

Rapid Communication

## STUDY ON 1-HEXENE POLYMERIZATION BASED ON ZIEGLER-NATTA CATALYSTS WITH DOPED SUPPORT\*

Xue Jiang and Zhi-qiang Fan\*\*

The Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China

**Abstract** A series of Ti/Mg supported catalysts are prepared by using ball-milled mixtures of  $\text{MgCl}_2$ -ethanol adducts and NaCl as supports, and 1-hexene polymerizations catalyzed by the novel catalysts are studied. It is found that the molecular weight distribution of poly(1-hexene) becomes apparently narrower when catalysts with doped supports are used, indicating that changing the structure of the support is an effective way to regulate the active center distribution of heterogeneous Ziegler-Natta catalyst.

**Keywords** Ziegler-Natta catalyst, Doped support, 1-Hexene polymerizations

### INTRODUCTION

The molecular weight distribution (MWD) of polypropylene (PP) plays an important role in determining the processibility and material performance of PP. The polyolefins prepared by Ziegler-Natta catalysts usually have broad MWD. Keii *et al.* attributed this to the non-uniformity of physical or chemical properties of the catalyst surface<sup>[1]</sup>. Auriemma *et al.* reported that the active sites of supported Ziegler-Natta catalysts were produced at the few defects on the surface of  $\text{MgCl}_2$ <sup>[2]</sup>, and the kinds of active sites and the properties of each kind are usually invariable, because they were determined by the surface properties of  $\text{MgCl}_2$  crystal<sup>[3]</sup>. From the above points of view, we attempted to change the surface character of  $\text{MgCl}_2$  crystal by doping NaCl into  $\text{MgCl}_2$ , with the aim of controlling the polyolefin's MWD. 1-Hexene has been used as the monomer because its polymerization is less influenced by diffusion limitation than that of propylene<sup>[3]</sup>. The results of propene polymerization, which may be different from those of 1-hexene systems, will be discussed in the following study. Fregonese and Garoff *et al.* reported the method of doping inorganic compounds, but they didn't pay attention to the control of polymer molecular weight distribution in their work<sup>[4, 5]</sup>.

Many methods and models have been reported for the study of the surface of Ziegler-Natta catalysts and their active sites. Seong *et al.* applied TPD (temperature-programmed desorption) to investigate the surface structure of  $\text{TiCl}_x/\text{MgCl}_2$ <sup>[6]</sup>. They concluded that the minor site was tentatively attributable to a coordinative unsaturated site at the basal plane boundaries or defects on supports<sup>[6]</sup>. Mauro *et al.* studied the micro kinetics of ethylene polymerization by heterogeneous Ziegler-Natta catalysts and proposed a model for the active sites<sup>[7]</sup>. Cavallo *et al.* reported chain propagation and termination models<sup>[8]</sup>. The distribution of active sites in heterogeneous Ziegler-Natta catalysts have been studied on the basis of non-linear fitting of MWD curves<sup>[3, 9, 10]</sup>.

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\*\* Corresponding author: Zhi-qiang Fan (范志强), E-mail: fanzq@zju.edu.cn

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## EXPERIMENTAL

### Catalyst Preparation

The preparation of catalyst was according to the patent<sup>[11]</sup>. 5 g supports were placed in a three-neck flask; about 50 mL titanium tetrachloride was injected into the flask, under stirring. Then the temperature was raised to 80°C in 10 min and 0.6 mL di-*n*-butyl phthalate (DNBP) was injected, the temperature raised to 130°C and kept there for 2 h. Then the system was cooled to 60°C, the temperature kept stable, the liquid was siphoned off and the remaining solid was washed. Next, the same volume of titanium tetrachloride was injected for a second time, and the system kept at the same temperature for the same time as in the first step. Finally, after cooled, washed and vacuum dried, the catalyst powder was transferred into a glass bottle, sealed off, and stored in an icebox.

### 1-Hexene Polymerizations

1-Hexene polymerization was carried out in 100 mL Schlenk flask that was immersed in a 50°C oil-bath. 50 mL petroleum ether was injected into the dried Schlenk vessel protected by argon, then 5 mL monomer and a certain quantity of co-catalyst were injected into the bottle in turn and, after magnetic stirring for 3 min, the catalyst was added and the reaction was started. The reaction was terminated after 30 min, and the polymerization solution was poured into 200 mL industrial alcohol with 1 mL hydrochloric acid. The polyhexene was precipitated, washed and vacuum dried at 50°C, weighed and stored in desiccator.

