

Study of Propylene Polymerization Catalyzed by a Spherical MgCl_2 -Supported Ziegler–Natta Catalyst System: The Effects of External Donors

Zhenli Ma, Li Wang, Wenqin Wang, Lianfang Feng, Xueping Gu

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

Received 2 October 2003; accepted 31 May 2004

DOI 10.1002/app.21247

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

ABSTRACT: Spherical MgCl_2 -supported Ziegler–Natta catalysts containing internal donors, such as diethyl phthalate, diisobutyl phthalate, and di-*n*-octyl phthalate, have been prepared. The effects of external donors, phenyltrimethoxysilane, phenyltriethoxysilane, and diphenyldimethoxysilane, on the propylene polymerization catalyzed by these catalysts were studied. The results indicate that the

external donors not only led to an increase in the isotactic index, but also affected the morphology of resultant polymer particles. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 738–742, 2005

Key words: Ziegler–Natta catalysts; propylene polymerization; spherical catalysts; external donor

INTRODUCTION

Polyolefins, which account for more than half of the worldwide polymer production of approximately 200 million metric ton per year, are well recognized as economically attractive and environmental friendly polymeric materials.¹ The key to the development of polyolefins is the renovation of catalysts. Ziegler–Natta catalysts have experienced four major generations since their discovery:^{2,3} using MgCl_2 as a support; using electron donors for propylene polymerization; using a chemical reaction method to prepare MgCl_2 -supported catalyst; and using spherical catalysts to control the morphology of polymer particles. However, the specific role of the internal and external donors in a catalyst system is still open to discussion.

The electron donors have several functions, such as to make a complex or to react with MgCl_2 , TiCl_4 , and cocatalyst, to stabilize MgCl_2 crystallites, and to deactivate astereospecific polymerization sites or to convert astereospecific sites to stereospecific ones, thus increasing the isotactic index.^{4,5}

Control of the polymer particle morphology is based on the fact that polyolefins tend to replicate the shape of the catalyst particles on which they are pro-

duced.^{3,6} By using spherical catalyst particles the resultant polymer replicates the catalyst pellets; it is able to avoid the granulation process.⁷ Therefore, the preparation of spherical support is important for obtaining spherical polymer pellets.

In this paper, we describe the effects of the spherical supports prepared via a chemical route. The effects of an external donor on the performance of MgCl_2 -supported spherical catalyst are evaluated by comparing phenyltrimethoxysilane (PTMS), phenyltriethoxysilane (PTES), and diphenyldimethoxysilane (DPDMS) with three catalysts containing diethyl phthalate (DEP), diisobutyl phthalate (DIBP), and di-*n*-octyl phthalate (DNOP), respectively, as internal donors.

EXPERIMENTAL

Materials

Anhydrous ethanol, paraffin oil, methyl siloxane (its viscosity is 500 cp at 25°C), and petroleum ether were dried over 4-Å molecular sieves before use. Hexane was refluxed over Na-K alloy. DEP, DIBP, DNOP, and DPDMS were used after distillation. Anhydrous MgCl_2 , PTMS, PTES, TiCl_4 , triethylaluminum, and *n*-heptane were used without further purification. All manipulations were all carried out using dry, oxygen-free argon gas.

Preparation of the spherical MgCl_2 -support

A typical preparation procedure for a spherical MgCl_2 support is as follows: in a three-neck 250-mL flask

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

Contract grant sponsor: National Natural Science Foundation of China.

Contract grant sponsor: The Science and Technology Commission of Zhejiang Province.

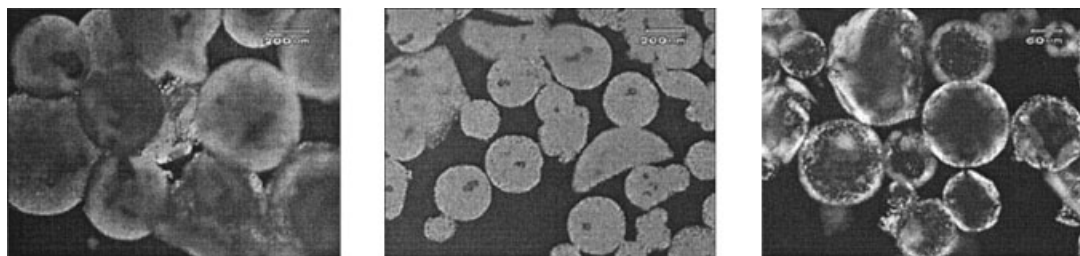


Figure 1 Photograph of spherical supports, from left to right: 030228S, 030106S, and 030226S.

