

Propylene polymerization catalyzed by novel supported titanium catalysts $\text{MgCl}_2/\text{NaCl}/\text{DNBP}/\text{TiCl}_4$ with different NaCl content

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Abstract

A series of $\text{MgCl}_2/\text{NaCl}/\text{ID}/\text{TiCl}_4$ type supported catalysts were prepared by comilling NaCl with $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct and reacting the mixture with TiCl_4 and internal electron donor (ID = di-*n*-butyl phthalate). Crystallites of NaCl were found in the doped catalysts as revealed by WAXD analysis. The NaCl doped catalysts showed lower catalytic activity and higher isospecificity in catalyzing propylene polymerization. There was a marked change of the molecular weight distribution (MWD) of polymer with NaCl content. Catalyst containing 16 mol% NaCl produced PP with much broadened MWD (PDI = 1.3) than the undoped catalyst when TEA was used as the activator, while the TIBA activated catalyst produced PP with much narrower MWD. The changes in catalyst's active center distribution were studied based on non-linear fitting of the polymer MWD curve by multiple Flory functions. Stereochemical structure of the polymer was studied by thermal analysis. Selective and reversible deactivation of active centers by Cl^- from NaCl is proposed to be the main reason for the observed changes in polymerization behaviors and polymer structure caused by doping NaCl in the catalyst.

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1. Introduction

After 50 years of studies on olefin polymerization catalyzed by heterogeneous Ziegler–Natta catalysts, the importance of further improving the catalysts and developing novel catalysts is still highly recognized. The multiplicity of active centers in heterogeneous Z–N catalysts [1], including the $\text{TiCl}_4/\text{MgCl}_2$ based high-yield supported catalysts, has become the main concern in today's study in the field, because great successes have been made in improving catalyst activity and controlling the morphology of the product particles [2]. In most cases, 3–6 types of active center can be identified in heterogeneous Z–N catalysts [3,4], each produces polymer

with molecular weight and chain structure different from the others. Many experiments show that the molecular weight distribution (MWD) and chain structure distribution of the polymer are mainly determined by the active center distribution (ACD) of the catalyst. As a series of important properties of the polymer are determined by its structure distribution, controlling ACD of the catalyst has become a great challenge and will significantly influence polyolefin production by the traditional Z–N catalysts [5]. In spite of many difficulties, the surface structures of MgCl_2 and ACD of the MgCl_2 supported catalyst have been studied by several approaches, including kinetic studies [6–9], XPS and temperature programmed desorption (TPD) studies [10–12] and deconvolution of polymer MWD by multiple Flory functions [3,4,13–15].

However, it is still difficult to regulate the ACD of a heterogeneous Ziegler–Natta catalyst, especially when the aim is to

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form a single-site catalyst. It has been found that the ACD can be influenced in a limited extent by changing the polymerization condition [13], changing the cocatalyst [16], and introducing internal or external electron donor to the catalyst system [15,16]. There are a few literatures reporting modification of $\text{TiCl}_4/\text{MgCl}_2$ based catalyst by doping inorganic compounds in the support, such as ZnCl_2 [17] and MnCl_2 [18]. A theoretical study on $\text{TiCl}_4/\beta\text{-MgCl}_2$ based catalyst [19] has also been reported. In these reported works, MWD of the polymer was not studied and regulation of ACD was not taken as the main task.

It was well recognized that the active centers of supported Z–N catalyst locate on different surface sites of the MgCl_2 crystallites, like cuts, edges, and surface defects. If the crystal structure of MgCl_2 is changed, the distribution of potential active sites will also be changed, and the ACD of the supported catalyst will be modified. Therefore, doping the catalyst support may become an effective way of regulating ACD. In this work, we have prepared a series of $\text{MgCl}_2/\text{NaCl}/\text{ID}/\text{TiCl}_4$ type supported catalysts, in which the MgCl_2 support was doped with different amount of NaCl [20,21]. The doping of NaCl into MgCl_2 was realized by ball-milling NaCl with $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct, the precursor of the support. Such a way of doping has not been reported before. The MWD of polypropylene (PP) produced by the catalysts was determined and the changes in ACD were studied based on non-linear fitting of the MWD curve by multiple Flory functions.

2. Experimental

2.1. Preparation of the catalysts

To prepare the $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct, anhydrous MgCl_2 (donated by a catalyst producer in Ningbo, China) and anhydrous ethanol (distilled and dried over 4A molecular sieve before use) in a molar ratio of 1:3 were added into a flask, and equal volume of dry petroleum ether was also added. The flask was then heated to 100–130 °C under magnetic stirring and protected by an atmosphere of argon, until MgCl_2 was completely dissolved. After the system was cooled to room temperature, the solvent and the remained ethanol was removed by evacuation. The dried adduct powder was sealed in a glass bottle and stored. By comparing the weight of adduct and the weight of MgCl_2 used, and assuming that no MgCl_2 is removed in the process of vacuum drying, it was found that the molar ratio of MgCl_2 to ethanol in the dried adduct is 1:2.65.

About 15 g adduct and a weighed amount of NaCl were sealed in a 120 ml ball-milling can containing 35 vol.% of steel balls of 10 mm and 5 mm diameters, and ball-milled for 24 or 72 h under a dry argon atmosphere. By changing the amount of NaCl, $\text{MgCl}_2 \cdot n\text{EtOH}/\text{NaCl}$ mixtures with different level of doping were prepared and used as catalyst support in the following steps.

About 4–6 g ball-milled $\text{MgCl}_2 \cdot n\text{EtOH}/\text{NaCl}$ mixture was added to a three-neck flask, and 50 ml TiCl_4 was injected into the flask at temperature lower than 10 °C under stirring. The temperature was then raised to 80 °C in 10 min, and 0.5–0.8 ml di-*n*-butyl phthalate (DNBP, distilled and dried over molecular sieve before use) was injected in. The temperature was then raised to 130 °C and maintained for 2 h. Then the flask was cooled to 60 °C. The liquid was siphoned off and the solid part was washed three times with petroleum ether. Then, a second batch of TiCl_4 (20 ml) was injected into the flask and stirred at 130 °C for 2 h. After the same cooling, separation and washing operations as before, the catalyst was vacuum dried to form a powder in gray color and stored under argon.

