

The Roles of Grignard Reagent in the Ziegler–Natta Catalyst for Propylene Polymerization

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ABSTRACT: Grignard reagent PhMgCl was added during the preparation of the catalyst system $\text{MgCl}_2/\text{di-}n\text{-butyl phthalate (DNBP)}/\text{TiCl}_4\text{—AlEt}_3/\text{diphenyl dimethoxyl silane (DPDMS)}$ to improve its performance. It was found that PhMgCl could enhance both the activity of the catalyst and the isotacticity of the products, but decreased the Ti content of the catalysts under the same preparation conditions. The polymerization kinetics showed that PhMgCl accelerates the decay in the same time that it increased the initial and final polymerization rates. By means of UV-vis spectroscopy, electron spin resonance (ESR) spectroscopy, and the Ti content determination of the catalysts, the multiple roles of PhMgCl were disclosed: reduction of Ti^{4+} to Ti^{3+} , association with MgCl_2 to replace part of TiCl_4 in aspecific active sites, and complexing with the original active sites to form new active sites. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 925–930, 1997

INTRODUCTION

The present catalysts for propylene polymerization in industry are mainly MgCl_2 -supported Ti-based catalysts containing internal and external electron donors. Both high activity and high stereospecificity are the main purposes of the research on the catalysts for propylene polymerization. To obtain a highly isotactic polymer, electron donors must be added.^{1,2} Unfortunately, this is usually at the cost of the activity of the catalyst,^{3–7} especially in the case of benzoate compounds. Many efforts have been made to enhance the activity of the catalyst, such as improving the activation method of the support and the addition of other compounds.^{8,9} The Grignard reagent was used to increase the activity of the catalyst for ethylene (co)polymerization by some investigators.^{10,11} However, these catalysts were directly

prepared by reduction of TiCl_4 and the Grignard reagent, which were not suitable for propylene homopolymerization. Moreover, the emphases in these articles were focused on the catalytic behavior, and the roles of the Grignard reagent was not well studied. In the present work, the catalyst $\text{MgCl}_2/\text{di-}n\text{-butyl phthalate (DNBP)}/\text{TiCl}_4$, which had been used for propylene polymerization, was treated with the Grignard reagent PhMgCl at different PhMgCl/Ti ratios to improve its performance and the influence of PhMgCl was investigated by various methods.

EXPERIMENTAL

Preparation of PhMgCl

PhMgCl in the absence of an ether compound was synthesized according to Ref. 12. Under a dry N_2 atmosphere, magnesium powder was premixed with a small amount of chlorobenzene (BzCl). AlEt_3 , 0.05 mL, and a grain of I_2 was used as the initiator. The temperature was increased to 120–

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130°C accompanied with agitation. Then, the rest of the BzCl was added dropwise under this temperature and the reaction was maintained for 6 h. After the reaction was completed, the concentration of PhMgCl was determined by the decomposition of PhMgCl with excessive 0.2N H₂SO₄, followed by titration with 0.2N NaOH.

Preparation of the Catalyst

The preparation of MgCl₂-supported catalysts containing DNBP as an internal electron donor was described in Ref. 13. Under a N₂ atmosphere, 1 g of anhydrous MgCl₂ and 6 mL BuOH were added to 50 mL *n*-octane. This suspension was heated to 80°C and stirred until the MgCl₂ was dissolved. The solution was then held at 100°C for 2 h after 50 mL TiCl₄ was added dropwise. Subsequently, the resulting solid product was separated by filtration and was washed with *n*-octane. Internal electron donors were added and the mixture was stirred for 2 h. Then, the suspension was washed and 50 mL TiCl₄ was added again. After 2 h, the operations of filtration and washing were repeated. The Ti content of the catalysts was determined by UV-vis spectroscopy at $\lambda = 410$ nm. According to the Ti content and PhMgCl/Ti ratios, prescribed PhMgCl was added in the end. The mixture was stirred for 1 h, then washed with *n*-octane. The Ti content in the final catalyst was measured. The morphology of the catalyst was nearly globularlike,¹³ the average particle diameter was 50 μ m, and the particle diameter distribution was 2.7.