### Measurement

Poly(1-hexene) was tested by Gel Permeation Chromatography (GPC) to characterize molecular weight and MWD. A Waters 150C instrument with 103-105 ultra-styragel columns was used, with tetrahydrofuran (THF) as solvent at 30°C. The universal calibration method was used to calculate the MWD data based on polystyrene standards.

## RESULTS AND DISCUSSION

The MgCl<sub>2</sub>-ethanol adducts were prepared and ball-milled with certain amount of NaCl to make a series of supports. The doped supports were examined by X-ray diffraction (XRD) and several kinds of mixed crystals were found in the doped compound, as reported in a previous paper<sup>[12]</sup>. Superfluous titanium tetrachloride was used to react with supports and a series of catalysts were prepared<sup>[12]</sup>. Then the prepared catalysts, with aluminum triisobutyl as co-catalyst, were used to catalyze the 1-hexene polymerizations. GPC was applied to examine the molecular weight distribution of poly(1-hexene). The MWD curves were non-linearly fitted utilizing multiple Flory functions to obtain information like the number of active center types and their distribution<sup>[3, 9, 10]</sup>.

Table 1 lists the molecular weight, polydispersity index (PDI) and catalyst efficiency data of the polymers prepared with catalysts having different NaCl content. The number of Flory components obtained in the non-linear fitting of MWD curves is also listed. It is shown that doping of the support resulted in an increase in the molecular weight of poly(1-hexene). Meanwhile the PDI decreased obviously with the doping of support.

**Table 1.**  $M_n$ ,  $M_w$ , and PDI of poly(1-hexene)

| NaCl dosage (wt%) | Activity ( $\text{g} \cdot \text{g}^{-1} \text{Ti} \cdot \text{h}^{-1}$ ) | $M_n \times 10^{-4}$ | $M_w \times 10^{-4}$ | PDI | $N^*$ |
|-------------------|---------------------------------------------------------------------------|----------------------|----------------------|-----|-------|
| 0                 | 459                                                                       | 4.0                  | 32.6                 | 8.2 | 3     |
|                   |                                                                           | 3.9                  | 32.3                 | 8.3 |       |
| 5.4               | 280                                                                       | 16.3                 | 55.3                 | 3.4 | 2     |
|                   |                                                                           | 16.0                 | 56.4                 | 3.5 |       |
| 11.8              | 236                                                                       | 16.2                 | 55.6                 | 3.4 | 2     |
|                   |                                                                           | 16.6                 | 55.8                 | 3.4 |       |
| 18.3              | 244                                                                       | 11.4                 | 45.2                 | 4.0 | 2     |
|                   |                                                                           | 10.9                 | 45.3                 | 4.2 |       |

\* $N$  is the number of peaks obtained in non-linear fitting of MWD.

Figure 1 shows the MWD curves and the results of Flory function fitting for the poly(1-hexene) samples. The only difference among the four samples is the dosage of NaCl in catalysts' supports, being 0, 5.4%, 11.8%

and 18.3%, respectively. The MWD curve of the poly(1-hexene) prepared by the non-doped support catalyst is fitted by 3 peaks (Fig. 1a), showing that the catalyst system may have three types of active sites in 1-hexene polymerization, which are named as A, B and C. When the supports were doped, the number of Flory peaks decreased to 2 (Fig. 1b, Fig. 1c, Fig. 1d).