2.2. Analysis of the catalyst

The catalysts were analyzed by wide-angle X-ray diffraction (WAXD) in a Rigaku D/max 2550PC diffractometer with Cu K α target and 40 kV voltage. The catalyst powder was mounted on the sample holder in glove box and covered by a thin LDPE film during the analysis.

Morphology of the catalyst was observed by scanning electron microscope (SEM) in a Leika Cambridge S260 SEM. The samples were gold plated before analysis.

Ti content of catalyst was determined by conventional spectrophotometry method.

2.3. Propylene polymerization

A 100 ml Schlenk bottle, which was immersed in a 50 °C oil-bath, was evacuated and purged by argon for three times and then filled with propylene at 1 atm. 50 ml petroleum ether as solvent, a certain volume of cocatalyst ($\text{Al}(\text{C}_2\text{H}_5)_3$ (TEA) or $\text{Al}(i\text{-C}_4\text{H}_9)_3$ (TIBA)) and external donor ($\text{Ph}_2\text{Si}(\text{OCH}_3)_2$) in petroleum ether were added in that order under stirring. 40–50 mg catalyst was added into the flask after 1 min to start the polymerization. Propylene at 1 atm was continuously supplied into the flask to maintain a constant pressure. After 30 min, propylene was stopped and the polymerization slurry was poured into 200 ml ethanol containing 1 ml hydrochloric acid to terminate the reaction and settling down the polymer. The polymer particles were filtered, washed with ethanol and vacuum dried at 50 °C.

2.4. Polymer characterization

Molecular weight and MWD of the PP samples were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories Ltd.) at 150 °C in 1,2,4-trichlorobenzene. Three PL mixed B columns (500–10⁷) were used. Universal calibration against narrow polystyrene standards was adopted.

Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 thermal analyzer. The polymer (about 4 mg) was sealed in aluminum pan, which was then sealed in a glass tube at argon atmosphere. The glass

tube was immersed in an oil bath and heated to 180 °C, kept at that temperature for 30 min, and then annealed at 140, 130, 120, 110, 100, 90, 80, 70, and 60 °C, respectively, each for 12 h. The treated samples were then scanned in DSC from 50 to 180 °C at a heating rate of 10 °C/min.

The isotacticity index of PP was determined by extraction of the sample by boiling *n*-heptane in Kumagawa extractor for 12 h. The weight percentage of insoluble part was taken as the isotacticity index (I.I.). The soluble part was precipitated by pouring the heptane solution into excess of ethanol, and both the soluble and insoluble parts were collected for the DSC analysis.

3. Results and discussion

3.1. Characterization of the catalysts

By ball-milling the $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct with different amount of NaCl and using the $\text{MgCl}_2 \cdot n\text{EtOH}/\text{NaCl}$ mixture as the catalyst support, a series of NaCl doped Ti based supported catalysts were prepared. The Ti content of the catalysts was determined and listed in Table 1. It can be seen that most of the catalysts contain more than 3.5% of Ti, which is higher than the Ti content of similar catalysts prepared using ungrounded support. Increase in the surface area

Table 1
Titanium content of catalysts containing different amount of NaCl

NaCl content (mol%) ^a	Titanium content (wt.%)	
	24 h ^b	72 h ^b
0	5.5	5.4
16	4.7	4.9
29	3.5	5.2
48	3.8	4.5
61	2.5	4.2

^a Mole percentage of NaCl in the ($\text{MgCl}_2 + \text{NaCl}$) mixtures.

^b Time of ball-milling of the (adduct + NaCl) mixtures.

of the support by ball-milling may be responsible for this change.

When the ball-milling time was 24 h, introducing NaCl into the support caused a marked decrease in Ti content, while only slight decrease in Ti content is observed when the milling time is prolonged to 72 h. Because NaCl is not an effective support for anchoring TiCl_4 , it can be considered as a kind of inert filler in the catalyst, and only MgCl_2 act as the support for the Ti species. Taking this factor into consideration, the density of supported Ti on MgCl_2 was only slightly lowered by the doping treatment after 24 h of ball-milling, and even increased after 72 h of milling.

WAXD patterns of two NaCl doped catalysts and an undoped catalyst are shown in Fig. 1. In the WAXD of doped