Polymerization of Propylene

Polymerization was carried out in slurry at atmospheric pressure for 1 h. Propylene was rapidly bubbled through the stirred *n*-heptane solvent in a reactor. AlEt₃ was used as a cocatalyst and diphenyl dimethoxysilane (DPDMS) was employed as an external electron donor. Typical polymerization conditions were 100 mL of *n*-heptane, 30 mg catalysts, [AlEt₃]/[Ti] = 100, [Si]/[Al] = 0.04, and polymerization temperature = 50°C. The polymerization reaction was terminated by addition of ethanol containing HCl. The products were washed and filtrated, then dried *in vacuo* at 80°C overnight.

Polymerization Kinetics

The kinetics of slurry polymerization was conducted in a closed system, which included a three-

necked flask, an electromagnetic valve, and a tank full with propylene gas. The pressure in the tank was maintained constant. The prescribed amount of solvent, AlEt₃, and the electron donor were charged into the flask. The pressure in the flask was the same as that in the tank and the diluent was saturated with propylene. Then, the catalysts were introduced. After the polymerization started, the entrance of propylene was controlled by an electromagnetic valve. The opening time of the electromagnetic valve was recorded. When the pressure in the tank is invariant, the amount of propylene gas entering the flask each time the electromagnetic valve opens can be considered to be the same¹⁴ and it is equal to the whole weight of the polymer divided by open times. Therefore, the consumption of propylene vs. time, e.g., polymerization-time profile, is obtained.

Analytical Procedures

ESR spectra were recorded at room temperature on a JEOL JES-FEIXG spectrometer under a N₂ atmosphere. The values of the *g* factor were determined by comparison with those of the Mn²⁺ standard. The UV-vis spectrum was obtained on a Du-50 Beckman spectrometer. Polymer samples were extracted with boiling *n*-heptane in a Soxhlet apparatus for 6 h. The percentage by weight of the insoluble polymer was taken as the isotactic index (I.I.) of the polymer.

RESULTS AND DISCUSSION

Reduction of Ti⁴⁺

While preparing the catalyst, the color of the catalyst immediately changed into brown from white after PhMgCl was added. The ESR spectra of the catalyst before and after treatment with PhMgCl are shown in Figure 1. Only one ESR signal, which had a *g* value of 2.002 and might originate from free radicals, is presented in Figure 1(a). This indicates that Ti ions are all four valent in the catalyst before being treated with PhMgCl. However, in Figure 1(b), several Ti³⁺ ESR signals were observed, which shows that Ti⁴⁺ ions are reduced into Ti³⁺ ions by PhMgCl. The UV-vis spectrum of the liquid phase after addition of PhMgCl is shown in Figure 2. Two absorption peaks appear at $\lambda = 210.0$ nm and $\lambda = 246.5$ nm,

