

Control of the molecular weight distribution and tacticity in 1-hexylene polymerization catalyzed by $\text{TiCl}_4/\text{MgCl}_2\text{-NaCl/TEA}$ catalysis system

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Abstract

NaCl doped MgCl_2 supported TiCl_4 catalysts were used for 1-hexylene polymerizations in this paper. The catalysts' activity, the molecular weight distribution and the tacticity of polyhexylene are influenced strongly by the doping of NaCl in MgCl_2 , based on the polymerization experiment, the deconvolution analysis of molecular weight distribution (MWD) profiles and the ^{13}C NMR analysis. The results show that it is possible to control the active center distribution of supported $\text{TiCl}_4/\text{MgCl}_2$ catalysts by doping of support with NaCl .

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1. Introduction

MgCl_2 supported TiCl_4 catalyst is one of the most important catalysts for α -olefin polymerizations [1]. It is well known that the control of the molecular weight (MW) and molecular weight distribution (MWD) of polyolefin and the control of the tacticity of poly(α -olefin) are the most two important target of the study on the α -olefin polymerization [2,3]. Recently, several kinds of polyolefins that have controllable molecular weight distribution [4] or special tacticity [5] have been studied and reported, e.g., the syndiotactic polyolefin, which is used as elastic, is an important developing novel product [5]. However, as the molecular weight distribution controlling is a key factor in olefin polymerization [6–9], the studies should be carried on in detail and profoundly. There are several ways to control the molecular weight distribution of polyolefin, wherein doping of MgCl_2 is an effective means but not be reported so much

[10,11]. A series of novel catalyst supported by doped MgCl_2 (NaCl doped $\text{MgCl}_2\text{-C}_2\text{H}_5\text{OH}$ composite) have been prepared and characterized in our group [4,12]. There was a short communication had been published earlier by us, which reported the primary results of 1-hexylene polymerization catalyzed by the novel catalyst [13]. After that, we have made more detailed study on 1-hexylene polymerization with the novel supported catalyst, including the activity of the catalysts, the molecular weight distribution, and the tacticity of the polyhexylene. The results are very important for the more study about the active center distribution of the novel catalysts.

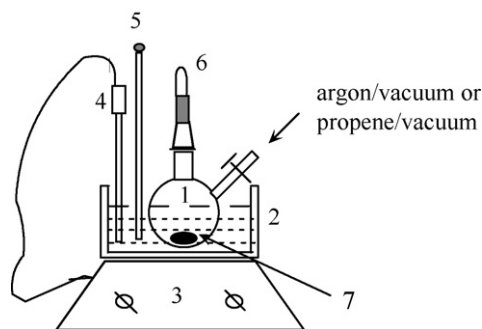
2. Experimental

2.1. Preparation of catalysts and polyhexylene

The preparation and characterization of the catalysts with doped MgCl_2 as support can be referred to the published literatures [4,11].

1-Hexylene polymerization was processed in the apparatus shown as Scheme 1. A clean and dried Schlenck bottle 1

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Scheme 1. The olefin polymerization apparatus. (1) Schlenk bottle; (2) oil bath; (3) heater and magnetic stirrer; (4) temperature sensor; (5) thermometer; (6) catalyst container; (7) rotator.

was set as Scheme 1, and then vacuumed and ventilated argon to remove the air in the bottle before added the chemicals. Next, 45 mL petrol ether, about 5 mL 1-hexylene and calculated quantity of co-catalyst solution were injected in turn. The apparatus 3 was magnetic stirrer with heater, the heater was powered on to keep the temperature of the oil bath 2 at 50 °C and the magnetic stirrer was turned on at a certain speed to mix the reaction agents homogeneously. After that, 20–30 mg catalyst was added and began to time as soon as possible. The polymerization was ended after 30 min and the polymer solution was poured into 200 mL isopropanol containing 2 mL HCl solution. The polyhexylene was precipitated and taken out, washed by ethanol and then dried in vacuum oven, weighed.

2.2. Calculation of activity of catalysts

The activity of the catalyst was calculated based on the equation below,

$$A = \frac{W_2}{W_1 Ti t};$$

wherein, A is the activity of catalyst, W_1 the weight of catalyst, W_2 the weight of polymer, Ti the titanium content of the catalyst that was determined in the past experimental [4], and t is the polymerization time.

