Formation Mechanism of Stereoblocks in Polypropylene Produced by Supported Ziegler−Natta Catalysts

Junting Xu,* Linxian Feng, and Shilin Yang

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: Stereoblock structures are found in the poly(propylene) fractions of low isotacticity produced by supported Ziegler−Natta catalysts. The influences of electron donors on the length of stereoblock and $AlEt_3$ on the isotactic index of polymer were investigated. The formation of stereoblock structures is correlated to the interaction between $AlEt_3$ and active sites. The nature of the active sites which produce different stereostructures and the reason that they can interconvert are explained with the concept of equilibrium. When electron donors are present in the catalysts, electron donors may exist in the environment of aspecific active sites and can be extracted by $AlEt_3$, and these reactions are reversible. In the case of catalyst containing no electron donor, $AlEt_3$ can complex with active sites, and there is an equilibrium reaction between monometallic and bimetallic active sites. These equilibrium reactions are responsible for the formation of stereoblock structures.

Introduction

Stereoblock polypropylene (PP), consisting of isotactic and atactic sequences, was first synthesized by Natta with a conventional titanium and vanadium catalyst.[1] Collette et al. obtained a similar polymer by using alumina-supported group IVB metal tetraalkyls as catalysts.[2,3] Another type of stereoblock PP, consisting of isotactic and syndiotactic sequences, was found by Busico in the pentane-soluble fraction produced by a $MgCl_2$-supported catalyst.[4] The amount of such a fraction increased when the cocatalyst AlR_3 was replaced with NaR.[5] Recently, we have found that stereoblock structures mainly exist in the fraction with low isotacticity.[6] It is generally believed that the interconversion of two kinds of active sites leads to the formation of the stereoblock structure,[7] but there is still no report on the nature of these active sites and the reason why these active sites can interconvert.

Both internal and external electron donors are necessary in supported Ziegler−Natta catalysts for propylene polymerization. It is widely accepted that the internal donor can be extracted by cocatalyst $AlEt_3$ to some extent, and there existed many equilibria in the heterogeneous catalytic system.[8,9] However, the influence of these equilibria on the microstructure of polymer has not been extensively studied.

Up to now, the studies on stereoblock structure and electron donors have been reported separately in the literature. In our previous work,[10] it was found that an electron donor can also be present in aspecific active sites. Therefore, we believe that there may be some relationship between the stereoblock structure and the electron donor. This paper is an attempt to correlate the effects of electron donors on the stereoblock structures.

Experimental Section

Preparation of Catalysts. The preparation of $MgCl_2$-supported catalysts has been described in refs 10 and 11. Under N_2 atmosphere, 1 g of anhydrous $MgCl_2$ and 6 mL of BuOH were added in 50 mL of *n*-octane. This suspension was heated to 80 °C and stirred until $MgCl_2$ was dissolved. The solution was then heated at 100 °C for 2 h after 50 mL of $TiCl_4$ was introduced. Subsequently, the resulting solid product was separated by filtration and was washed with *n*-octane. The internal electron donor (if needed) di-*n*-butyl phthalate (DNBP) was added at DNBP/Mg = 0.2 and stirred for 2 h. Then the suspension was washed and 50 mL of $TiCl_4$ was added again. After 2 h, the operations of filtration and washing were repeated.

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. $AlEt_3$ was used as cocatalyst and diphenyldimethoxylsilane (DPDMS) was employed as an external electron donor. Typical polymerization conditions were as follows: 100 mL of *n*-heptane, 30 mg of catalysts, $[AlEt_3]/[Ti] = 100$, $[Si]/[Al] = 0.04$, and polymerization temperature = 50 °C. The polymerization reaction was terminated by addition of ethanol containing HCl. The products were washed and filtered and then dried *in vacuo* at 80 °C overnight. Four catalysts were used for polymerization: $MgCl_2/TiCl_4-AlEt_3$(Cat-A), $MgCl_2/TiCl_4$/DNBP−$AlEt_3$(Cat-B), $MgCl_2/TiCl_4-AlEt_3$/DPDMS(Cat-C), and $MgCl_2/TiCl_4$/DNBP−$AlEt_3$/DPDMS (Cat-D). The corresponding polymer samples were A, B, C, and D.

Preparative TREF. Preparative TREF apparatus was used to collect a sufficient amount of polymer fractions. The polymers were dissolved in xylene at a concentration of 0.005 g/mL at 130 °C. This solution was deposited on an inert support, sea sand packed in a steel column. The column was cooled to room temperature at a rate of 1.5 °C/h. Then the deposited polymer was heated in incremental steps of temperature and eluted with xylene. The polymer fractions were recovered by evaporating the xylene solvent and drying in a vacuum oven. Because a small amount of antioxidant had been added, the total recovery of polymer was around 105%.