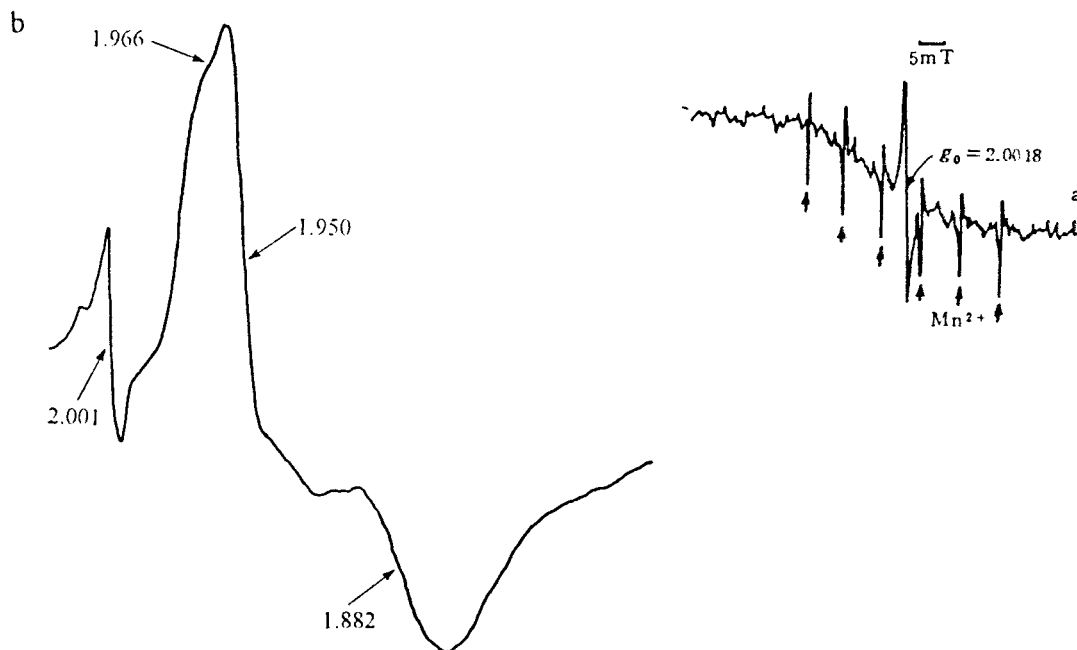


Figure 1 ESR spectra of the catalyst $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4$ (a) before and (b) after being treated with PhMgCl .

respectively. The peak at $\lambda = 210.0$ nm is the absorption of BzCl , which was used as a solvent during the preparation of PhMgCl . The absorption band at $\lambda = 246.5$ nm is attributed to biphe-

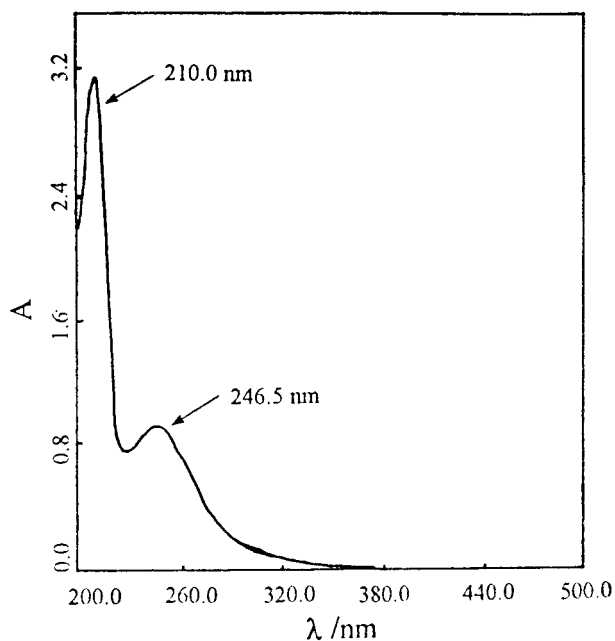


Figure 2 UV-vis spectrum of the liquid phase of the catalyst $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4$ treated with PhMgCl .

nyl.¹⁵ This suggests that biphenyl forms during the reduction of Ti^{4+} to Ti^{3+} by PhMgCl . Therefore, the reaction occurs as shown in Scheme 1.

The Effect of PhMgCl on Activity and Kinetics

On the basis of the titanium content of the catalysts, the activity of the catalysts treated with different amounts of PhMgCl is shown in Figure 3. No matter whether an external electron donor is added or not, PhMgCl increases the catalytic activity. Around $\text{PhMgCl}/\text{Ti} = 2.0$, the activity reaches its maximum. As mentioned above, only 1 mol of PhMgCl is needed to reduce 1 mol of Ti^{4+} into Ti^{3+} (Scheme 1); thus, it is necessary to study the effect that more than 1 mol PhMgCl takes. Figure 4 shows the ESR spectrum of the $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4\text{-AlEt}_3$ catalyst. Comparing Figure 4 and Figure 2(b), one can see that the shape of the spectrum changes and the values of the g factor shift. In Figure 2(b), four signals were observed with $g = 2.001$, 1.966, 1.955, and 1.882, respectively. However, for the $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4\text{-AlEt}_3$ catalyst, five signals with $g = 1.975$,



Scheme 1 Reaction between PhMgCl and TiCl_4 .

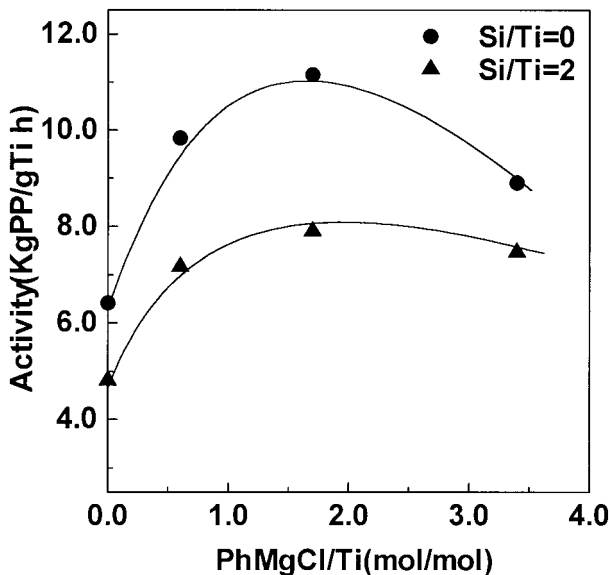


Figure 3 The dependence of catalytic activity on PhMgCl/Ti ratios.