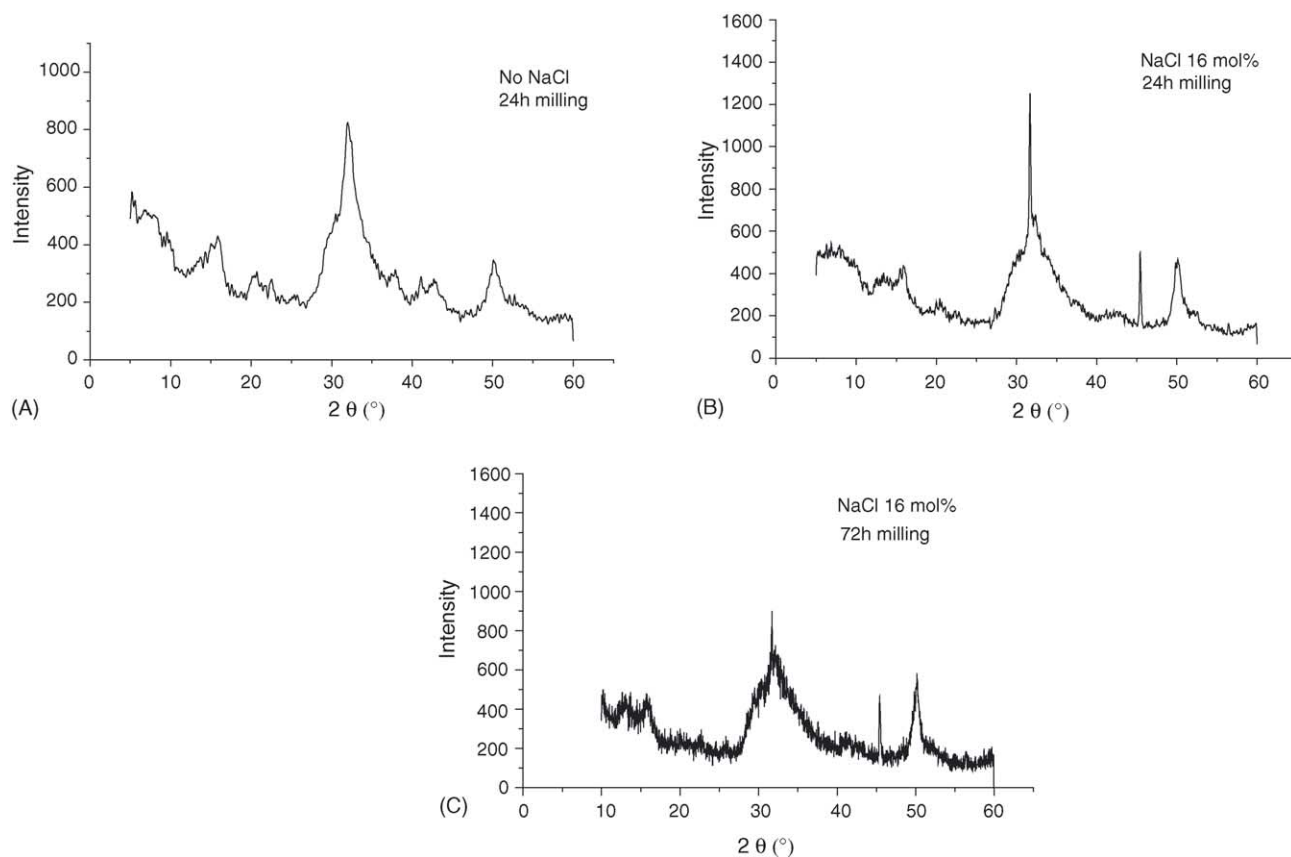


Fig. 1. WAXRD patterns of the catalysts without NaCl (A) and with doped NaCl (B, C).

catalyst with 16% NaCl, there are two sharp peaks at $2\theta = 31.7$ and 45.4° , respectively. These peaks correspond to the 2 2 0 and 2 0 0 planes of NaCl crystal [22]. However, the peak at 27.4° does not appear, which represent the 1 1 1 plane of NaCl and is a strong peak in pure NaCl. On the other hand, the strong “helo” appearing at $2\theta = 25\text{--}40^\circ$, which is characteristic of undoped MgCl_2 supported catalysts, keeps almost unchanged in the doped catalyst. Therefore, it appears that most of the NaCl is not dispersed in the lattices of MgCl_2 in isolated state, but exists in the form of crystallites. The disappearance of the peak of 1 1 1 plane may implies that there is strong interaction between the NaCl crystallites and the MgCl_2 crystallites. As compared to the doped catalyst with 24 h ball-milling, the doped catalyst prepared with 72 h ball-milled support showed much weaker peaks of the 2 2 0 and 2 0 0 planes of NaCl (see Fig. 1(C)). This means that long time of ball-milling may effectively reduce the size of NaCl crystallites, and seriously break up the lattice of a part of NaCl.

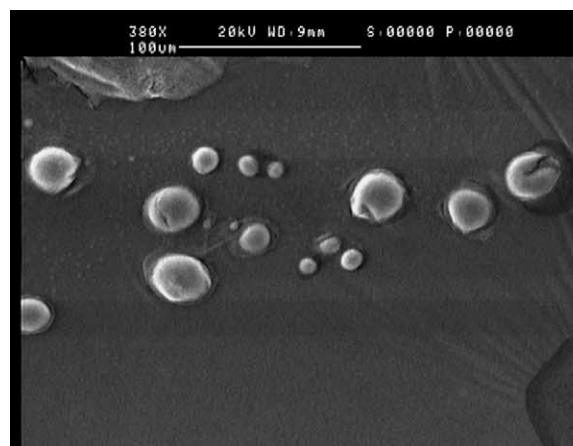
The morphology of both undoped and doped catalysts is shown in Fig. 2. Both catalysts show near-spherical particle shape and a relatively broad size distribution. The doping treatment exerted little influences on the catalyst morphology.

3.2. Propylene polymerization

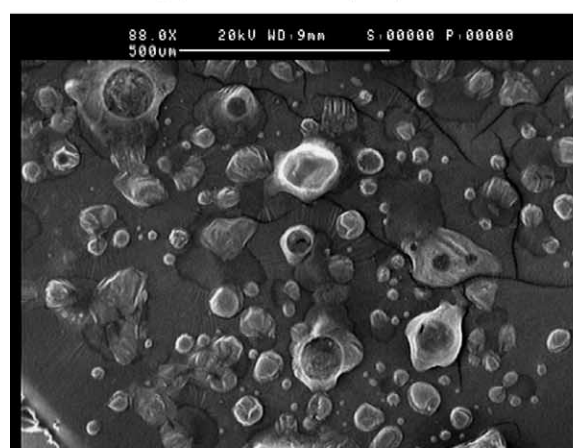
The NaCl doped catalysts were used in propylene polymerization activated by either TEA or TIBA, and the results are shown in Tables 2 and 3.

As shown in Table 2, when TEA was used as cocatalyst, the catalyst activity decreased with the increase of NaCl content. Comparing to the catalysts prepared by 24 h of ball-milling, catalysts of the same NaCl content and ball-milled for 72 h showed much higher activity based on catalyst weight (g/g cat h). However, when compare the activity based on Ti, the 24 h ball-milled series showed activity similar to the 72 h ball-milled catalysts, and even give higher value when the NaCl content is higher than 40%. The molecular weight of polymer produced by both the 24 h ball-milled and the 72 h ball-milled catalysts slightly increase with increasing NaCl content, while the polydispersity of polymer changes with NaCl content in a complicated way. Using the 72 h ball-milled catalysts, the polydispersity index rose at first with NaCl content and then decreased as NaCl further increased. The isotacticity of polypropylene also changed with NaCl content in a complicated way. When the ball-milling time was 72 h, the catalysts made from doped supports gave polymer with higher isotacticity than the catalyst without NaCl.

