

# Preparation of Novel MgCl<sub>2</sub>-Adduct Supported Spherical Ziegler–Natta Catalyst for $\alpha$ -Olefin Polymerization

Li Wang, Hao-Jie Yu, Zhen-Li Ma, Zhao-Yang Ye, Shan Jiang, Lian-Fang Feng, Xue-Ping Gu

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

Received 26 January 2005; accepted 26 May 2005

DOI 10.1002/app.22332

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

**ABSTRACT:** In this article, preparation of novel MgCl<sub>2</sub>-adduct supported spherical Ziegler–Natta catalyst for  $\alpha$ -olefin polymerization is reported. The factors affecting the particle size (PS) and particle size distribution (PSD) of the prepared support were investigated. In this method, the internal donor added while preparing MgCl<sub>2</sub>-adduct support was supposed to act as a crosslinking agent. Therefore it provided a reasonable way to enhance the morphology

and control the PS of the resultant polymer particles. The possible mechanism is discussed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 945–948, 2006

**Key words:** spherical MgCl<sub>2</sub>-adduct support; morphology; spherical Ziegler–Natta catalyst; particle size; propene polymerization

## INTRODUCTION

Polyolefin is one of the most widely used polymer materials. The ultimate key to the development of industrial olefin polymers is the renovation of catalyst. Generations of Ziegler–Natta catalyst for propene polymerization brought about spectacular progress. The concept of the total control of polymer by using Ziegler–Natta catalyst gradually gained ground.<sup>1–4</sup> Recently, by making use of the replication phenomenon reported many years ago,<sup>2</sup> active species supported on spherical MgCl<sub>2</sub> support have made great progress in controlling polymer morphology as spherical particles.<sup>5–10</sup> This has led to the invention of the fourth-generation catalyst, which can produce polymers with controlled morphology. By using this kind of catalyst, the resultant polymer can replace the pellets, thereby avoiding the granulation phase,<sup>6</sup> which will greatly simplify the posttreatment process and save energy.

To fulfill this aim, research work was performed focusing on synthesizing the “ideal” support, which is indispensable for the “ideal” catalyst, for the morphology and composition of the support play the determining role on the morphology of the final product. Much interest has been taken in the recrystallization method, which involves dissolving MgCl<sub>2</sub> in electron-

donor solvents, e.g., alcohols and ethers, then recrystallizing MgCl<sub>2</sub> from the solution.<sup>5,10–14</sup> In our previous work, different factors affecting the preparation of spherical MgCl<sub>2</sub> support were investigated. It was found that the spherical morphology is easy to achieve, but the firmness of the support was rather difficult to control. One of the basic requirements for the catalyst is to have enough mechanical resistance to withstand manipulations and enough looseness to allow the pores developed by the growing polymer to break down the catalyst into microscopical particles that remain entrapped in the polymer. How to modulate the firmness of the catalyst to a proper extent in the recrystallization method still remains a big problem.

Here we deal with this problem through a novel route of synthesizing the spherical MgCl<sub>2</sub> adduct support material containing di-*i*-butylphthalate. By applying this technology the sequent spherical catalyst was prepared, and furthermore, the spherical polypropene product was obtained. The resultant polypropene product showed good morphology.

## EXPERIMENTAL

### Materials

Anhydrous MgCl<sub>2</sub>, AlEt<sub>3</sub> (Fluka, Buchs, Switzerland), and di-*i*-butylphthalate (DIBP) (Acros, Geel, Belgium) were used as received. Diphenyldimethoxysilane, ethanol, paraffin oil, and methyl siloxane were dried over 4-Å molecular sieves before use. Hexane, toluene, and petroleum ether were refluxed over a Na–K alloy before use. Polymerization-grade propene was further

Correspondence to: L. Wang (opl\_wl@diel.zju.edu.cn).

Contract grant sponsors: The National Natural Science Foundation of China and the Science and Technology Commission of Zhejiang Province.

