *in-situ*, copolymers.

In-reactor blending of two different catalysts may share the advantages of both[1,2]. Ziegler-Natta catalysts are mature in industry, but a larger amount of comonomer has to be introduced in preparing low density polyethylene. Late transition metal catalysts have the advantage in preparing highly branched polyethylene[3]. While late transition metal catalyst has to be used with combination of MAO.

In this study, the new type combined catalyst system $TiCl_4$-(α-diimine)nickel(II) complex/$MgCl_2$-SiO_2/AlR_3 was prepared based on the former described procedure[4]. The diimine compound (C_6H_5-N=C(CH_3)-C(CH_3)=N-C_6H_5)$NiBr_2$was prepared according to the reference[5]. Measured by ICP(Inductively Coupled Plasma), Ni content in the combined catalyst is 0.3～2.0％(wt%) and Ti content is 0.6～1.2％(wt%).

The combined catalysts were used in slurry copolymerization of ethylene/1-butene to synthesize low-density PE in the absence of MAO. The results of copolymerization were listed at the **Table 1**. Compared with single immobilized $TiCl_4$ catalyst(entry 1), the combined catalysts show higher catalytic efficiency in ethylene copolymerization. With same 1-butene content(entry 1,3,6,7), the molecular weight and the density are lower and branched degrees are higher in the resulting copolymers with combined catalyst. The branched degrees are even higher with more 1-butene content when catalyzed with the same catalyst(entry 2~5). The results in entry 6,3,7 indicate that with higher Ni/Ti ratio, the catalytic efficiencies decrease, but the branched degrees do not increase.

* E-mail: ceswhh@zsu.edu.cn

Table 1 Copolymerization results of ethylene/1-butene with combined catalyst*

Entry	Ni/Ti (mol/mol)	1-butene (%)	Cat. efficiency gPE/g (Ni+Ti)·h	Mv ($\times 10^4$)	Density g/cm^3	Branches/ 1000 C
1**	/	10	2295	7.45	0.934	10.4
2	1.04	5	5280	3.01	0.924	16.0
3	1.04	10	5619	1.46	0.913	34.3
4	1.04	15	5202	6.01	0.919	46.9
5	1.04	20	4221	1.78	0.918	55.1
6	0.32	10	8370	3.46	0.920	24.2
7	2.56	10	2446	1.74	0.927	24.8

* Polymerization reaction was cocatalyzed with $AlEt_2Cl/Al(i\text{-}Bu)_3$(1/1) hybrid catalyst, at first $AlEt_2Cl$ was introduced, after 0.5 h, $Al(i\text{-}Bu)_3$ was added to continue the reaction.
Polymerization condition: $M_{Al}/M_{(Ni+Ti)}$=100, T=40℃, t=1.5 h,P=106.7 kpa
Ni/Ti was measured by ICP. Mv was calculated with $[\eta] = 6.67\times10^{-4} M_v^{0.67}$. Densities were determined in density gradient column. Branched degree was measured by IR spectrum.
**The polymerization was catalyzed with traditional $TiCl_4$ catalyst

^{13}CNMR was recorded by Varian INOVA 500NB NMR at 120 ℃ in *o*-dichlorobenzene. **Figure 1** and **Figure 2** give the ^{13}CNMR spectra of the copolymers obtained in entry 1 and 3. It can be seen that the microstructure of the copolymer prepared with combined catalyst is different from that with traditional Z-N catalyst. There is only ethyl branch in ethylene/1-butene copolymer with $TiCl_4$ catalyst. While with combined Ni-Ti catalyst, there are different kinds of branches: ethyl, butyl and longer branches (see **Figure 2**). This suggests that ethylene exhibited the property of oligomerization and copolymerization *in-situ* with the combined catalysts bearing Ti-Ni bimetal active sites[6].

Figure 1 ^{13}CNMR spectra of copolymer in entry 1

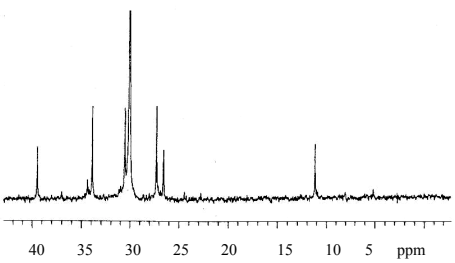
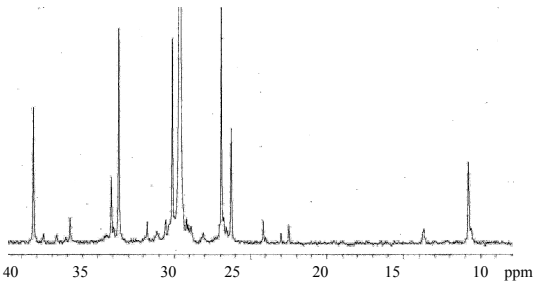


Figure 2 ^{13}CNMR spectra of copolymer in entry 3



Acknowledgment

This project is supported by the National Natural Science Foundation of China(29874039) and the Foundation of Guangdong Province(001280).

References

1. S. Mecking, *Macromol. Rapid Commun.*, **1999,** *20*, 139.
2. J. A. M. Canich, G. A. Vaughan, P. T. Matsunaga, D. E. Gindelberger, *et al.,* WO Patent Application 9748735 to Exxon, priority date June 17, **1996.**
3. S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.*, **2000** , *100*, 1169.
4. Z. M. WANG, W. XIAO, Q. X. ZHANG, *etal., Chem. J. Chin. Univers.,* **1998**, *19* (2), 295.
5. L. K. Johnson, C. M. Killian，M. Brookhart, *J. Am. Chem. Soc.,* **1995,** *117*, 6414.
6. J. M. Hu, H. H. Wang, J. L. Wu, Q. X. Zhang, *Chin. Chem. Lett.,* **2000,** *11* (1), 85.

Received 31 January, 2002
Revised 10 February, 2003