TABLE I
Preparation Condition and Mg Content in the Support Samples

Support samples	EtOH/MgCl ₂ (molar ratio)	Stirring speed of predispersion (rpm)	Stirring speed of second dispersion (rpm)	Mg content (wt %)
030228S	3.0	—	1100	12.99
030106S	3.5	800	1200	12.44
030226S	3.0	800	1200	11.74

with a mechanical stirrer, MgCl₂ was completely dissolved in ethanol at 80°C and then dispersed in a mixture of methyl siloxane and paraffin oil (1/1, v/v) at 120°C. In another flask, a mixture of methyl siloxane and paraffin oil (1/1, v/v) at 120°C was prepared and then this mixture was transferred into the first reactor. The MgCl₂ solution was dispersed further in the inert medium at 120°C. The resultant mixture was introduced into a large amount of *n*-hexane at -30°C in the third reactor, and the final MgCl₂ adducts were recrystallized, rinsed with *n*-hexane three times, and dried in a vacuum.^{8,9}

Preparation of the spherical Ziegler–Natta catalyst

A typical preparation procedure of the spherical Ziegler–Natta catalysts is as follows: TiCl₄ was added into a three-neck glass reactor with a reflux condenser and maintained at -15~-20°C. The spherical MgCl₂ adduct obtained in the above preparation step was added. When the temperature reached 40°C, an internal donor was added to the reactor and the reactor was heated to 130°C and kept for 2 h. After the liquid was removed at 80°C, another aliquot of TiCl₄ was added into the reactor, and the temperature was kept

at 130°C for another 2 h. The product was then cooled to 50°C, the liquid was removed, and the solid was washed with hexane three times. The resultant catalysts were dried in a vacuum at room temperature.⁸

Propylene polymerization

Polymerization of propylene was carried out in slurry reactors at 50°C for 30 min. A magnetic stirrer was used to promote the monomer diffusion. Propylene was continuously introduced to the reactor to maintain the total pressure at 1 atm. Measured amounts of triethylaluminum and external donor (if needed), followed by the solid catalyst, were added into the reactor containing 50 mL petroleum ether. Polymerization was terminated by the addition of a dilute solution of hydrochloric acid in ethanol, and then products were collected by filtration and dried in a vacuum oven at 50~60°C.

Characterization

The content of magnesium in the support and catalyst was estimated by titration. Titanium content

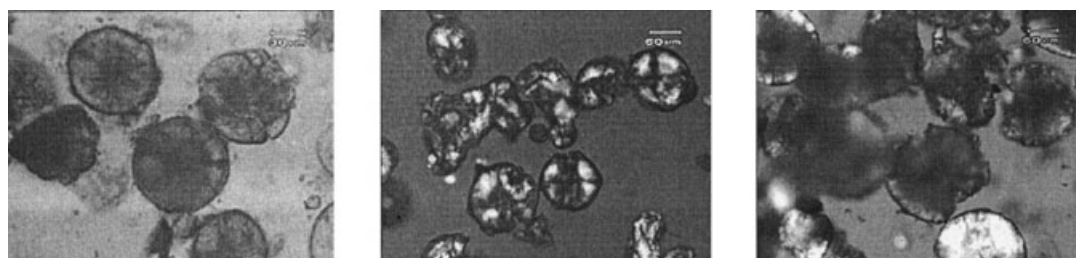


Figure 2 Photograph of spherical catalysts, from left to right: 030304C, 030116C, and 030311C.

TABLE II
Component of the Catalysts

Catalyst samples	Support samples	ID	ID/Mg (molar ratio)	Component (wt %)	
				Ti	Mg
030304C	030228S	DEP	0.09	5.71	20.9
030116C	030106S	DIBP	0.13	6.84	17.6
030311C	030226S	DNOP	0.10	6.12	—

was estimated by Cary UV at 410 nm. Photographs of supports, catalysts, and polymers were taken on an Olympus DP12 optical microscope. Polypropylene samples were fractionated with boiling heptane by Soxhlet extraction for 12 h. The isotactic index reported for each sample is the weight percentage of insoluble polymer.