**TABLE I**  
Preparation Conditions of Spherical  $\text{MgCl}_2$  Adducts

Sample no.	EtOH/ $\text{MgCl}_2$ (mol/mol)	DIBP/ $\text{MgCl}_2$ (mol/mol)
1s	2.8	0.177
2s	2.8	0.091
3s	3.2	0.090
4s	3.2	0

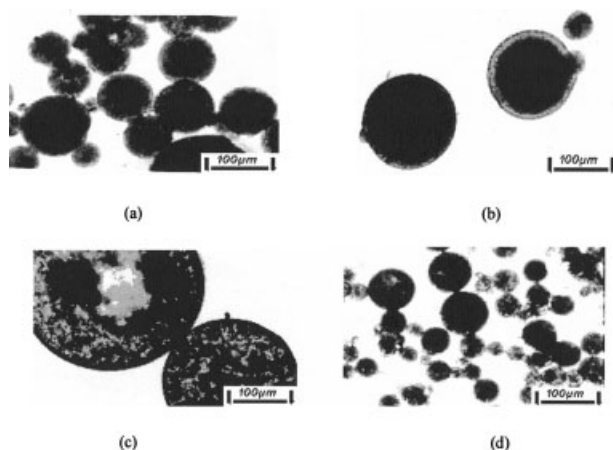
purified by passing over 4-Å molecular sieves. Preparation and manipulation were all carried out under dry, oxygen-free argon gas, using standard Schlenk technique.

### Preparation of the spherical $\text{mgcl}_2$ adducts

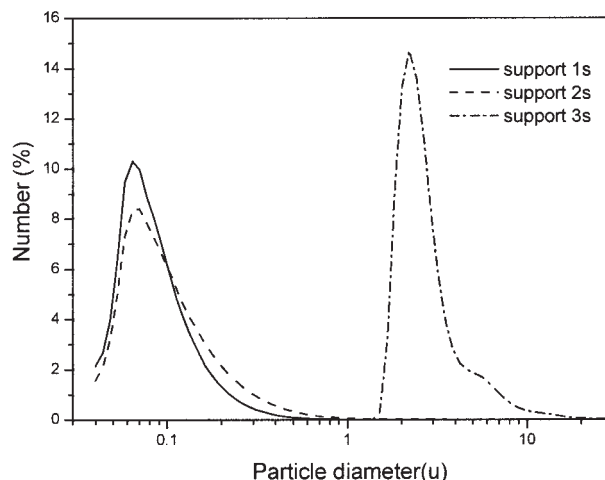
First, in a three-necked, 250-mL flask (the first reactor) with a mechanical stirrer, 8 g of  $\text{MgCl}_2$  was completely dissolved in ethanol at 70–80°C and then DIBP was added to the solution (the mole ratio of the reactants are shown in Table I). In another flask, a mixture (150 mL) of methyl siloxane and paraffin oil (1/1 v/v) was prepared at 120°C, and then the mixture in the first reactor was transferred into this reactor (the second reactor). Here, the  $\text{MgCl}_2$  solution was dispersed in the inert medium at 120°C (the final dispersion). In the end, the resultant mixture was introduced into 300 mL of *n*-hexane at –20°C in the third reactor, and the final  $\text{MgCl}_2$  was recrystallized, rinsed with *n*-hexane three times, and dried in vacuo. In the previous ordinary methods no internal donor was added.<sup>15</sup>

### Characterization

The procedures of preparing the catalyst and polymerizations are the same as described in an earlier article.<sup>15</sup> Photographs of  $\text{MgCl}_2$  adducts, catalysts, and



**Figure 1** Morphology of spherical  $\text{MgCl}_2$ : (a) 1s, (b) 2s, (c) 3s, and (d) 4s.



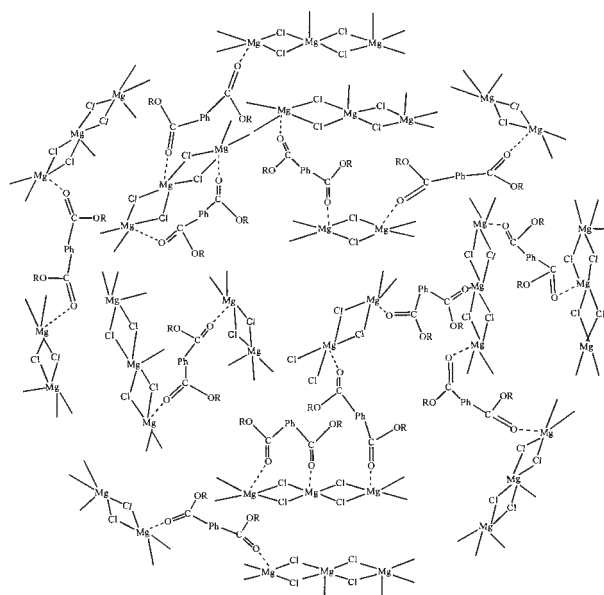
**Figure 2** The particle size distribution of supports prepared by adding DIBP.