2.3. Analysis of polyhexylene

Molecular weight and MWD of the polyhexylene samples were measured by gel permeation chromatography in a Waters 150C GPC instrument (Waters Co. Ltd., USA) at 30 °C in tetrahydrofuran. Three mixed columns (10^2 – 10^7) were used. Universal calibration against narrow polystyrene standards was adopted.

Polyhexylene's ^{13}C NMR analysis was performed on an Avance DMX500 NMR (Bruker Co. Ltd., Germany). Deuterium substituted chloroform (DCCl_3) was used as solvent, the relaxation time was 5 s and overlaid 1000 times in room temperature.

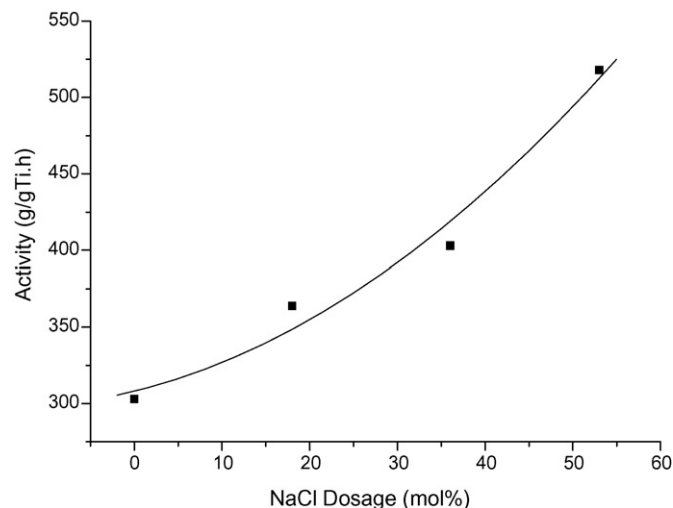


Fig. 1. The effect on 1-hexylene polymerization activity of NaCl dosage in the support of the doped-support catalyst as TEA was co-catalyst. Polymerization conditions: $[M] = 1 \text{ mol/L}$, m (catalyst) = 20–30 mg, $\text{Al/Ti} = 60$, $T = 50 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$, V (solvent) = 50 mL.

3. Results and discussions

3.1. The catalysts' activity

The catalysts' activity is influenced dramatically by the NaCl's dosage, as shown in Fig. 1. The samples in Fig. 1 were synthesized by MgCl_2 supported TiCl_4 catalysts in which MgCl_2 was doped with different content of NaCl, combining with triethyl aluminum (TEA) as co-catalyst. Fig. 1 showed that the catalysts' activity was almost linearly increased with the NaCl's dosage. Based on the study of our group [4,12–14], the doping of NaCl may generate more defects on the surface of MgCl_2 so that active centers can be formed more. Moreover, the Na^+ introduced by the doping of NaCl may affect the property of the active Ti^{n+} and improve its activity [15], that is to say, it is possible that the Na^+ change the electron effect of titanium ion combined with the defects on the surface of MgCl_2 , which is the active center of polymerization. Therefore, the catalyst's activity was increased with the increasing of the NaCl's dosage in MgCl_2 when TEA was used as co-catalyst. However, the property of the active center that resulted by doping of supports was still not well understood, it might be necessary to make more experiment or theoretical analysis.

3.2. The molecular weight and MWD of polyhexylene

The molecular weight and molecular weight distribution data of the polyhexylene prepared by the novel catalysts with TEA as co-catalyst were listed in Table 1.

It was shown in Table 1 that the average molecular weight of polyhexylene became less as the support MgCl_2 was doped by NaCl; in the case of the co-catalyst was TEA. The number average molecular weight was decreased from above 50,000 to below 30,000, and the weight average molecular weight was decreased from about 300,000 to about 200,000. The decreasing

Table 1
Molecular weight and PDI of polyhexylene obtained with doped-supported catalyst and TEA as co-catalyst^a

Dosage/mol%	$\bar{M}_n/10^4$	$\bar{M}_w/10^4$	PDI ^b
0	5.3	29.6	5.6
	5.1	29.7	5.8
18	3.1	20.4	6.5
	3.1	19.1	6.3
36	3.2	20.3	6.3
	3.2	20.5	6.4
53	2.6	20.9	7.9
	2.7	20.2	7.5

^a Polymerization conditions: $[M] = 1 \text{ mol/L}$, m (catalyst) = 20–30 mg, Al/Ti = 60, $T = 50^\circ\text{C}$, $t = 30 \text{ min}$, V (solvent) = 50 mL.