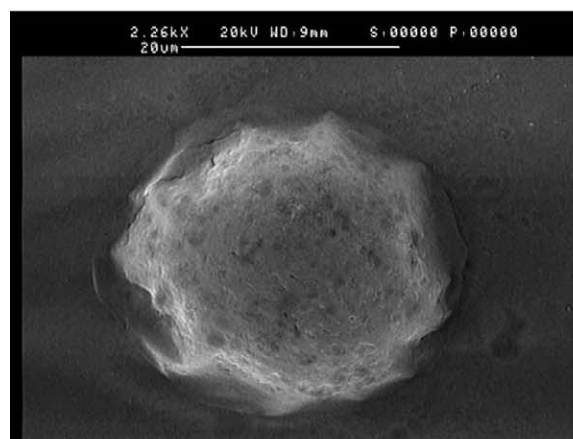
When TIBA was used as cocatalyst, the changes of polymerization activity with NaCl content looked similar to the situation in the TEA activated polymerization runs, but the molecular weight was much higher than the TEA series. There was a faster decrease of polydispersity index with increasing the NaCl amount. The change of molecular weight with NaCl% was also complicated. In these series the doping treatment also increased the isotacticity of polymer,



(A) NaCl content = 0 (x300)



(B) NaCl content = 16% (x88)



(C) NaCl content = 16% (x2260)

Fig. 2. SEM picture of catalyst particles without NaCl (A) and with doped NaCl (B, C) (72 h ball-milling).

though the isotacticity was lower than the TEA activated system.

From the above mentioned results it can be said that, doping NaCl in the catalyst caused decrease in activity, increase in polymer stereoregularity (especially when TIBA was used), and complicated changes in MWD.

Table 2
Results of propylene polymerization by catalysts with different NaCl content^a

Ball-milling time (h)	NaCl content (mol%)	Activity (g/g cat h)	Activity (kg/gTi h)	I.I. ^b (%)	$M_w \times 10^{-4}$	PDI ^c
24	0	179	3.2	90	18.4	11.3
	16	92	2.0	88	15.8	12.0
	29	40	1.1	88	19.5	9.6
	48	72	1.9	90	21.6	10.7
	61	76	3.1	92	25.0	8.5
72	0	163	3.0	92	18.8	10.1
	16	123	2.5	93	16.3	13.1
	29	121	2.3	94	22.4	7.9
	48	100	2.2	96	21.3	7.2
	61	65	1.6	94	18.6	7.6

^a Polymerization conditions: catalyst weight: 30–40 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 90, Si/Ti = 2, propylene pressure: 1 atm, solvent: petroleum ether (50 ml), temperature: 50 °C, time: 30 min.

^b Isotacticity index, percentage of boiling *n*-heptane insoluble part.

^c Polydispersity index (M_w/M_n) determined by GPC.

3.3. Influences of NaCl doping on the active center distribution

It has been proved in previous works that deconvolution of polymer MWD by multiple Flory functions [3,4] is an effective method to study the ACD of catalyst. In Fig. 3 the MWD curves and their deconvolution results of PP synthesized by TEA activated catalysts are shown. The time of ball-milling was 72 h.

It is seen that all the MWD curves are deconvoluted into five Flory components, excepting the sample synthesized by the catalyst with 16% NaCl. Considering that the polymerization was conducted under mild conditions, 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. 3 we can see that peaks A in samples synthesized by different catalysts are all located in the molecular weight range of 3×10^4 to 3×10^6 , peaks B in the range of 1×10^4 to 1×10^6 , peaks C in the range of 3×10^3 to 3×10^5 , peaks D in the range of 1.5×10^3 to 1×10^5 , and peaks E in the range of 5×10^2 to 2×10^4 . In the MWD

curve of polymer from the catalyst with 16% NaCl, there is a peak F which has the lowest molecular weight. 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 (see Table 4. Variations in the position of the peak of the lowest molecular weight, i.e. peak E are larger, possibly because of its low intensity and high experimental error in this part of GPC curve). This may be taken as an evidence that all the peaks A in Fig. 3 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 ACD, namely, change in relative intensity of different peaks.

On this basis, we can get a deeper insight into the effect of NaCl doping treatment on ACD of the catalyst. At relatively low NaCl content, the ACD was much broadened comparing to the undoped catalyst. Besides the newly emerged peak F, the intensities of peaks E and D also increased, and that of the peak C decreased after doping 16% of NaCl in the catalyst (see Fig. 3(2)). The polydispersity index was as high as 13.1. However, when the NaCl content was further increased, the peak F disappeared and the peaks E and D weakened again. The ACD of the catalyst looked similar to that of the undoped

Table 3
Results of propylene polymerization by catalysts with different NaCl content^a

Ball-milling time (h)	NaCl content (mol%)	Activity (g/g cat h)	Activity (kg/gTi h)	I.I. (%)	$M_w \times 10^{-4}$	PDI
24	0	203	3.7	76	39.7	7.4
	16	104	2.2	84	33.6	5.1
	29	49	1.4	83	34.7	5.0
	48	124	3.2	81	38.7	5.2
	61	84	3.4	80	44.8	5.5
72	0	190	3.5	81	38.4	8.6
	16	133	2.7	88	21.7	5.1
	29	73	1.4	90	25.4	6.1
	48	113	2.5	89	35.8	7.5
	61	79	1.9	94	49.3	5.6

^a Polymerization conditions: catalyst weight: 30–40 mg, cocatalyst: TIBA, Al/Ti (mol/mol) = 90, Si/Ti = 2, propylene pressure: 1 atm, solvent: petroleum ether (50 ml), temperature: 50 °C, time: 30 min.