polymers were taken on a Nitachis-450 optical microscope. The catalyst particles were dispersed in anhydrous hexane and polymer particles in anhydrous ethanol. The particle size (PS) and particle size distribution (PSD) of the spherical support were measured on a Coulter LS-230 particle size analyzer.

## RESULTS AND DISCUSSION

### Spherical $\text{mgcl}_2$ support material

The  $\text{MgCl}_2$  spherical adduct support material produced by the novel route shows a better morphology



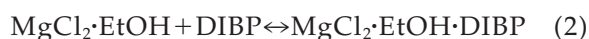
**Scheme 1** Possible structure of  $\text{MgCl}_2$ -adduct support material.

**TABLE II**  
The Influence of DIBP/MgCl<sub>2</sub> (mol/mol) on Ti Loading Content During Support Treatment with Titanium

Catalyst	Support	Adding DIBP/MgCl <sub>2</sub>	Total DIBP/MgCl <sub>2</sub>	Ti (% w/w)
3c1	3s	0	0.090	2.93
3c2	3s	0.180	0.270	8.24

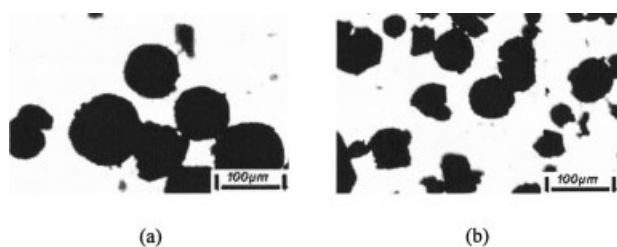
than the support prepared by the ordinary way (Fig. 1), and fewer broken pieces were observed.

The possible reactions of preparation process and the composition of the MgCl<sub>2</sub> adducts are shown as eqs. (1) and (2).<sup>16</sup>

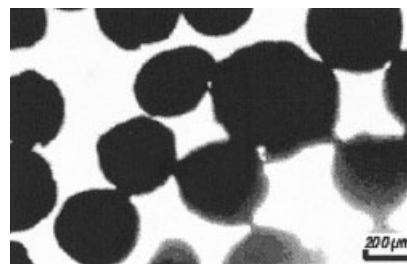


Different conditions of preparing the support were investigated (Table I). It is found that DIBP/MgCl<sub>2</sub> ratio may change the PS and PSD of the prepared MgCl<sub>2</sub> adducts (Fig. 2), therefore this novel route provides a way to control the PS of the final product.

Equation (2) shows that after adding DIBP into the MgCl<sub>2</sub> alcohol solution, MgCl<sub>2</sub>·EtOH and MgCl<sub>2</sub>·EtOH·DIBP complexes will reach an equilibrium in the reactor. In this way, the addition of DIBP may change the surface tension and viscosity of the solution, and therefore affect the formation of the spherical particles. Furthermore, DIBP may also influence the crystallization process in the precipitation step. The reaction of DIBP with MgCl<sub>2</sub> has long been reported.<sup>2,4,17,18</sup> It was supposed that DIBP was more likely to absorb on the 110 face of the MgCl<sub>2</sub>. When DIBP reacts with two different microcrystallites, it plays a role of a crosslinking agent (Scheme 1), thereby strengthening the intensity of the recrystallizing particles and controlling the PS. The support prepared by this route is in favor of getting rid of the fragility of catalyst, which is preferable in the sequential preparation of catalyst and the polymerization reaction. What is more, it is easy to adjust the crosslinking extent or the firmness of the MgCl<sub>2</sub>-adduct support by changing the amount of DIBP added.