RESULTS AND DISCUSSION

Spherical supports and catalysts

The supports preparation involved a chemical route to produce an active form of $MgCl_2$. In the process, better spherical supports (Fig. 1) were obtained only with simple instrumentations. The morphologies of these samples were similar on the whole. Preparation conditions and the Mg content in the supports are shown in Table I.

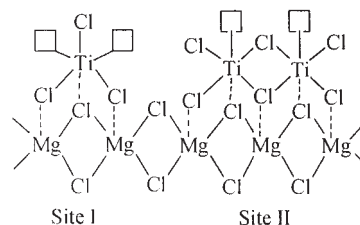


Figure 3 Plausible Ti^{3+} species on the $MgCl_2$ (100) face¹¹ (\square : vacant site).

We found that an EtOH/ $MgCl_2$ ranging from 3.0 to 3.5 was suitable for preparing spherical support, which is avoided by removing redundant ethanol before treatment with $TiCl_4$. The stirring speed of dispersion was another important factor controlling the morphology of the support: better spherical supports were prepared with lower stirring speed of dispersion (600–2000 rpm) in our laboratory.

Spherical catalysts were prepared by bubbling argon at the bottom of the reactor instead of mechanical stirring. The morphology of the resultant spherical catalysts is shown in Figure 2. Compared with Figs. 1 and 2, the morphology of the spherical catalysts is similar to that of the support. It was believed that internal donor could affect the titanium loading content and its distribution in the catalyst. The composition of the catalyst is given in

TABLE III
Polymerization Activity and Isotactic Index of Polypropylene

Catalyst	ID	Run	ED	ED/Ti (molar ratio)	Activity Kg PP/(g Ti \times h)	I.I. (%)
030304C	DEP	030304P9	NONE	—	2.01	81.7
		030304P8	PTMS	1.0	1.76	83.6
		030304P5	PTMS	2.0	1.49	89.0
		030304P15	PTES	1.0	1.68	86.6
		030304P17	PTES	2.0	1.39	87.1
		030304P11	DPDMS	1.0	1.22	88.9
		030304P13	DPDMS	2.0	1.43	93.2
		030116C	DIBP	030116P6	NONE	—
030116P4	PTMS	1.0		0.79	82.7	
030116P1	PTMS	2.0		1.02	91.6	
030116P12	PTES	1.0		0.96	81.1	
030116P14	PTES	2.0		0.83	85.6	
030116P8	DPDMS	1.0		0.76	90.4	
030116P10	DPDMS	2.0		0.84	94.0	
030311C	DNOP	030311P12		NONE	—	1.90
030311P22		PTMS	1.0	0.95	85.6	
030311P23		PTMS	2.0	0.89	91.8	
030311P18		PTES	1.0	1.31	88.8	
030311P20		PTES	2.0	0.94	95.1	
030311P14		DPDMS	1.0	1.53	91.5	
030311P16		DPDMS	2.0	0.90	91.6	

Note. Polymerization conditions: petroleum ether 50 ml, 50°C, 30 min, Al/Ti = 100.

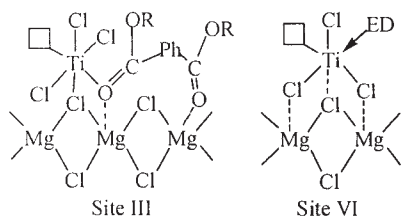


Figure 4 Plausible structure models of potentially stereospecific sites¹³ (□: vacant site).

Table II. Compared with a catalyst without internal donor, the titanium content of these catalyst samples was lower (for a catalyst samples without internal donor: Ti (wt %) = 9.55%).

Effects of external donor on stereospecificity and activity of polypropylene

The results of propylene polymerization are shown in Table III. When the external donor was added, the activity of catalyst decreased, while the isotacticity increased. With an increase of the external donor concentration, the activity of the atactic fraction decreased sharply, whereas that of isotactic polymer fraction comparatively increased. This increase is mainly due to the increased number of stereospecific sites and the decreased number of nonstereospecific sites in the presence of ED.¹⁰

There may exist two types of Ti^{3+} species on $MgCl_2$ (100) faces in the absence of internal donor, as shown in Figure 3;¹¹ one is a mononuclear species with two vacant sites (Site I) and the other is a bi- or multinuclear species with one vacant site (Site II). The former may produce the atactic polymer and the latter the isotactic polymer.¹²

In the presence of internal donors and external donors, according to ESR results,¹³ the mononuclear sites changed into potential highly isospecific centers that had only one vacant site on Ti^{3+} (Fig. 4, sites III and IV). It is necessary to use ID and ED simultaneously to increase the isotactic index of polypropylene.