1.967, 1.955, 1.951, and 1.946 appears in Figure 4. The value of the g factor is related to the structure of active sites and the shift of the g factor means that some structural changes of the active site take place after addition of PhMgCl. Therefore, it is believed that the residual 1 mol PhMgCl may interact with the original active sites and new active sites are formed. Since phenyl is a group of an electron donor, it will increase the electron density of the Ti atom and activate the Ti—R bond in the resulting active sites; thus, the insertion rate of the monomer accelerated and the activity of catalyst was enhanced.

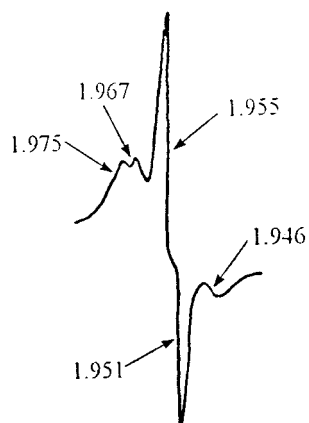


Figure 4 ESR spectrum of $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4-\text{AlEt}_3$.

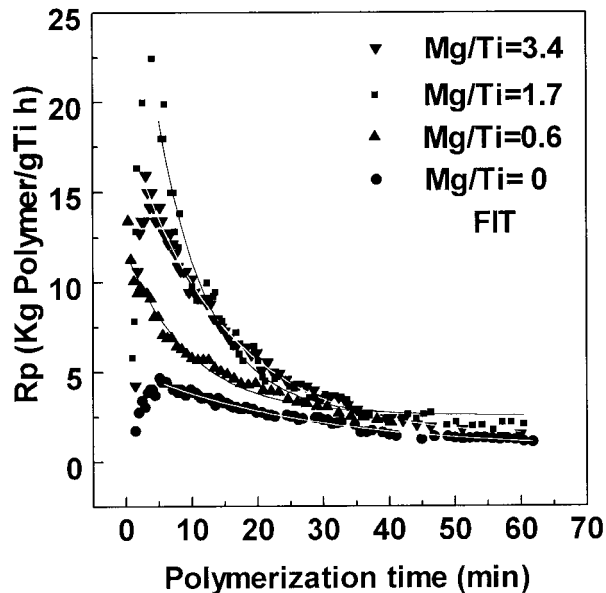


Figure 5 Polymerization kinetics of different catalysts.

The rate-time profiles for propylene polymerization using the catalysts treated with different amounts of the Grignard reagent are illustrated in Figure 5. The kinetic curves of all these catalysts are of the decay type. The experimental kinetics in the period of decaying can fit the following equation quite well¹⁶:

$$\frac{R_t - R_S}{R_0 - R_S} = \exp[-k_d \cdot (t - t_0)] \quad (1)$$

where R_0 is the maximum of polymerization rate; R_t , the polymerization rate at time $t = t$; R_S , the polymerization rate at the steady state; k_d , the decay rate constant; and t_0 , the time polymerization reaches its maximum.

The obtained parameters k_d , R_0 , and R_S are listed in Table I, which shows that PhMgCl enhances both R_0 and R_S . k_d also increases when the Grignard reagent is added. This indicates that PhMgCl accelerates the decay of the catalysts. The possible reason is that as PhMgCl enhances the electron density of the Ti atom the Ti—R bond becomes more active, but more unstable, which leads to a more rapid rate of deactivation. When PhMgCl/Ti is over 2, the activity and k_d decrease. This may result from the overreduction of Ti^{3+} to Ti^{2+} by PhMgCl, which is inactive to propylene polymerization.¹⁷

Table I The Effect of PhMgCl on the Polymerization Kinetics

No.	PhMgCl/Ti Ratio (mol/mol)	k_d (min^{-1})	R_0 (kg PP/g Ti h)	R_s (kg PP/g Ti h)
1	0	0.036	4.13	0.63
2	0.6	0.069	11.75	1.34
3	1.7	0.128	19.08	2.56
4	3.4	0.102	15.60	2.60