^b Polydispersity index, \bar{M}_w/\bar{M}_n .

rate of the former was a little larger so that the molecular weight distribution of the polymer (shown by polydispersity index, PDI) became a little wider along with the doping of MgCl_2 .

The molecular weight and the molecular weight distribution of polyhexylene were changed by NaCl doping of MgCl_2 . Those changes could be attributed to the influence of the NaCl doping in MgCl_2 on the combination of the titanium ion together with the MgCl_2 surface, just as the explanation of the change of activity in Section 3.1. It was probable that the doping of MgCl_2 formed some new active sites that produce low molecular weight polymer. Thus, the activity of catalysts was increased and the polymer's molecular weight was decreased along with the doping of NaCl into MgCl_2 . The molecular weight distribution demonstrated the active center distribution in Ziegler-Natta polymerizations based on many studies before [1,4–7]. It can be

inferred that the active sites of the novel Ziegler-Natta catalyst were changed very much by the doping of MgCl_2 . More study about the new active center's property might be necessary to be carried on in detail.

3.3. The non-linear fitting of the MWD profiles of polyhexylene

The multiple most probable distribution functions (Flory functions) were adopted to deconvolute the MWD profile of the polyhexylene, in order to get a more review of the distribution rule of the catalyst's active center. The basic theory of the deconvolution of the MWD profile is: the MWD of the polymer produced by one kind of active center in Ziegler-Natta polymerization is accord with Schulz-Flory distribution, and the distributing index is 2, thus the MWD of the polymer produced by multiple active center catalyst is superposition of the distribution of each kind of active center [16]. Therefore, the distribution index of each component deconvoluted by the Flory function is 2, the number of peaks denotes the species of active centers and the peak height proportion denotes the relative weight of the polymer produced by each kind of active centers. It has been proved in previous works that deconvolution of polymer MWD by multiple Flory functions is an effective method to study the active center distribution of catalyst [6,16].

Fig. 2 is GPC curve of polyhexylene samples and their deconvolutions, which were produced by NaCl doped supported catalysts with different NaCl dosage, in which TEA was used as co-catalyst. It is seen that all of the MWD curves are deconvoluted into four Flory components, excepting the sam-

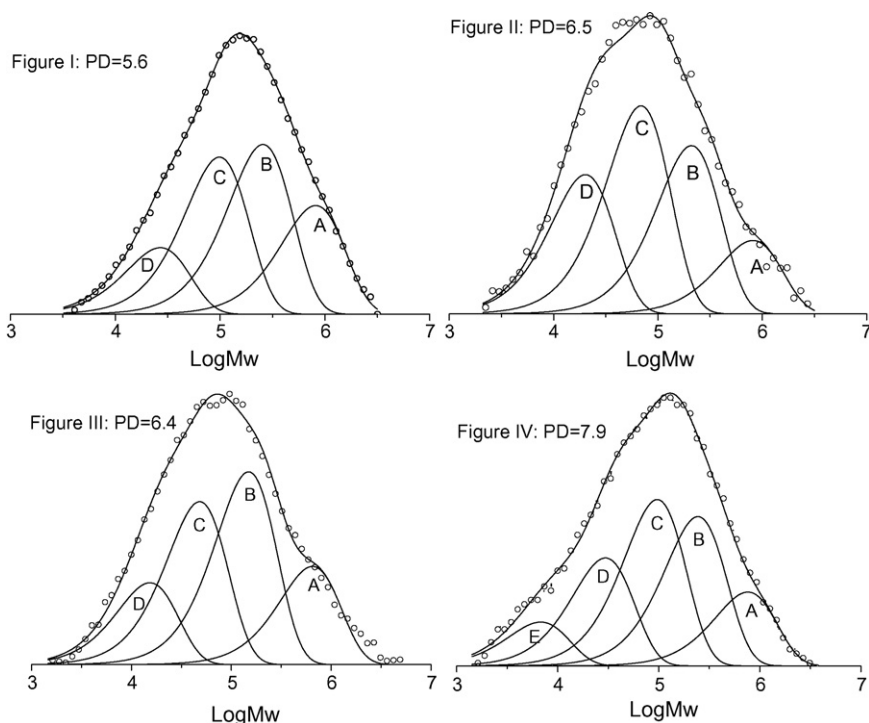


Fig. 2. MWD of polyhexylene synthesized by different doping supports' catalysts with TEA as co-catalyst and the deconvolution results: the NaCl dosage in the support of the sample (I) is 0 and that of (II) is 18 mol%, of (III) is 36 mol% and of (IV) is 53 mol%, respectively.