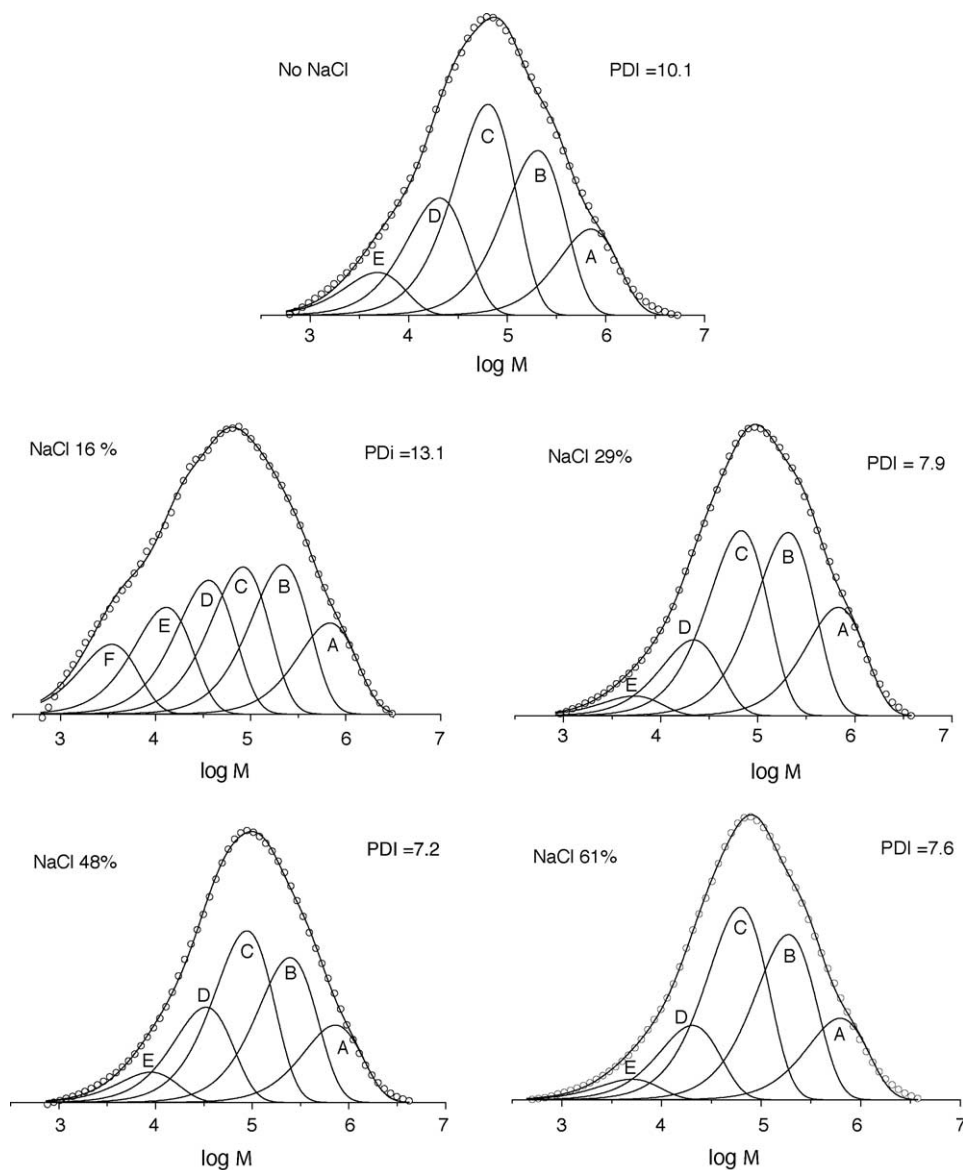


Fig. 3. MWD of PP synthesized with TEA as cocatalyst and the deconvolution results. (The PP samples are synthesized by catalysts treated by 72 h ball-milling. Circles: experimental data; lines: the Flory peaks and their sum.)

Table 4

Results of MWD deconvolution by multiple Flory peaks^a

NaCl content (mol%)	M_w of the Flory peaks ($\times 10^{-4}$) ^b					
	A	B	C	D	E	F
0	34.7 (14) ^c	10.0 (26)	3.14 (34)	1.02 (19)	0.24 (7)	–
16	33.7 (13)	10.8 (21)	4.10 (21)	1.79 (19)	0.64 (15)	0.17 (10)
29	33.2 (19)	10.1 (32)	3.33 (32)	1.08 (13)	0.27 (3)	–
48	35.6 (15)	12.1 (28)	4.33 (33)	1.64 (18)	0.44 (6)	–
61	30.7 (15)	9.29 (31)	3.06 (36)	1.01 (14)	0.25 (4)	–

^a Polymerization conditions of the PP samples are the same as Table 2. Catalysts prepared by 72 h ball-milling are used, and TEA is the cocatalyst.

^b Weight average molecular weight of the deconvoluted Flory peaks A, B, C, D, E, F.

^c Data in each parentheses are the percentage of peak area in the whole MWD peak.

system (Fig. 3(3–5)). This means that the doping treatment can change the ACD of catalyst, but the mechanism must be rather complicated.

Fig. 4 shows the MWD curves and the deconvoluted Flory components of the polymer synthesized by TIBA activated catalysts. It can be seen that the ACD of the undoped catalyst is quite similar to that of the same catalyst activated by TEA, meaning that influences of cocatalyst on the ACD of undoped catalyst is rather limited. However, when 16% of NaCl was doped in the catalyst, there was a great difference in ACD between the TEA activated system and TIBA activated system. After analyzing the deconvolution results (see Fig. 4 and also Table 5), a working hypothesis is proposed, that is: though the average molecular weight of a certain Flory component in TIBA activated system was higher than that of

the corresponding Flory component in TEA activated system, there is a close connection between the active centers in TEA activated catalysts and in TIBA activated catalysts. For example, the Flory component of the highest molecular weight in both series represents the same type active center, which may originate from the same type of surface site. The difference in molecular weight should be caused by the lower chain transfer constant of TIBA than TEA. Therefore, the Flory components in the TIBA series are named as A', B', C', and so on, implying that the active centers "I" and "I'" originate from the same type of active site.

