

Copolymerization of Ethylene and 1-Dodecene Catalyzed by Novel Low-Ti-Loading Ziegler–Natta Catalysts and Their Microstructures

Zhenrong Zhao,¹ Li Wang,¹ Jianfeng Wang,² Xiaochen Dong,¹ Haojie Yu¹

¹State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

²Ningbo University of Technology, Ningbo 315011, People's Republic of China

Received 1 April 2006; accepted 3 November 2006

DOI 10.1002/app.25756

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ethylene–1-dodecene copolymers were synthesized with novel low-Ti-loading (0.8 wt %) Ziegler–Natta catalysts prepared by a one-pot balling method. ¹³C-NMR was applied for the quantitative determination of the compositions and microstructures of the resultant ethylene–1-dodecene copolymers. The results showed that (1) the ethylene–1-dodecene copolymers obtained from both the MgCl₂-supported low-Ti-loading Ziegler–Natta catalyst and the MgCl₂/SiO₂-bisupported low-Ti-loading Ziegler–Natta catalyst at a 0.6M 1-dodecene concentration had high levels of 1-dodecene

and (2) most of the 1-dodecene units were separated by ethylene units in the copolymer chains obtained from the MgCl₂-supported low-Ti-loading Ziegler–Natta catalyst, whereas there were some continuous 1-dodecene repeat units in the copolymer chain obtained from the MgCl₂/SiO₂-bisupported low-Ti-loading Ziegler–Natta catalyst. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1200–1204, 2007

Key words: catalysts; copolymerization; microstructure; polyolefins

INTRODUCTION

Research on the copolymerization of ethylene and other high olefins is becoming one of the most active research fields.^{1–4} Through copolymerization, polymers with different structures and significant properties can be obtained.^{5–8} The difference in the microstructures of ethylene–1-dodecene (E–D) copolymers greatly affects the properties of the obtained copolymers.^{9–11} Recently, we developed a novel one-pot balling method for preparing novel Ziegler–Natta (Z–N) catalysts.^{12–16} This study focuses on E–D copolymerizations catalyzed by low-Ti-loading catalysts [MgCl₂-supported low-Ti-loading Ziegler–Natta (M Z–N) and MgCl₂/SiO₂-bisupported low-Ti-loading Ziegler–Natta (M/S Z–N) catalysts] to determine the effect of this kind of catalyst on the composition and structure of the resultant copolymer.

EXPERIMENTAL

Materials

Anhydrous MgCl₂ was used as received. SiO₂ was calcinated at 600°C for 4 h and then cooled slowly under

a nitrogen flow. Hexane was refluxed over a Na–K alloy before use. AlEt₃ was obtained commercially and used as a cocatalyst without further purification. Petroleum ether was dried over 4-Å molecular sieves before use. Polymerization-grade ethylene was further purified by passage through two columns of preactivated 4-Å molecular sieves. Extra-pure-grade (99.99%) nitrogen was dried by passage through two columns of preactivated 4-Å molecular sieves to remove the residual moisture and oxygen. 1-Dodecene was purchased from Aldrich, purified by the addition of sodium, and kept under a dry nitrogen atmosphere.

Preparation of the low-Ti-loading Z–N catalysts

The procedure for preparing the M/S Z–N catalyst was divided into three stages (Fig. 1): grinding a mixture of MgCl₂ with SiO₂, grinding the mixture after the addition of a TiCl₄ solution in hexane, and grinding after the removal of hexane. All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere.

The route for preparing the M Z–N catalyst was the same as that for the M/S Z–N catalyst, except that only MgCl₂ was ground in the first stage.

Copolymerization procedure

Ethylene and 1-dodecene copolymerizations were carried out in a 100-mL, three-necked glass reactor equipped with a magnetic stirrer. The required amounts of

Correspondence to: L. Wang (opl_wl@dial.zju.edu.cn).

Contract grant sponsor: Science and Technology Commission of Zhejiang University.

Contract grant sponsor: Ningbo Science and Technology Program.

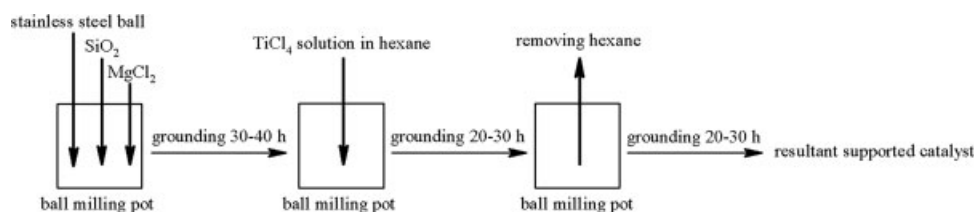


Figure 1 Preparation of the M/S Z-N catalyst with the one-pot ball-milling method.

petroleum ether, 1-dodecene, AlEt_3 , and the catalyst were introduced sequentially. Ethylene was continuously supplied to keep the pressure at 1 atm, and the ethylene consumption was detected and recorded online by a monitoring system. The copolymerization reactions were quenched after 0.5 h, and the products were precipitated by the addition of acidified alcohol. The resultant copolymers were washed with alcohol, filtered, and dried *in vacuo* to a constant weight.