ple synthesized by the catalyst with 53% NaCl, whose dosage is the most. Considering that the polymerization was conducted under mild conditions in solution, influences of diffusion limitation on MWD can be neglected, and each Flory component should correspond to polymer produced on a certain type of active center. Therefore, it is possible to deduce the distribution of active center and its changes by tracing the position and relative peak intensity of each deconvoluted Flory component. In Fig. 2 we can see that peaks A in samples synthesized by different catalysts are all located in the molecular weight range of 3×10^4 – 3×10^6 , peaks B in the range of 1×10^4 – 1×10^6 , peaks C in the range of 3×10^3 – 3×10^5 , and peaks D in the range of 1.5×10^3 – 1×10^5 . In the MWD curve of polymer from the catalyst with 53 mol% NaCl, there is a peak E which has the lowest molecular weight, in the range of 1×10^3 – 3×10^4 . Though the MWD of polymer samples differ a lot from each other, the average molecular weight of a certain peak (e.g., peak A) changes only a little. Variations in the position of the peak of the lowest molecular weight, i.e. peak D is larger, possibly because of its low intensity and high experimental error in this part of GPC curve. This may be taken as evidence that all the peaks A in Fig. 2 represent a certain type of active center (center A); all the peaks B represent the B type center, and so on. The differences between MWD of different samples seem to be the results of changes in active center distribution, namely, change in relative intensity of different peaks.

Moreover, we can get a deeper insight into the effect of NaCl doping treatment on active center distribution of the catalyst using in hexylene polymerization, which is very different from propylene polymerization [4]. Comparing to the undoped catalyst, the distribution of active center was not broadened at relatively low NaCl content as much as in propylene polymerization (the polydispersity index is as high as 13.1 as the NaCl dosage is just 16 mol% in propylene polymerization [4]). The polydispersity index was increased from 5.6 to 6.5 as the dosage was raised from 0 to 18 mol%, while it was hardly changed when the dosage of NaCl was raised from 18 to 36 mol%. However, the polydispersity index was increased to 7.9 as the dosage was as high as 53 mol%. It was more important that a new Flory component appeared that was the peak E in Fig. 2IV. It showed that a new kind of active center appeared as the NaCl dosage was 53 mol%, furthermore, the hexylene polymerization catalyzed by the new active center produced the lowest molecular weight polymer, thus the MWD was broadened.

3.4. The tacticity of polyhexylene

The ^{13}C NMR of polyhexylene was adopted to characterize the tacticity, which the isotactic pentad (mmmm) content in C3 methylene could be calculated based on the NMR [17]. The ^{13}C NMR of polyhexylene synthesized by different doping supports' catalysts with TEA as co-catalyst is shown in Fig. 3. The NaCl dosage in support used in each samples is 0.18 and 53 mol%, respectively.

From Fig. 3 it can be seen that six C atoms exist in all of three samples, and the chemical shift of each is very similar, which can be corresponding to the six C atoms in hexylene structural