Based on this hypothesis, we can find that the ACD of catalyst containing 16% of NaCl and activated by TIBA is much narrower than the TEA activated catalyst. Both the peaks A' and F' disappeared, and the peak E' became very small in

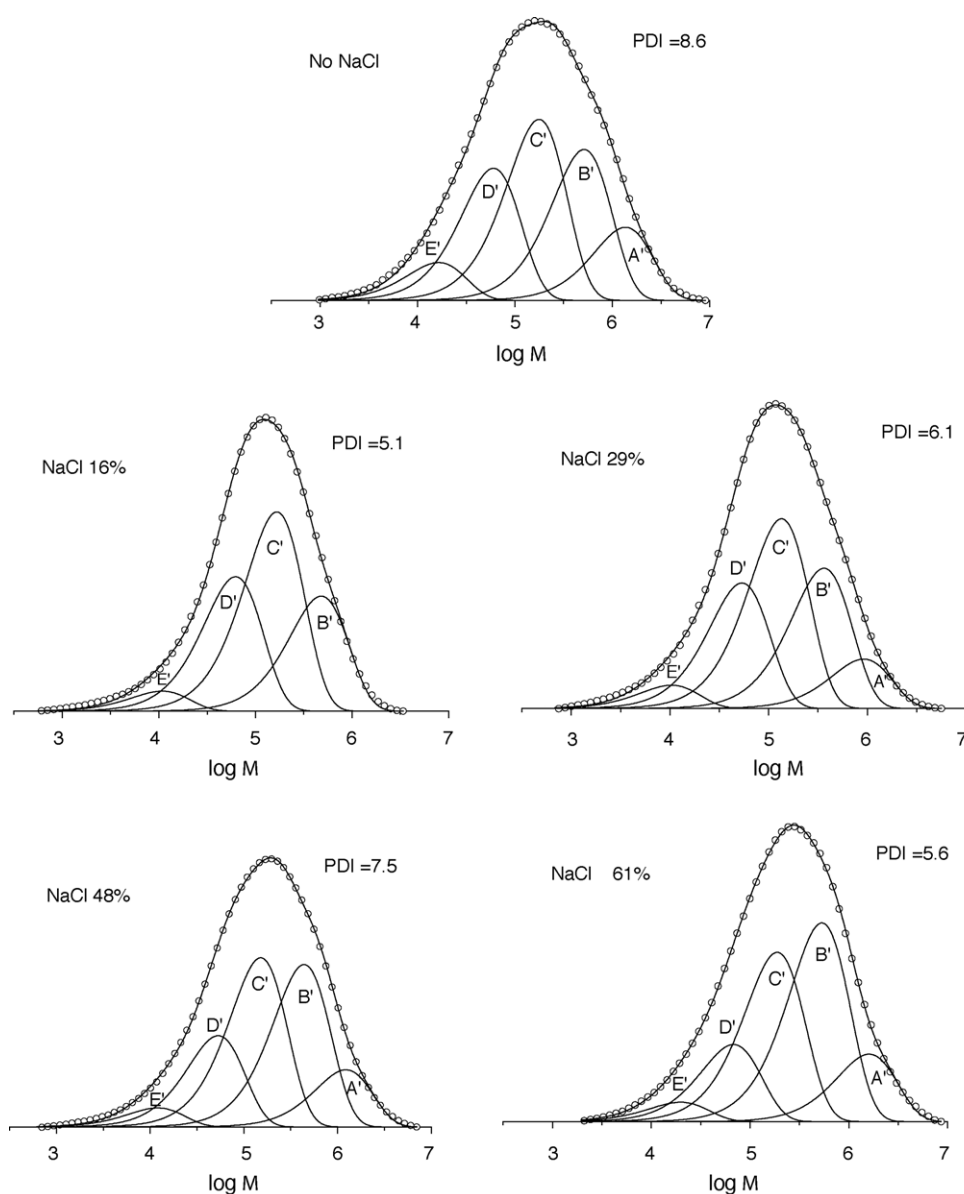


Fig. 4. MWD of PP synthesized with TIBA as cocatalyst and the deconvolution results. (The PP samples are synthesized by catalysts treated by 72 h ball-milling. Circles: experimental data; lines: the Flory peaks and their sum.)

Table 5
Results of MWD deconvolution by multiple Flory peaks^a

NaCl content (mol%)	M_w of the Flory peaks ($\times 10^{-4}$) ^b				
	A'	B'	C'	D'	E'
0	67.1 (13) ^c	25.3 (26)	8.74 (31)	2.98 (23)	0.81 (7)
16	–	23.6 (25)	8.19 (42)	3.07 (29)	0.53 (4)
29	45.0 (9)	17.9 (27)	6.66 (36)	2.65 (24)	0.51 (4)
48	60.2 (11)	21.6 (33)	7.46 (34)	2.62 (18)	0.59 (4)
61	78.7 (13)	26.3 (37)	9.28 (32)	3.35 (14)	0.98 (4)

^a Polymerization conditions of the PP samples are the same as Table 3. Catalysts prepared by 72 h ball-milling are used, and TIBA is the cocatalyst.

^b Weight average molecular weight of the deconvoluted Flory peaks A, B, C, D, E.

^c Data in each parentheses are the percentage of peak area in the whole MWD peak.

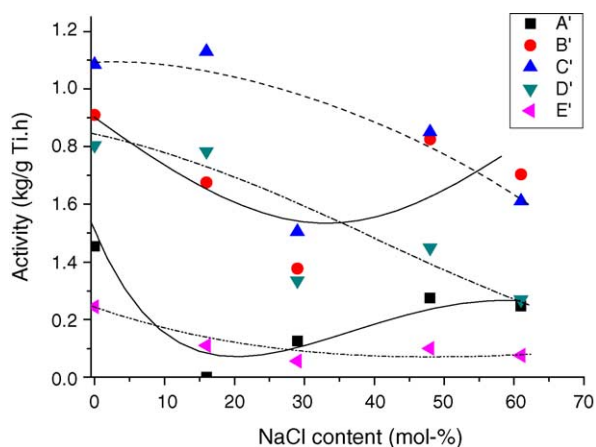


Fig. 5. Activity of five types of active centers calculated based on the polymerization activity and MWD deconvolution results. (The catalysts are treated by 72 h ball-milling. TIBA are used as cocatalyst. The polymerization conditions are the same as Table 3, and the MWD deconvolution results are listed in Table 5.)

the TIBA activated catalyst. This implies that in this catalyst the active centers A', E' and F' are highly sensitive to the cocatalyst. However, when the content of NaCl was further increased, peak A' appeared again and gradually increased with the NaCl content. There is also a gradual increase of peak B' with NaCl amount. Because there is a gradual decrease of catalysts efficiency with NaCl content (see Table 3), a more precise description should be: the activity of active center B' doesn't change much with NaCl content, but the activities of active centers C', D' and E' decrease markedly with NaCl content (see Fig. 5).

