

SUPPORTED CATALYST WITHOUT EXTERNAL ELECTRON DONOR FOR PROPYLENE POLYMERIZATION II. TACTICITY DISTRIBUTION AND MICROSTRUCTURE OF POLYPROPYLENE*

XU Juntong (徐君庭) Feng Linxian (封麟先) Wang Senhui (王森辉)
and Yang Shilin (杨士林)

(Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China)

Abstract Propylene was polymerized with a novel supported Ziegler-Natta catalyst containing 2,2-di-iso-butyl-1,3-dimethoxy-propane (DIBDMP) as internal donor and in the absence of external donor. The tacticity distribution of polypropylene was obtained by using temperature rising elution fractionation (TREF) technique and microstructure of fractions was studied with ^{13}C -NMR. Compared with the catalyst without electron donor, this catalyst gives a considerably narrower tacticity distribution. Fractionation data demonstrate that DIBDMP shows better performance than aromatic diester DNBP (di-n-butyl phthalate). Chemically inverted propylene units and less stereoblockiness are found in the first fraction. Possible reasons for these were presented.

Keywords Polypropylene; Ziegler-Natta catalyst; Electron donor; Tacticity distribution

INTRODUCTION

Electron donors play an important role in supported Ziegler-Natta catalyst for propylene polymerization and the fundamental research on electron donors has led to the continuous development of it. Supported Ziegler-Natta catalyst is believed to undergo two stages based on the electron donors used. The catalyst in combination with ethyl benzoate as electron donor exhibits a high activity and a high stereospecificity^[1-2]. The use of phthalate and alkoxy silane compounds as an internal and an external donor, respectively, further enhance the activity and the stereospecificity of the catalyst^[3-4]. Recently, new classes of bifunctional donors such as 1,3-diethers and β -diketones have been synthesized and studied^[5-6]. When these compounds are used as internal donors, external donor is not needed. Some studies show that the O-O distance may be the key factor that influences the performance of these new electron donors^[7]. However, the effect of these compounds on the microstructure of polypropylene was rarely reported. In our previous

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work, when 2,2-di-iso-butyl-1,3-dimethoxy-propane (DIBDMP) was used as internal donor, highly isotactic polypropylene was produced by this catalyst in the absence of external donor, and the activity of this catalyst is comparable with that of the catalyst containing both aromatic diester as internal donor and siloxane compound as external donor^[8]. In the present paper, the obtained polypropylene was fractionated with preparative temperature rising elution fractionation (TREF) technique and the microstructure of polymer was investigated.

EXPERIMENTAL

Preparation of catalyst

The preparation of catalysts containing either DIBDMP or DNBP as internal electron donor was described in ref.[8,9].

Polymerization of propylene

Propylene polymerization procedure was described in ref.[9]. Typical polymerization conditions were: 100 ml of *n*-heptane, 30 mg catalysts, $[AlEt_3]/[Ti]=100$, $[Si]/[Al]=0.04$, polymerization temperature= 323 K.

Preparation TREF

Preparative TREF apparatus was used to collect plenty amount of polymer fractions. The polymers were dissolved in xylene to a concentration of 0.005 g/ml at 130°C, and 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%.

NMR analysis

¹³C 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 C₆D₄Cl₂. Hexamethyldisiloxane (HMDS) 1% 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 32 K.

RESULTS AND DISCUSSION

The TREF curves of polypropylenes produced by the catalyst containing DIBDMP as electron donor is shown in Fig.1. Since TREF method fractionated polypropy-

lene mainly according to its tacticity, the resulting TREF curve reflects the tacticity distribution of PP. From the shape of $W_i\%/\Delta T \sim T$ curve, one can see that, with the exception of the peak near 388 K, other peaks are not pronounced. This suggests that this sample has a relatively narrow tacticity distribution in comparison with that of polymer produced by the catalyst containing no electron donor^[10]. Some fractionation data of polymers produced by different catalysts are summarized in Table 1. The fractions eluted below 373 K is of low isotacticity and the fractions eluted above 373 K are generally believed to be produced by isospecific active sites^[11].

As shows in Table 1, DIBDMP decreases the amount of fractions with low isotacticity and increases the proportion of fractions with high isotacticity. It suggests that DIBDMP shows better performance than aromatic diester compound DNBP.

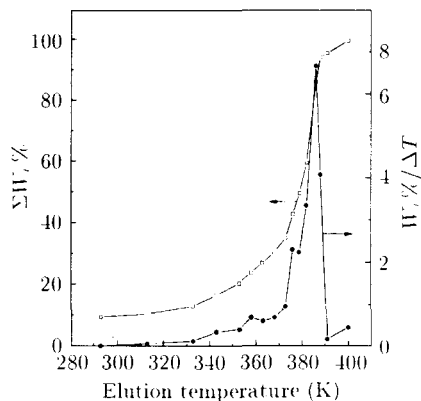


Fig.1. TREF curves of polypropylene prepared with $\text{MgCl}_2/\text{TiCl}_4$ /DIBDMP- AlEt_3 catalyst

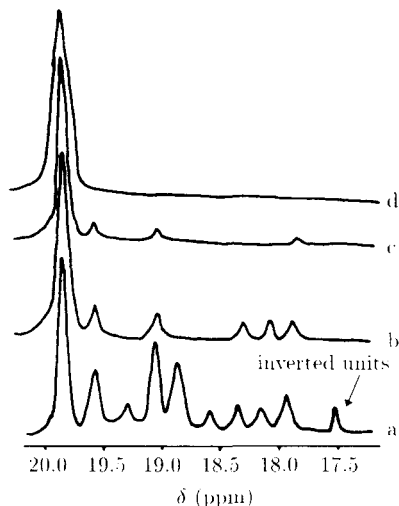


Fig.2 Expanded methyl region ^{13}C -NMR spectra of (a) fraction 1, (b) fraction 5, (c) fraction 10 and (d) fraction 14

Some fractions of this sample were selected for ^{13}C -NMR analysis. The expanded methyl region ^{13}C NMR spectra are shown in Figure 2 and pentad distributions are listed in Table 2. It can be seen that the isotacticity of fractions increases with the increase of elution temperature. This is in agreement with the conclusion that the fractionation is mainly based on tacticity^[11,12].