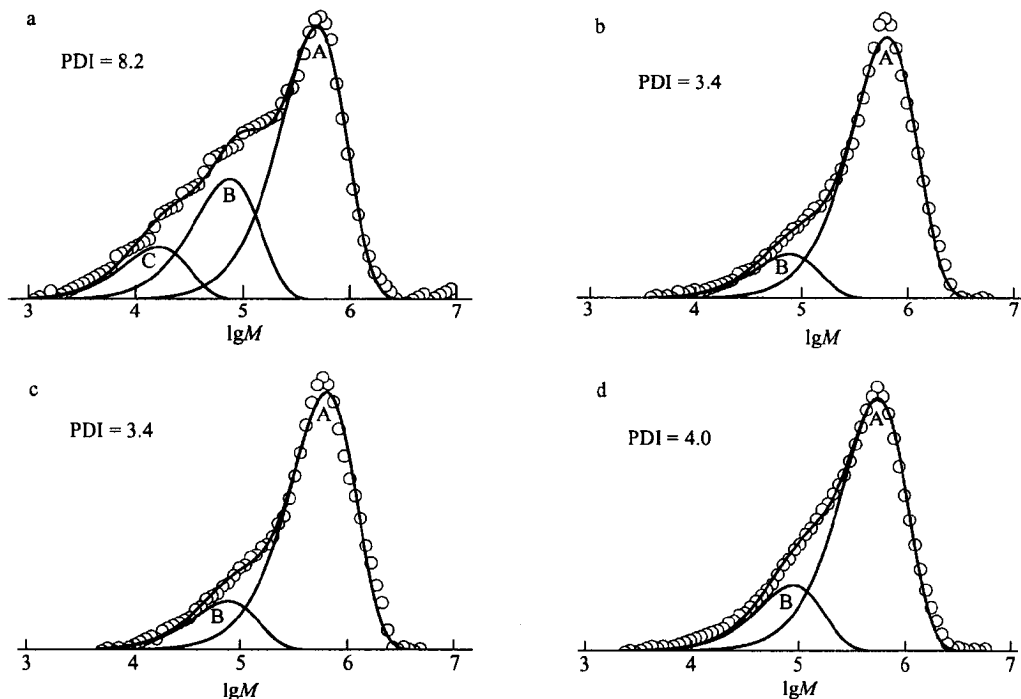
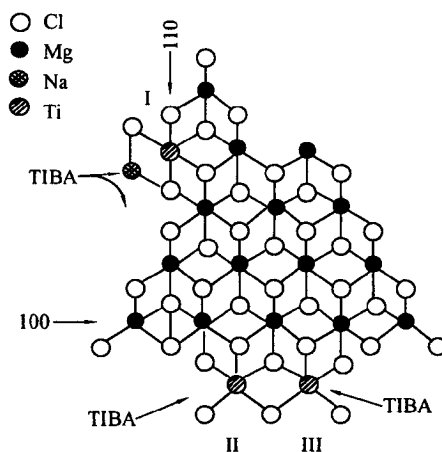


**Fig. 1** MWD and its Flory components of poly(1-hexene) synthesized using catalysts of different NaCl dosage  
NaCl dosage in support is 0, 5.4%, 11.8% and 18.3% (wt%) in a, b, c, d, respectively.

It is reasonable to say that the Flory components A, B and C represent three types of active centers<sup>[3]</sup>. Therefore, it is quite clear that doping NaCl into the catalyst caused complete deactivation of active center C and partly deactivation of center B. The polydispersity of the polymer is thus markedly lowered when doped catalyst is used. The MWD curves of poly(1-hexene) synthesized by the doped catalysts are actually very close to that of



**Scheme 1** The active site models of doped support catalyst

a real single site system, as more than 70% of the polymer has been produced by the active center A. Doping the catalyst support may become an effective way of regulating the active center distribution of heterogeneous Ziegler-Natta catalysts.

Based on the experimental data and the results of Flory function fitting of the MWD curves of poly(1-hexene), we proposed an active site model of the doped supported catalyst system, as shown in Scheme 1. Because mixed crystals were only found in supports with low NaCl dosage<sup>[11]</sup>, most part of the support is still  $\text{MgCl}_2$ . In this model, we think that a part of NaCl may combine with Ti species on the catalyst surface that is highly coordination unsaturated (surface site I in Scheme 1). This kind of surface site may form active center type C or B when NaCl is not present, but will be deactivated when NaCl blocks the site. On the other hand, the bi-titanium sites II and III may be more stable and have low tendency of combining with NaCl. This model can explain the lower catalyst efficiency and lower content of polymer produced by centers C and B when NaCl dosage in the catalyst increases.

In conclusion, doping with NaCl may cause selective deactivation of certain types of active center in the  $\text{TiCl}_4/\text{MgCl}_2$  type supported catalyst when TIBA is used as co-catalyst. Studies on the doping effects in polymerization systems with different monomers and different co-catalysts are underway.

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