The active center distribution of doped catalysts made from 24 h ball-milled supports has also been analyzed using the same method. It was found that the changes of ACD with increasing NaCl content followed the same trend as in the series of 72 h ball-milling, but the extent of the changes was much smaller. This means that only 24 h of milling is not long enough to fully break up the NaCl crystallites and disperse them in the support. It can be assumed that, after 72 h of ball-milling the distribution of NaCl in the catalyst may be closer to the equilibrium state, and the effect of NaCl on the catalyst can be fully displayed.

3.4. Influences of NaCl doping on polymer structure

It has been shown in Tables 2 and 3 that doping NaCl in the catalyst resulted in increased isotacticity of the polymer. To further investigate the changes in microstructure of the product, both the boiling *n*-heptane soluble part and the insoluble part of the PP were analyzed by DSC thermal analysis. As described in the experimental part, samples for DSC analysis have been annealed in a stepwise mode under a series of temperatures to let the isotactic sequences crystallize and form crystalline lamella with different melting temperatures [23]. The DSC thermogram can thus reflect the distribution of isotactic sequences in the sample.

Fig. 6 shows the DSC thermograms of PP synthesized by the undoped and the NaCl doped catalysts activated by TEA. It is seen that using doped catalysts resulted in great increases in the area of melting peaks in the *n*-heptane soluble part, and appearance of a new endothermic peak at around 155 °C. The crystallinity calculated from the DSC data was greatly increased, as shown in Table 6. The DSC thermograms of the heptane insoluble part also changed with the NaCl content. A new peak at around 171 °C appeared in the samples synthesized by the doped catalysts, which existed only as a shoulder at 167.1 °C in the samples of the undoped catalyst. The crystallinity of the insoluble part is also increased by the doping treatment.

These results mean that, doping NaCl not only changed the isotacticity index, but also changed the stereochemical structure of all the polymer fractions. Because the soluble part from doped catalysts has rather high crystallinity but still high solubility, it should have a stereoblock structure, namely, there are alternatively connected isotactic and atactic sequences in the chains. This is much different from the almost completely atactic structure of the soluble part formed by undoped catalyst.

In Fig. 7 the DSC thermograms of polypropylene synthesized by TIBA activated catalysts are shown, and the data of crystallinity are listed in Table 6. It is clear that the stereosequence distribution of the soluble part was not changed much by the doping treatment, while the stereoregularity of the insoluble part was slightly increased. The formation of a new peak at 173.1 °C in the insoluble part implies that a little PP

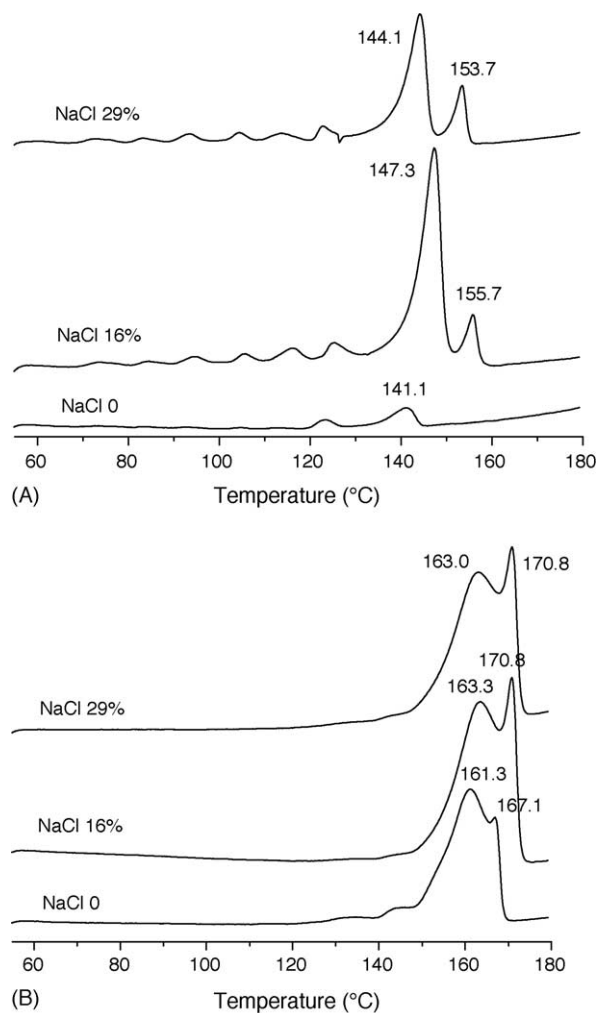


Fig. 6. DSC diagrams of the boiling heptane soluble (A) and insoluble (B) fractions. (The PP samples are synthesized by catalysts treated by 72 h ball-milling and activated by TEA.)

sequences of the highest isotacticity are formed in the doped system.

Based on these results, it is still difficult to draw unambiguous conclusions on mechanism of the doping treatment and structure of the active centers in the doped catalysts. However, it is possible to get some useful clues. At first, NaCl doped in the catalyst may be considered as a source of free Cl^- anions. These Cl^- anions from NaCl can occupy the vacancies on the surface of the MgCl_2 crystallites and reduce the number of undercoordinated Mg^{2+} , which provides the vacancy needed to form the active centers. This should be the main reason for the decrease of catalyst activity. The increase of catalyst stereospecificity may also be explained on this basis, as active sites with two vacancies are non-stereospecific, and blockage of one of the vacancies will convert the site into isospecific ones. On the other hand, the differences in chemical properties between TEA and TIBA should be noted. The higher Lewis acidity and lower bulkiness of TEA than TIBA let the former to be coordinated by Cl^- more tightly

Table 6
Thermal properties of the PP fractions^a

Cocatalyst	PP fraction ^b	NaCl content (mol%)	ΔH_f^c (J/g)	χ_c^d (%)
TEA	Soluble	0	8.3	3.5
		16	47.2	20.0
		29	36.9	15.6
	Insoluble	0	106.5	44.9
		16	117.2	49.6
		29	110.9	47.0
TIBA	Soluble	0	13.8	5.8
		61	6.5	2.8
	Insoluble	0	86.4	36.6
		16	71.3	30.2
		61	92.2	39.1

^a Polymerization conditions of the PP samples are the same as Tables 2 and 3. Catalysts prepared by 72 h ball-milling are used.