**Figure 3** Morphology of catalyst: (a) 3c1 and (b) 3c2.



**Figure 4** Morphology of polymer catalyzed by catalyst 3c1; P, 1.0 atm.

The process of support preparation is supposed to be a complex one. There still exist a lot of factors that can influence the PS and PSD of the resultant MgCl<sub>2</sub> support.<sup>15</sup> However, adding DIBP provides a reasonable way to adjust the firmness of the MgCl<sub>2</sub> adduct support and to improve the morphology of the resultant support as well.

### Spherical catalyst

It is found that the addition of DIBP during the support treatment with titanium was in favor of the titanium loading (Table II). Yang et al.<sup>19</sup> reported a possible mechanism by which DIBP may complex with titanium. In this mechanism, DIBP took part in the formation of the active species. The amount of DIBP added in preparing the catalyst has little influence on the morphology of the catalyst (Fig. 3). And the prepared catalyst kept the spherical morphology of the support.

### Resultant polypropylene

Polymers produced by using catalyst 3c1 present a good morphology (Fig. 4). The most outstanding advantage was that the polymerization of 3c1 was carried out under a normal pressure. It means that the catalyst can produce polymers with good morphology and large size even under low monomer concentration, which will be very beneficial in industrial application.

### CONCLUSIONS

The spherical MgCl<sub>2</sub> adduct support material was synthesized by a novel route. It is supposed that the addition of DIBP in this new method provides a way to adjust the firmness of the MgCl<sub>2</sub> adduct, and to control the morphology and the PS of the support. The resultant polymers show a good morphology. Though the mechanism is still a matter of discussion, the application of this novel method in industrial field is quite promising.

## References

1. Galli, P.; Luciani, L.; Cecchin, G. *Angew Makromol Chem* 1981, 94, 63.
2. Galli, P.; Barbe, P. C.; Noristi, L. *Angew Makromol Chem* 1984, 120, 73.
3. Sobota, P. *Polym Plast Technol Eng* 1989, 28, 493.
4. Wang, L.; Feng, L. X.; Xu, J. T.; Yang, S. L. *Chin J Polym Sci* 1995, 13, 41.
5. Rerraris, M.; Rosati, F.; Parodi, S.; Giannetti, E.; Motroni, G.; Albizzati, E. U.S. Pat. 4,399,054 (1983).
6. Covezzi, M. *Macromol Symp* 1995, 89, 577.
7. Wu, L.; Lynch, D. T.; Wanke, S. E. *Macromol* 1999, 32, 7990.
8. Simonazzi, T.; Cecchin, G.; Mazzullo, S. *Prog Polym Sci* 1991, 16, 303.
9. Yu, H. J.; Wang, L.; Ye, Z. Y.; Ma, Z. L.; Jiang, S.; Wang, J. F.; Feng, L. F. *Poly-Plast Tech Eng* 2004, 43, 1115.
10. Mao, B. Q.; Yang, J. X.; Li, Z. L.; Yang, A. C.; Zheng, Y.; Xia, X. Z. Chinese Pat. CN 1091748A (1994).
11. Handlir, K.; Holeck, J.; Klukorka, J.; Bocek, V. *Int Polym Sci Tech* 1986, 13, 1.
12. Magalhães, D. N. T.; Filho, O. D. C.; Coutinko, F. M. B. *Eur Polym Mater* 1991, 27, 827.
13. Rerraris, M.; Rosati, F. U.S. Pat. 4,469,648 (1984).
14. Mario, S.; Illaro, C.; Gianni, P. Eur Pat. 0553805 A1 (1993).
15. 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, 18, 3112.
16. Hu, Y. L.; Chien, C. W. *J Polym Sci Part A: Polym Chem* 2003, 1988, 26.
17. Busico, V.; Corradini, P.; Martino, L. D.; Proto A.; Savino V. *Makromol Chem* 1985, 186, 1279.
18. Soga, K.; Shiono, T.; Doi, Y. *Mackromol Chem* 1987, 189, 1531.
19. Yang, C. B.; Hsu, C. C.; Park, Y. S.; Shurvell, H. F. *Eur Polym Mater* 1994, 30, 205.