Copolymer characterization

^{13}C -NMR spectra of the resultant polymers were recorded on a Bruker DMX-500 at 90°C . The ethylene and 1-dodecene copolymer solutions were uniformly prepared (10 wt %) in *o*-dichlorobenzene- d_4 .

RESULTS AND DISCUSSION

In our previous works,^{12–16} we have found that it is effective to control the Ti loadings of catalysts prepared by a one-pot ball-milling method.

As the surface structures of MgCl_2 are different from those of SiO_2 , some of the Mg component will probably react chemically with the surface hydroxyls of SiO_2 during ball milling:¹⁷



Therefore, the surface structures of the M/S Z-N catalyst may be more complicated than those of the M Z-N catalyst (see Fig. 2).

Both the MgCl_2 -supported and $\text{MgCl}_2/\text{SiO}_2$ -bisupported Z-N catalysts have high copolymerization activities and significant comonomer effects, as

shown in Table I. The catalytic activity is maximum at a polymerization temperature of 50°C or so. A possible reason for the maximum activity is as follows. With an increase in the polymerization temperature, the polymerization rate constant increases, and thus the catalytic activity increases. However, with an increase in the polymerization temperature, the solubility of the ethylene monomer in petroleum ether decreases, and this causes the reduction of the catalytic activity. Figures 3 and 4 show the kinetic curves of the consumed ethylene in E-D copolymerization catalyzed by the M Z-N and M/S Z-N catalysts, respectively. Figure 5 shows the ^{13}C -NMR spectra of the E-D copolymers obtained from the low-Ti-loading (0.8 wt %) Z-N catalyst at a 1-dodecene concentration of 0.6 mol/L. The complete chemical-shift assignments encompassing all possible arrangements of ethylene and 1-dodecene in the E-D copolymers were calculated with the Grant–Paul formulation^{18,19} and compared with those obtained from the ^{13}C -NMR spectra of the E-D copolymers synthesized by the low-Ti-loading Z-N catalyst; they are all shown in Table II.

Table III lists the triad, dyad, and monad distributions in the E-D copolymers obtained with the M Z-N and M/S Z-N catalysts. Table IV shows the average sequence lengths for ethylene (n_E) and 1-dodecene (n_D) and the reactivity ratios for ethylene (r_E) and 1-dodecene (r_D) calculated from ^{13}C -NMR sequence data. The contents of 1-dodecene in both E-D copolymer chains were high and reached 16.7 and 17.8%, respectively; the contents of the [DD] dyads and [DDD] dyads (triads) in the E-D copolymers prepared with the M/S Z-N catalyst were higher than the contents in the copolymers prepared with the M Z-N catalyst, indicating that there were more continuous 1-dodecene repeat

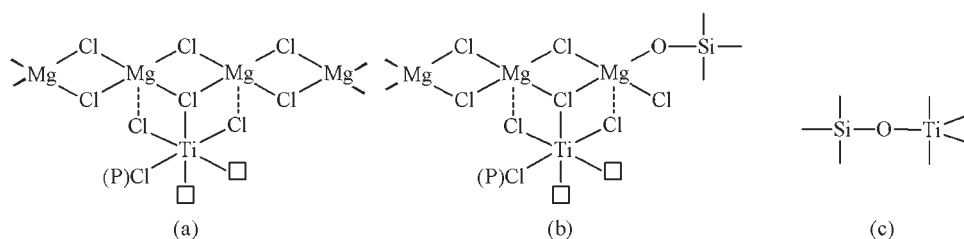


Figure 2 Plausible structures of active centers in the supported Z-N catalysts.

TABLE I
Activity of E–D Copolymerizations Catalyzed by the M Z–N and M/S Z–N Catalysts

1-Dodecene (mol/L)	Temperature (°C)	Activity (10^3 g of polymer/g of Ti h)	
		M Z–N catalyst	M/S Z–N catalyst
0.0	50	7.4	5.2
0.1	50	10.8	7.4
0.2	50	14.6	8.5
0.4	50	18.4	9.4
0.6	50	24.4	10.9
0.2	40	—	7.6
0.2	60	—	6.6

Polymerization conditions: time = 30 min; [Ti] = 1.0 mmol/L; [Al] / [Ti] = 200.

units in the chains of the copolymers obtained with the M/S Z–N catalyst, and there were more isolated 1-dodecene units in the chains of the copolymers obtained with the M Z–N catalyst. It is reasonable to assign this difference to the difference between the active centers in the M Z–N catalyst and M/S Z–N catalyst.