^b Soluble and insoluble fractions of PP obtained by extraction with boiling *n*-heptane.

^c Heat of fusion based on the sum of endothermic peaks in the DSC diagram.

^d Crystallinity (weight percentage of crystalline phase in the whole sample).

than the latter. Therefore, the free Cl^- anions from NaCl get high mobility with the help of TEA, as shown in the equilibrium:



The broadening of ACD in the TEA activated catalyst containing 16% NaCl can thus be understood, as a part of active sites previously occupied by the free Cl^- may be released by the complexation of Cl^- with TEA. When higher amount of NaCl was doped in the catalyst, the size of NaCl crystallites become larger. This change may reduce the number of free Cl^- , because Cl^- in the inner part of the NaCl crystallites cannot be easily released. Complexation of Cl^- with TEA can also result in the formation of steroblock PP chains. When a part of active centers with two vacancies are coordinated by one Cl^- , they will be still active and become isospecific. If the coordinated Cl^- is removed by TEA, the active center will become aspecific again. Fast equilibrium between two-vacancy state and one-vacancy state will result in steroblock propagation of the PP chains.

When the catalysts are activated by TIBA, because the complexation of TIBA with Cl^- is weak, the active centers occupied by Cl^- cannot be released in the polymerization process. This makes the ACD of doped catalysts narrower than the undoped one. However, the disappearance of active center A in the catalyst with 16% NaCl and its gradual recovery in the catalysts with higher NaCl content is difficult to understand. A tentative explanation is that, the size of the NaCl crystallites may determine the selectivity of Cl^- complexation. When NaCl aggregate into larger crystallites in the catalysts with high NaCl content, the formation of free

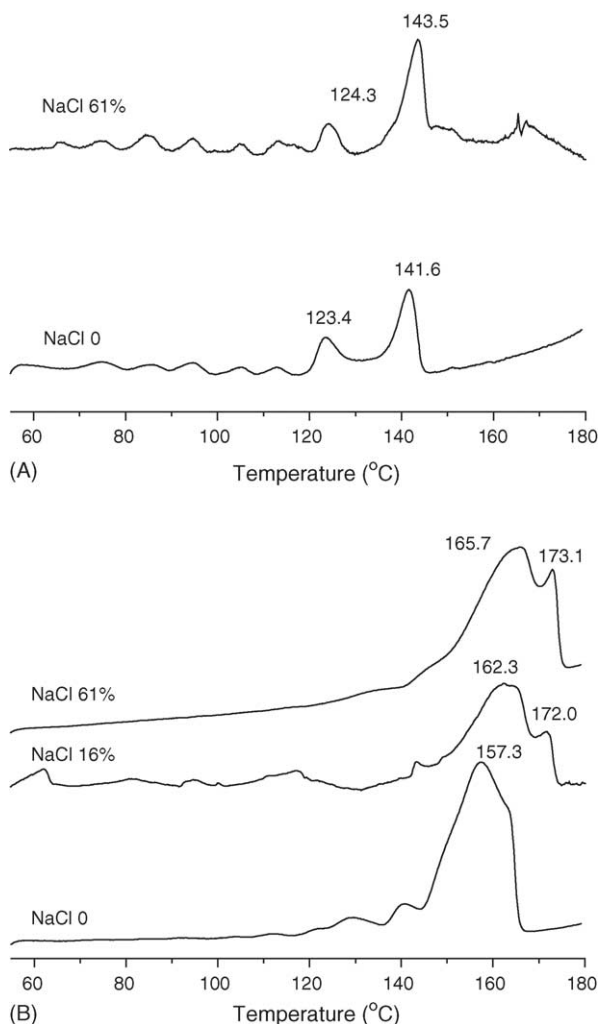


Fig. 7. DSC diagrams of the boiling heptane soluble (A) and insoluble (B) fractions. (The PP samples are synthesized by catalysts treated by 72 h ball-milling and activated by TIBA.)

Cl^- may be depressed. We have also noted that, in most cases increasing NaCl content resulted in deactivation of the active centers E and D. With TIBA as cocatalyst, the center C is also slightly deactivated. This means that the centers E, D and C have stronger tendency to be coordinated by Cl^- than the centers A and B. As reported in our previous work [4], active centers producing polymer of the highest molecular weight, namely, the A and B type centers, have the lowest concentration in the catalyst. They are likely located on the corners or edges of the MgCl_2 crystallites. Cl^- coordinated on these sites are therefore less stable. It seems that the center A' will not be deactivated when there are not enough free Cl^- (high NaCl content), but the center E' are easily deactivated when there are only a small number of free Cl^- .

In summary, the main roles of NaCl doped in the catalyst are to provide free Cl^- anions that can occupy vacancies on the catalyst surface and selectively deactivate a part of the active centers. Some of the active centers may be deactivated

reversibly. This will cause marked changes in ACD and the polymer chain structure.

4. Conclusions

A series of $\text{MgCl}_2/\text{NaCl}/\text{ID}/\text{TiCl}_4$ type supported catalysts were prepared by comilling NaCl with $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct and reacting the mixture with TiCl_4 . Crystallites of NaCl were found in the doped catalysts as revealed by WAXD analysis. The NaCl doped catalysts showed lower catalytic activity and higher isospecificity in catalyzing propylene polymerization. Molecular weight of the polymer decreased at first and then increased with the increasing of NaCl content. There was a marked change of MWD with the NaCl content. At NaCl content of 16 mol%, the MWD of PP was much broadened (PDI = 13) than the undoped catalyst when TEA was used as the activator, while the TIBA activated catalyst produced PP with much narrower MWD (PDI = 5). Selective deactivation of active centers by Cl^- from NaCl could be the main reason for the observed changes in polymerization behaviors and polymer structure caused by the doping treatment.

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