Extraction of PP. The polymers were extracted with boiling *n*-heptane in a Soxhlet extractor for 6 h. The weight percentage of the insoluble part was taken as the isotactic index. The absolute error of extraction is within ±1%.

NMR Analysis. ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 100.7 MHz in PFT mode at 370 K. The polymer solutions were prepared by dissolving ca. 50 mg of polymer in 0.5 mL of $C_6D_4Cl_2$. Then 1% hexamethyldisiloxane (HMDS) was added as internal reference. The pulse angle was 90°, the pulse repetition was 10 s, the spectral width was 5000 Hz, the number of scans was 6000, and the data points were 32K.

Results and Discussion

Extraction Results. The dependence of the isotactic index of PP on Al/Ti ratio is shown in Figure 1. It is

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Table 1. Pentad Distributions of the First Fractions and *n*-Heptane Soluble Fractions

polymer	mmmm	mmmr	rmmr	mmrr	mrmm + rrmr	mrmr	rrrr	rrrm	mrrm
A[a]	41.7	10.9	1.4	16.0	10.0	1.5	5.3	7.1	5.8
B[a]	33.7	8.1	3.9	13.8	17.2	2.4	8.9	4.3	7.7
C[a]	29.7	12.2	3.4	14.6	14.8	2.4	9.9	6.3	6.7
D[a]	22.9	12.5	2.7	16.3	14.1	2.7	10.3	9.9	8.6
A[b]	62.9	11.3	1.4	10.0	4.0	0.8	3.2	2.1	4.3
A[c]	68.2	9.3	0.8	9.1	3.2	0	2.9	2.2	4.1

[a] The first fraction obtained by TREF eluted at room temperature. [b] *n*-Heptane soluble fraction, Al/Ti = 50. [c] *n*-Heptane soluble fraction, Al/Ti = 150.

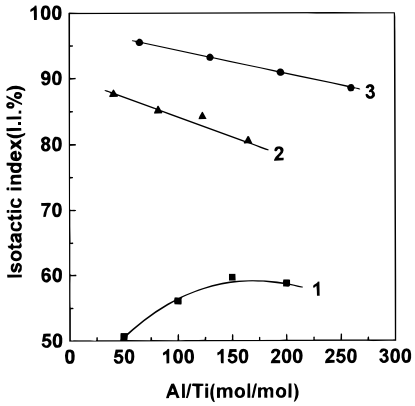

Figure 1. Dependence of isotactic index of polymers on Al/Ti ratio: (1) Cat-A; (2) Cat-B; (3) Cat-D.

found that when the catalysts contain an electron donor, the isotacticity of the polymer decreases with the increase of the Al/Ti ratio. Sacchi et al. measured the content of electron donors in the solid part of catalysts with GC and found that the internal electron donor can be partly removed by cocatalyst $AlEt_3$.[8] The polymerization results in the present work confirm this conclusion in a different way. Judging from the different slopes of two lines in Figure 1 (slope of line 3 < slope of line 2), one can see that introduction of an external donor in the catalyst can retard the declination of polymer isotacticity as the Al/Ti ratio increases. The external donor might influence the isotacticity in two ways: partial replacement of internal donor by the external donor on the catalyst surface as the former has been removed by $AlEt_3$ or complexation of external donor with $AlEt_3$ to reduce its ability to remove the internal donor. In contrast to the catalysts containing electron donors, the isotactic index of the polymer produced by the catalyst with no electron donor increases with the Al/Ti ratio. This indicates that $AlEt_3$ moieties are present in the environment of the active sites. A similar variation of isotacticity of PP with Al/Ti was observed by other authors.[9,12]

Microstructure of Polymers. As the stereoblock structure is mainly present in the fractions with low isotacticity, only the pentad distribution of the fist fractions obtain by TREF or *n*-heptane soluble fractions obtained by Soxhlet extraction are listed in Table 1. Common characteristics can be found for the catalysts containing electron donors in Table 1, that is, [*mmmm*] is larger than [*mmmr*] and [*rrrr*] is larger than [*rrrm*]. This is an indication of stereoblock structure. It should be noted that this stereoblock structure consists of isotactic and syndiotactic sequences,[4,5] instead of isotactic and atactic sequences.[1−3] If the presence of *mrrrm* is not considered, all the pentads *rrrm* should originate from $m(r)_n rrrm$ structures. In these structures, the ratio of [*rrrr*] to [*rrrm*] is 1:2 for $n = 1$, 2:2 for $n = 2$, 3:2 for $n = 3$, and 4:2 for $n = 4$.[6] Therefore, the average sequence length of racemic units in long racemic sequences can be estimated as

$$l(r) = 2[rrrr]/[rrrm] + 3 \qquad (1)$$

When the structure *mrrrm* is considered, the amount of *rrrm* resulting from $m(r)_n rrrm$ sequences should be less than the experimental [*rrrm*] value, then the actual average sequence length of racemic in long racemic sequences should be longer than what is estimated by eq 1.