CONCLUSIONS

Novel MgCl₂-supported and MgCl₂/SiO₂-bisupported Z–N catalysts with low Ti loadings were prepared with a new one-pot preparation route. With these catalysts, ethylene and 1-dodecene were copolymerized with high activity and with an evident comonomer effect, and the resultant copolymers had high contents of 1-dodecene.

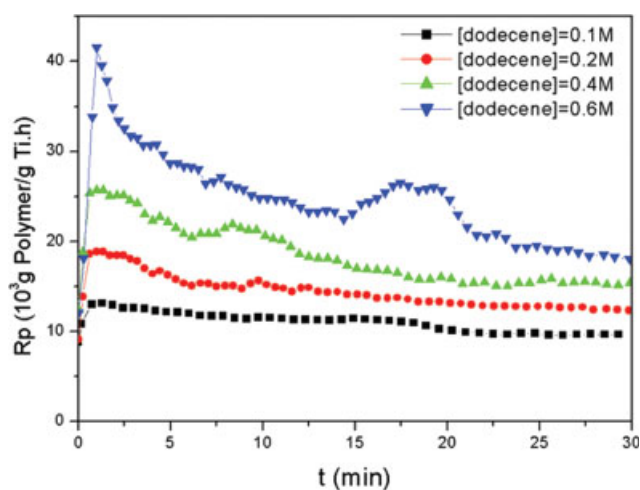


Figure 3 Kinetic curves of E–D copolymerizations catalyzed by the M Z–N catalyst (polymerization conditions: temperature = 50°C; [Ti] = 1 mmol/L; [Al]/[Ti] = 200). R_p is the rate of polymerization, and t is the time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

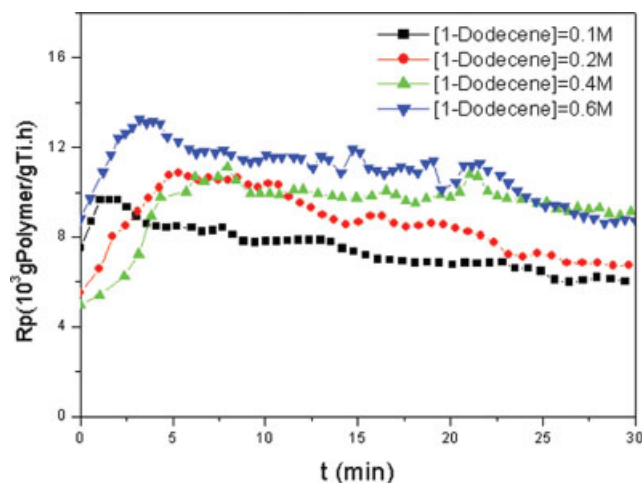


Figure 4 Kinetic curves of E–D copolymerizations catalyzed by the M/S Z–N catalyst (polymerization conditions: temperature = 50°C; [Ti] = 1 mmol/L; [Al] / [Ti] = 200). R_p is the rate of polymerization, and t is the time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Complete chemical-shift assignments encompassing all possible arrangements of ethylene and 1-dodecene in the E–D copolymers were calculated with the Grant–Paul formulation and obtained from the ¹³C-NMR spectra of the E–D copolymers synthesized by the low-Ti-loading Z–N catalysts. According