The Effect of PhMgCl on the Ti Content and Isotacticity

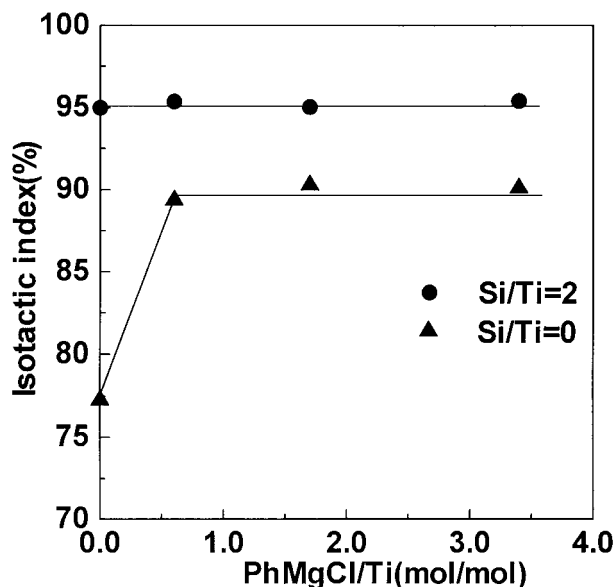
The Ti contents of the catalysts treated with different amounts of PhMgCl are listed in Table II. It can be seen that the addition of PhMgCl decreases the Ti content of the catalyst. Riis et al. reported that TiCl_4 supported on the surface of SiO_2 could be removed and TiCl_3 clusters formed.¹⁸ Zakharov et al.¹⁹ observed that AlEt_3 could remove some Ti ions on the surface of MgCl_2 into the solution and claimed that these Ti ions had four ligands. Wang⁹ also found an ESR signal in the liquid phase in the $\text{MgCl}_2/\text{TiCl}_4-\text{AlR}_3$ catalyst system. But an ESR signal was not observed in the liquid phase of the $\text{MgCl}_2/\text{TiCl}_4/\text{DNBP}-\text{AlEt}_3$ catalyst system, which may be due to the presence of an internal electron donor, DNBP. An internal electron donor can prevent the formation of some aspecific active sites. The amount of Ti ions, which is the easiest to remove, is reduced first by DNBP. In the meantime, due to the much stronger Lewis acidity of MgCl_2 than that of DNBP, AlEt_3 complexes with DNBP first and does not complex with MgCl_2 to replace TiCl_4 . But with regard to PhMgCl, its ability of complexing with MgCl_2 is stronger than that of AlEt_3 .

It is possible that part of the Ti ions, which cannot be removed by AlEt_3 , now can be replaced by PhMgCl. It is well known that MgCl_2 has two crystallinity faces: a 110 face and a 100 face. The coordination numbers of Mg on these faces are 4 and 5, respectively. Because of the different coordination number, which leads to the stronger

acidity of Mg atoms in the 110 face, PhMgCl first associates with the Mg atoms on the 110 face. Busico et al.²⁰ stated that TiCl_4 can be supported both on the 110 face and the 100 face of MgCl_2 . The active sites supported on the 110 face possess more than one vacant site and are aspecific active sites. Therefore, when PhMgCl coordinates with the Mg atom on the 110 face, part of aspecific active sites is replaced. This results in the decrease of the number of active sites and increase of the isotacticity of the polymer. Indeed, it was found that the isotactic index of the obtained polymers was enhanced after the catalyst was treated with PhMgCl (seeing Fig. 6). This effect is apparent when no external electron donor is added. Also, the participation of PhMgCl in active sites is partly responsible for the increase of isotacticity, since PhMgCl can increase the bulk of active sites. After an external electron donor is added, the ef-

Table II Ti Content of the Catalysts

	PhMgCl/Ti			
	0	0.7	1.7	3.4
Ti content (wt %)	4.28	3.42	2.75	2.49

**Figure 6** The effect of PhMgCl on the isotactic index (I.I.) of polymers.

fect of PhMgCl is not obvious. It may be shielded by the effect of external electron donor.

Since PhMgCl decreases the Ti content of catalysts, the activity calculated on the basis of total catalysts weight is enhanced not so largely as that based on the Ti content of catalysts. In fact, when an external donor is present in the catalysts, there is no substantial change in the activity based on the catalyst weight.

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