The first fraction contains mainly atactic polypropylene, for all pentads appear in Fig.2(a). In our previous work, we found that there existed stereoblock, which consists of in continuous *m* and *r* sequence, in the first fractions produced by supported Ziegler-Natta catalysts^[13]. The average length of continuous *m* and *r* sequence can be estimated from the following equations:

$$l(m) = 2[\text{mmmm}]/[\text{mmmr}] + 3 \quad (1)$$

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

(2)

Table 1 Fractionation data of PPs prepared by different catalysts

Internal donor	None ^{a)}	DNBP ^{b)}	DIBDMP ^{b)}
<i>m</i> dyad(%)	87.6	91.8	95.5
<i>W</i> ₁ %	15.27	9.74	9.37
Σ <i>W</i> _{<i>i</i>} % below 373 K	59.27	39.80	35.23
Maximal <i>W</i> _{<i>i</i>} %/Δ <i>T</i> near 376 K	1.87	1.98	2.29
Maximal <i>W</i> _{<i>i</i>} %/Δ <i>T</i> near 388 K	3.45	5.64	6.66

^{a)} neither internal nor external donor was added

^{b)} external donor was not added

Table 2 Pentad distributions of some fractions

Frac- tion	Elution temp.	<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mrmm</i> + <i>rrmr</i>	<i>mrmm</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrrm</i>	inverted units(%)
1	room temp.	22.4	19.5	3.9	16.9	15.6	2.9	3.0	3.3	6.7	5.6
5	353 K	71.5	8.8	0	4.9	0	0	4.6	4.9	5.3	0
10	373 K	92.8	2.9	0	2.9	0	0	0	0	1.4	0
14	388 K	~ 100	0	0	0	0	0	0	0	0	0

The product $l(m) * l(r)$ can be used to measure the blockiness of the first fractions. The values of $l(m)$, $l(r)$, and $l(m) * l(r)$ for the first fractions produced by the catalysts employing DNBP and DIBDMP as internal donor are listed in Table 3. It is found that the product $l(m) * l(r)$ is much lower when DIBDMP is used as internal donor, indicating that there is less blockiness in this fraction. Since the formation of stereoblock may be related to the removal of electron donor by cocatalyst $AlEt_3$ [13], we can reach the conclusion that DIBDMP is more difficult to be removed from the solid catalyst than DNBP. These results agree with the finding in our previous work that the declination of the isotacticity of products is the slowest when the catalyst only contains DIBDMP as internal donor, even in the absence of external donor[8]. A possible explanation is that the two steric iso-butyl groups in DIBDMP can prevent $AlEt_3$ from interaction with DIBDMP. This may be one important reason that explains why the catalyst can produce highly isotactic polypropylene in the absence of external donor. Since one of the roles of external donor is replacing the internal donor removed by $AlEt_3$, in the case of no removal of internal donor by $AlEt_3$ the amount of external donor needed is reduced, even external donor is not needed.

Table 3 Stereoblockiness in the first fractions of different samples

Internal donor	DNBP ^{a)}	DIBDMP ^{a)}
<i>l</i> (<i>m</i>)	11.32	5.30
<i>l</i> (<i>r</i>)	7.28	4.82
<i>l</i> (<i>m</i>) * <i>l</i> (<i>r</i>)	82.40	25.5

^{a)} external donor was not added

It is also found that there exists a small amount of chemically inverted units in the first fraction, which is similar to the first fraction produced by the catalyst containing bis(ethyl hexyl) phthalate as internal donor^[14]. The observation of inverted propylene units in the atactic fraction prepared with this catalyst system confirms our previous viewpoint that electron donor can also be present in the environment of aspecific active sites^[13,14].

The fraction eluted at 353 K possesses higher isotacticity than the first fraction, but it still contains a considerable amount of stereo-defects. Therefore it is also produced by active sites with less stereospecificity.

The fractions eluted at 376 K and 388 K are of high isotacticity, especially the fraction eluted at 388 K, which scarcely contains any chain defect. Thus, they may be produced by isospecific active site. Though, only a shoulder peak is observed in the $W_i\%/\Delta T \sim T$ curve of this polymer, there is an obvious peak in the $W_i\%/\Delta T \sim T$ curve of the polymer produced by the catalyst containing no electron donor. Kakugo et al. also suggested that there existed two kinds of isospecific active sites^[15]. Therefore, the fractions eluted at 376 K and 388 K may be produced by different isospecific active sites.

Since there is no chain defect in the fraction eluted at 388 K, no more information can be provided. From the structure of the fraction eluted at 376 K, the polymerization mechanism for the active site, which produces this fraction, can be inferred. Because four pentads *mmmm*, *mmmr*, *mmrr* and *mrrm* appear in its ¹³C NMR spectrum and the ratio of *mmmr* : *mmrr* : *mrrm* is 2 : 2 : 1, the chain propagation mechanism is active-site-controlled. If polymerization mechanism is chain-end-controlled, only three pentads *mmmm*, *mmmr* and *mrrm* should be observed in the ¹³C NMR and the ratio of *mmmr* : *mrrm* is 1 : 1^[16].

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