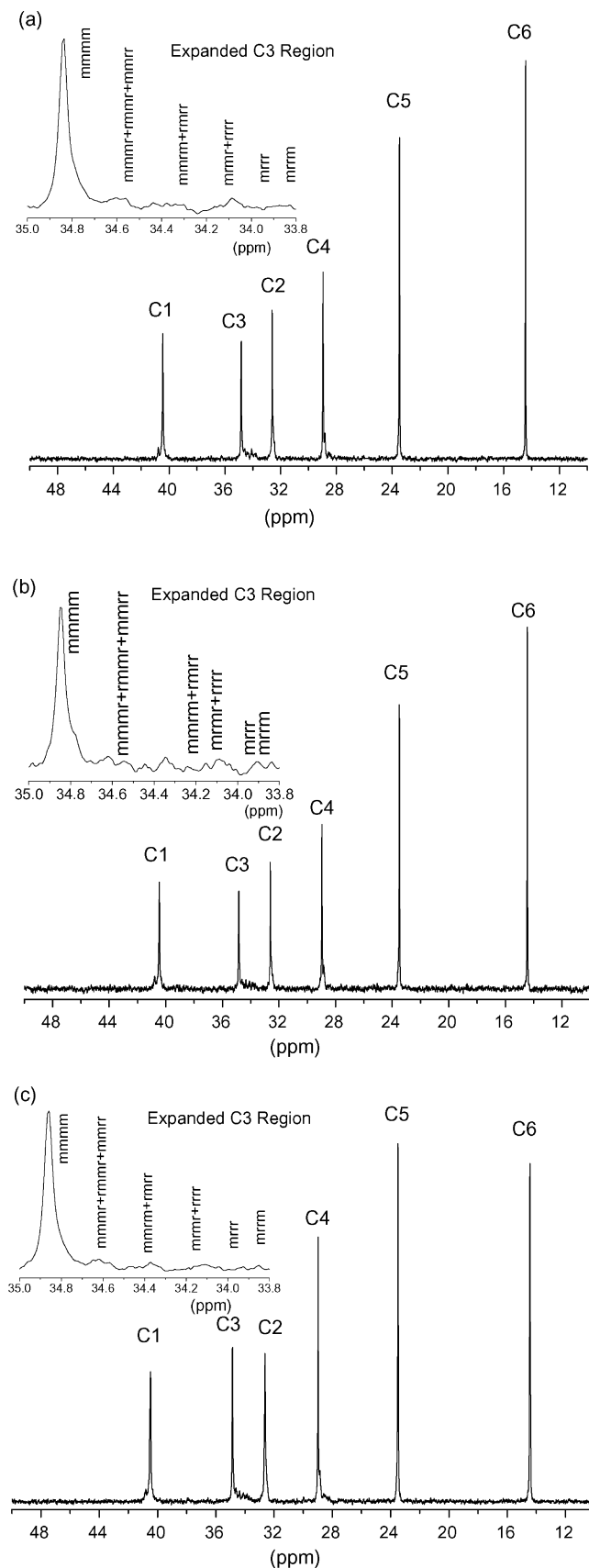
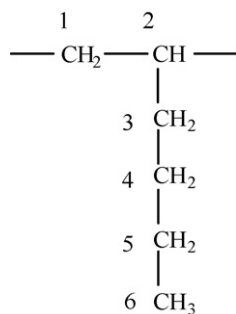


Fig. 3. The ^{13}C NMR of polyhexylene synthesized by different doping supports' catalysts with TEA as co-catalyst. The NaCl dosage in support is: (a) 0 mol%; (b) 18 mol%; (c) 53 mol%, respectively.



Scheme 2. The structure of C1–C6 in hexylene structural unit.

Table 2
The isotactic pentad (mmmm) content in C3 methylene region

NaCl dosage (mol%)	mmmm content (weight%)
0	61.1
18	59.4
53	55.6

unit [18–20], in which the chemical shift (δ) is 40.5 ppm is C1, and so on (see Fig. 3). The C1–C6 are shown in Scheme 2.

There is an expanded spectrum of C3 methylene region in Fig. 3 a–c. The character of the pentads can be seen clearly, in which the isotactic pentad “mmmm” is located at 34.7 ppm, the “mmmr + rmmr + mmrr” is at 34.5 ppm, the “mmrm + rmr” is at 34.3 ppm, “mrmr + rrrr” is at 34.1 ppm, the “mrrr” is at 34.0 ppm and “mrrm” is at 33.9 ppm, and so on [21]. The isotactic pentad content was calculated and shown in Table 2. It can be concluded easily that the isotactic pentad content was decreased with the doping of the supports, which showed that the doping decreased the tacticity of the polyhexylene. It is mostly because that the new active center formed by the doping of the NaCl catalyze hexylene polymerizing and forming polymer with the lower tacticity, which was shown as E active center in deconvolution of MWD profile. Therefore, the NaCl’s doping could not only broaden the molecular distribution, but also raise the atactic structure polymer’s content.

4. Conclusions

Several MgCl₂-NaCl supported TiCl₄ catalysts (TiCl₄/MgCl₂-NaCl) with different dosage of the NaCl were applied to hexylene polymerization, with TEA as co-catalyst. The catalysts’ activity was increased with the rising of the dosage of

NaCl, while the polyhexylene’s molecular weight was decreased and the polydispersity index was enlarged. The tacticity of the synthesized polyhexylene was lowered down by the doping of NaCl into MgCl₂ as the catalyst’s support. The changes of the catalysis activity, the molecular weight distribution and the tacticity are just the phenomenon, which the essentially change could be attributed to the change of the active center distribution of the catalysts with the doping of NaCl in MgCl₂. It showed that the active center distribution of the doped supported catalysts could be changed by the dosage of NaCl. Therefore, the control of the active center distribution of TiCl₄/MgCl₂-NaCl/TEA catalytic system in 1-hexylene polymerization has been realized.

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