Similarly, the average sequence length of meso units in long meso sequences can be estimated as

$$l(m) = 2[mmmm]/[mmmr] + 3 \qquad (2)$$

The values of $l(m)$, $l(r)$, and $l(m)l(r)$ of different catalytic systems are listed in Table 2. The product $l(m)l(r)$ is used to measure the total blockiness of the structure. It is found that electron donors can greatly influence $l(m)$, $l(r)$, and $l(m)l(r)$. In the catalyst containing only an internal donor, the value of $l(m)l(r)$ is the largest, while the value decreases drastically in the catalyst containing only an external donor, and it becomes the smallest when both internal and external donors are present in the catalyst.

By examining the reaction between $AlEt_3$ and the catalyst components, Sacchi et al. proposed some equilibrium reactions, shown in Scheme 1.[8] They suggested that electron donors coordinating with active sites could be removed by $AlEt_3$, but these reactions were reversible.

For a reasonable explanation of the influences of electron donors on the microstructure of atactic fractions, with a consideration of the previous finding that the electron donor may also be present in an aspecific active site,[10] we propose that the formation of the stereoblock structure is related to these equilibrium reactions. When the active sites supported on the (110) face of $MgCl_2$ do not interact with the electron donor, they possess more vacant sites and produce more *rrrr* structures. After these active sites have interacted with electron donors, because the resulted products are symmetric and nonchiral, they should be still aspecific.

Table 2. Estimation of the Average Length for Continuous *m* and *r* Sequences

	A	B	C	D
$l(m)$	10.65	11.32	7.86	6.66
$l(r)$	4.49	7.28	6.14	5.16
$l(m)l(r)$	47.82	82.4	48.26	34.36

Scheme 1. Equilibrium between $AlEt_3$ and Electron Donors

$$C^*\cdot IED + AlEt_3 \rightleftharpoons C^* + IED\cdot AlEt$$

$$C^*\cdot EED + AlEt_3 \rightleftharpoons C^* + EED\cdot AlEt$$

(C*: active site; IED: internal electron donor; EED: external electron donor)

Scheme 2. Equilibrium between Monometallic and Bimetallic Active Site

$$C^*\cdot AlEt_3 \rightleftharpoons C^* + AlEt_3$$

However, due to the presence of electron donor, they will be more steric and produce somewhat more *mmmm* structures. When these equilibrium reactions proceed on a time scale comparable with that of polymer chain growth, stereoblocks are formed. With the increase of the Al/Ti ratio, these equilibrium reactions shift to the right, and consequently the amounts both of the *n*-heptane soluble fraction and the *rrrr* structure increase.

If the internal donor in the active sites is removed, it is possible for the external donor to interact with the resulting active sites. This leads to decreased stereoblock structure.

The equilibrium between $AlEt_3$ and external electron donor in aspecific active sites was suggested by Pino et al.[13] Comparing the values of *l*(*m*)*l*(*r*), one can reach the conclusion that the external donor is not so easy to remove as the internal donor, which may result from its bulky groups and different functional groups for coordination.

In the catalyst A, in which there is no electron donor, the stereoblock structure is also produced in the first fraction. In comparison with other catalysts, its [*mmmm*] is larger and its [*rrrr*] is smaller. Since no electron donor is added in the catalyst, the formation of stereoblock structure in this polymer should have been proceeded by a different mechanism. Langer suggested that there were two kinds of active sites in the $TiCl_3$–$AlEt_3$ catalyst: one is the bimetallic complex of Ti^{3+} with $AlEt_3$, and the other is the monometallic active sites of alkylated Ti^{3+}.[14] He believed that these two kinds of active sites could interconvert and predicted the formation of the stereoblock structure. In the supported catalyst $MgCl_2/TiCl_4$–$AlEt_3$, a similar situation may occur (Scheme 2).

When active sites coordinate with $AlEt_3$, they are more steric and produce more *mmmm* structures, while more *rrrr* structures are produced by monometallic active sites. This mechanism leads to a different variation tendency of the isotacticity index with the Al/Ti ratio as compared to the catalysts containing electron donors. With the increase of the Al/Ti ratio, not only does the amount of *n*-heptane soluble fraction decrease but also [*mmmm*] in this fraction increases.

The equilibrium shown in Scheme 2 is in fact an equilibrium reaction between the bimetallic active site and the monometallic active site. In coordination polymerization, the nature of active site is still controversial. Cossee proposed a monometallic model,[15,16] while Natta believed that the active site was a bimetallic complex.[17] There are some evidences supporting both models. Judging from the polymer structure reported in this work, it is quite likely that there is an equilibrium reaction between the monometallic and the bimetallic active sites.

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