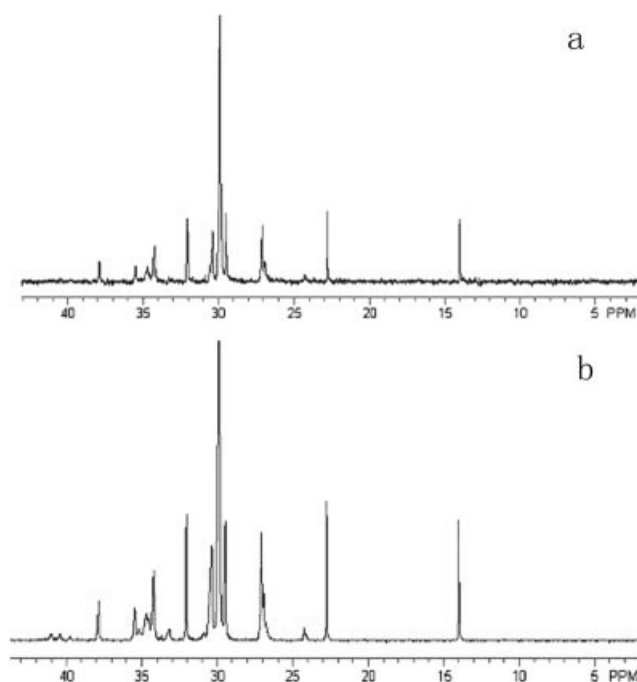


Figure 5 ¹³C-NMR spectra of E–D copolymers synthesized with (a) the M Z–N catalyst and (b) the M/S Z–N catalyst (polymerization conditions: temperature = 50°C; time = 30 min; [Ti] = 1.0 mmol/L; [Al] / [Ti] = 200; [1-Dodecene] = 0.6 mol/L).

TABLE IV
Average Sequence Lengths and Reactivity Ratios for the E-D Copolymers

Sample	n_E	n_D	r_E	r_D	$r_E r_D$
a	5.5	1.1	33.4	0.0072	0.24
b	7.0	1.5	44.6	0.035	1.56

Sample a was prepared with the M Z-N catalyst; sample b was prepared with the M/S Z-N catalyst. For the polymerization conditions, see Figure 5.

to the triad distribution, dyad distribution, and monad distribution, it could be presumed that the 1-dodecene unit was isolated basically in the copolymer chains synthesized by the M Z-N catalyst, whereas more continuous 1-dodecene repeat units existed in the copolymer synthesized by the M/S Z-N catalyst. It is reasonable to assign this difference to the difference between the active centers in the M Z-N catalyst and M/S Z-N catalyst.

References

- Ye, Z. Y.; Wang, L.; Feng, L. F.; Gu, X. P.; Chen, H. H.; Zhang, P. Y.; Pan, J.; Jiang, S.; Feng, L. X. *J Polym Sci Part A: Polym Chem* 2002, 40, 3112.
- Zohuri, G. H.; Mortazavi, M. M.; Jamjah, R.; Ahmadjo, S. *J Appl Polym Sci* 2004, 93, 2597.
- Galland, G. B.; Seferin, M.; Mauler, R. S.; Santos, J. H. Z. D. *Polym Int* 1999, 48, 660.
- Kissin, Y. V.; Mirabella, F. M.; Meverden, C. C. *J Polym Chem* 2005, 43, 4351.
- Lopez-Manchado, M. A.; Valle, M.; Sapunar, R.; Quijada, R. *J Appl Polym Sci* 2004, 92, 3008.
- Kim, J. D.; Soares, J. B. P. *J Polym Sci Part A: Polym Chem* 2000, 38, 1417.
- Fan, Z. Q.; Yasin, T.; Feng, L. X. *J Polym Sci Part A: Polym Chem* 2000, 38, 4299.
- Wang, L.; Yuan, Y. L.; Ge, C. X.; Wang, Y. X.; Ji, B.; Pan, J.; Ye, Z. Y.; Feng, L. X. *J Appl Polym Sci* 2000, 76, 1583.
- Rangwala, H. A.; Lana, I. G. D.; Szymura, J. A.; Fiedorow, R. M. *J Polym Sci Part A: Polym Chem* 1996, 34, 3379.
- Miyata, H.; Yamaguchi, M.; Akashi, M. *Polymer* 2001, 42, 5763.
- Czaja, K.; Bialek, M. *Polymer* 2001, 42, 2289.
- Wang, J. F.; Wang, L.; Ma, Z. L.; Wang, W. Q.; Jiang, G. H. *Chin. Pat. CN200410017170.7* (2004).
- Wang, J. F.; Wang, L.; Zhao, Z. R.; Wang, W. Q.; Chen, T. *J Zhejiang Univ Sci* 2004, 5(8), 912.
- Wang, J. F.; Wang, L.; Feng, L. F.; Gu, X. P.; Yu, H. J. *Polym-Plast Technol Eng* 2005, 44, 501.
- Wang, J. F.; Wang, L.; Feng, L. F.; Gu, X. P.; Yu, H. J. *J Polym Mater* 2004, 21, 401.
- Wang, J. F.; Wang, L.; Zhao, Z. R.; Chen, T.; Yu, H. J. *Chin. Pat. CN200410017171.1* (2004).
- Lu, H. L.; Xiao, S. *J Makromol Chem* 1993, 194, 421.
- Grant, D. M.; Paul, E. G. *J Am Chem Soc* 1964, 86, 2984.
- Randall, J. C. *Rev Macromol Chem Phys* 1989, 29, 201.