With regard to PTES and PTMS effects on the isotactic index of polypropylene, there was no evident distinction among the catalysts. In relation to the activity of the catalyst, the catalyst systems using PTMS and DIBP as an external donor and internal donor, respectively, were the best ones. In these systems, the I.I. increased with less decrease in activity. With regard to PTMS and DP-DMS effects on the isotactic index, we conclude that the latter, when used as an external donor, is better than the former regardless of any internal donor.

The morphology of the resultant polypropylene

Usually, polymer particles replicate the morphology of the particles of supported catalysts. Spherical polymer particles (Fig. 5) were obtained using our spherical catalysts. Polypropylene samples with high I.I. had better particle morphology.

CONCLUSION

With simple instrumentations, spherical $MgCl_2$ supports were prepared at a lower stirring speed of dispersion (600~2000 rpm). When the EtOH/ $MgCl_2$ ratio ranged from 3.0 to 3.5, the ethanol content in the resultant supports was suitable for preparing Ziegler-Natta catalysts without removing the redundant ethanol. Except for the component and morphology of the support, bubbling argon to the reactor bottom instead of mechanical stirring is an efficient technique to obtain spherical Ziegler-Natta catalyst.

External donors, coordinating on titanium atoms adjacent magnesium atoms, could poison atactic active sites or converted them into isotactic ones. As a whole, the percentage of the active sites in the system got the ascendancy. The activity of the catalyst decreased while the isotactic index of the resultant polypropylene increased. The polymers with a higher

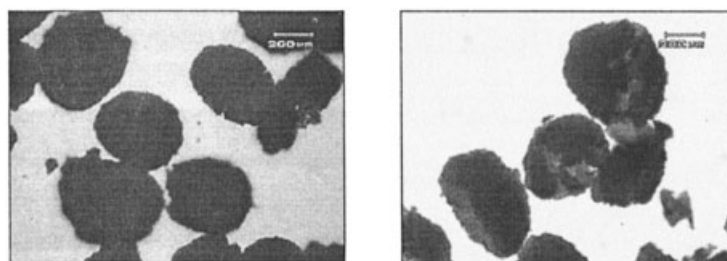


Figure 5 Photographs of spherical polymer particles produced by catalyst 030311C, left: 030311P20; right: 030311P16.

isotactic index better replicate the morphology of catalyst particles.

References

1. Mülhaupt, R. *Macromol Chem Phys* 2003, 204, 289.
2. Cecchin, G.; Morini, G.; Piemontesi, F. *Ziegler–Natta Catalysts*, in *KirkOthmer Encyclopedia of Chem Technology*; Wiley: New York, 2003.
3. Galli, P.; Vecellio, G. *Prog Polym Sci* 2001, 26, 1287.
4. Pakkanen, T. A.; Vahasaria, E.; Pakkanen, T. A.; Iiskola, E.; Sormunen, P. *J Catal* 1990, 121, 248.
5. Soga, K.; Shiono, T. *Prog Polym Sci* 1997, 22, 1503.
6. Pater, J. T. M.; Weickert, G.; Van Swaaij, W. P. M. *J Appl Polym Sci* 2003, 87, 1421.
7. Covezzi, M. *Macromol Symp* 1995, 89, 577.
8. 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 Pol. Chem* 2002, 40, 3112.
9. Mao, B. Q.; Yang, J. X.; Li, Z. L.; Yang, A. C.; Zheng, Y.; Xia, X. Z. CN 1036011C 1997.
10. Chadwick, J. C.; Morini, G.; Balbontin, G.; Camurati, I.; Heere, J. J. R.; Mingozzi, I.; Testoni, F. *Macromol Chem Phys* 2001, 202, 1995.
11. Busico, V.; Corradini, P.; Martino, L. D.; Proto, A.; Albizzati, E. *Makromol Chem* 1986, 187, 1115.
12. Soga, K.; Shiono, T.; Doi, Y. *Makromol Chem* 1988, 189, 1531.
13. Wang, L.; Feng, L. X.; Xu, J. T.; Yang, S. H. *Chinese J Polym Sci* 1995, 13, 41.