

EFFECTS OF EXTERNAL DONOR ON ACTIVE CENTER DISTRIBUTION OF SUPPORTED ZIEGLER-NATTA CATALYST

FAN Zhiqiang (范志强)*

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

M. Carmela Sacchi and Paolo Locatelli

(Istituto di Chimica delle Macromolecole, CNR, 20133 Milan, Italy)

ABSTRACT

The composition distribution (CD) and microisotacticity distribution (ID) of propene/1-hexene copolymer synthesized by $\text{MgCl}_2/\text{DIBP}/\text{TiCl}_4$ (DIBP: diisobutyl phthalate) were determined by fractionating the copolymers according to crystallinity and characterizing the fractions by ^{13}C NMR. The effects of two alkoxysilane donors, triethoxyphenylsilane (PTES) and dimethoxydi-tert-butylsilane (TBMS), on CD and ID of the copolymers were compared. Three main parts in the CD diagram of each copolymer were distinguished, which were correlated to active center distribution (ACD) based on three groups of different active centers. By studying the changes in 1-hexene content, microisotacticity and reactivity ratio product of three typical fractions, the effects of external donor on ACD were better elucidated. It was found that TBMS shows much stronger effects on ACD than PTES. In the former system, most fractions were produced on active centers with relatively lower r_1r_2 , higher reactivity to 1-hexene, and higher stereospecificity as compared to the system without external donor. It is concluded that the observed very extensive changes in ACD are mainly resulted by the formation of new types of active centers, possibly by coordination of external donor to certain positions on the catalyst.

INTRODUCTION

The multiplicity of active centers on MgCl_2 supported Ziegler-Natta catalysts has long been recognized^[1-4]. It has determinative influences on the structure inhomogeneity of the final polymer products^[3-6]. The control of active center distributions (ACD) is therefore one of the key problems in heterogeneous Ziegler-Natta catalysis. As a common example, in the polymerization of propene to isotactic product the

* The author to whom all correspondences should be addressed: Fan Zhiqiang.

Received November 6, 1996

ACD can be controlled by adding electron donors to the catalyst system with an aim to enhance its stereospecificity. Many different approaches have been reported so far for studying ACD^{[2],[3],[7-11]}, in which the most effective method may include fractionating the polymer and correlating its fraction distribution to ACD. The authors have reported on the reactivity distribution of active centers based on the fractionation of polymer according to molecular weight^[11]. For studying the stereospecificity distribution of active center, copolymerization systems have been proved to be more effective^[3]. In a previous work we have fractionated propene/1-hexene copolymers according to comonomer content, based on which the effects of alkoxy silanes as external donor on composition distribution (CD) and microisotacticity of the copolymer were studied^[12]. In this paper CD and distribution of microisotacticity of the same systems are further correlated with the copolymerization reactivity of active centers, and the effects of external donors are discussed based on the changes in active center distributions.

EXPERIMENTAL

The procedures of the copolymerizations, copolymer fractionation and NMR analysis of the fractions have been reported in a previous work^[12].

RESULTS AND DISCUSSION

Three copolymers produced under the same conditions were studied, one with no external donor in the polymerization system, and the others with triethoxyphenylsilane (PTES) and dimethoxydi-tert-butylsilane (TBMS) as external donors respectively. The catalyst used was $\text{MgCl}_2/\text{DIBP}/\text{TiCl}_4$ (DIBP=diisobutyl phthalate), and $\text{Al}(\text{C}_2\text{H}_5)_3$ was the cocatalyst. The copolymers containing about 5 mol-% 1-hexene were fractionated by extracting the samples with n-octane at different temperatures (20, 45, 65, 80, 90, 100, and 110° C, respectively). This is an improved Kumagawa extraction method which provides similar results as temperature-rising elution fractionation (TREF)^[7], so the fractionation is basically based on the crystallinity of the fractions. The cumulative fractionation curves were worked out, and 1-hexene content and microisotacticity (expressed in [mm]) of each fraction were determined by ^{13}C NMR. These results have been reported in the previous work^[12].

Composition distribution

A plot of cumulative weight fraction vs. 1-hexene content of the fraction is shown in Fig.1. According to the Schulz-Dinlinger procedure, the curve of $(1/2 W_j + \sum_{i=1}^{j-1} W_i)$

vs. hexene content is used to calculate the differential distribution curves (Fig.2), i.e. the slope of the curve (in broken-line form) is plotted against hexene content.

The curve has been reasonably extrapolated on both sides of the experimental hexene content range. This is a procedure usually used in precipitation fractionation experiments for molecular weight distribution determination. When the number of fractions is limited, only an approximative differential distribution can be obtained by this procedure. The differential composition distribution diagrams of the three copolymers are shown in Fig.2. As only seven fractions have been collected from each copolymer, the diagrams are quite approximative. But it is still possible to observe the following facts in Fig.2:

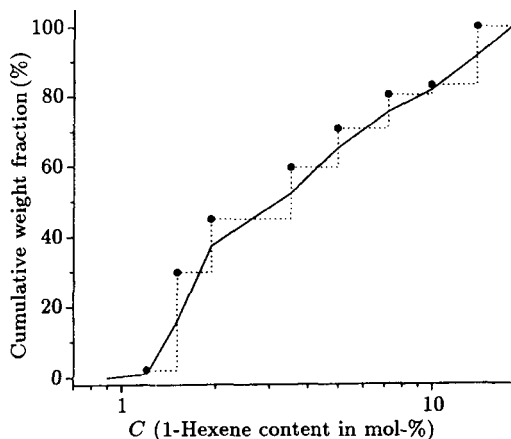


Fig.1 Cumulative composition distribution curve of propene/1-hexene copolymer synthesized with TBMS as external donor experimental cumulative weight fraction; — $1/2W_j + \sum_{i=1}^{j-1} W_i$ (cumulative weight fraction defined according to the Schulz-Dinlinger procedure, in which W_j is the weight fraction of the last fraction in the accumulated samples, W_i is the weight fraction of the other fractions)

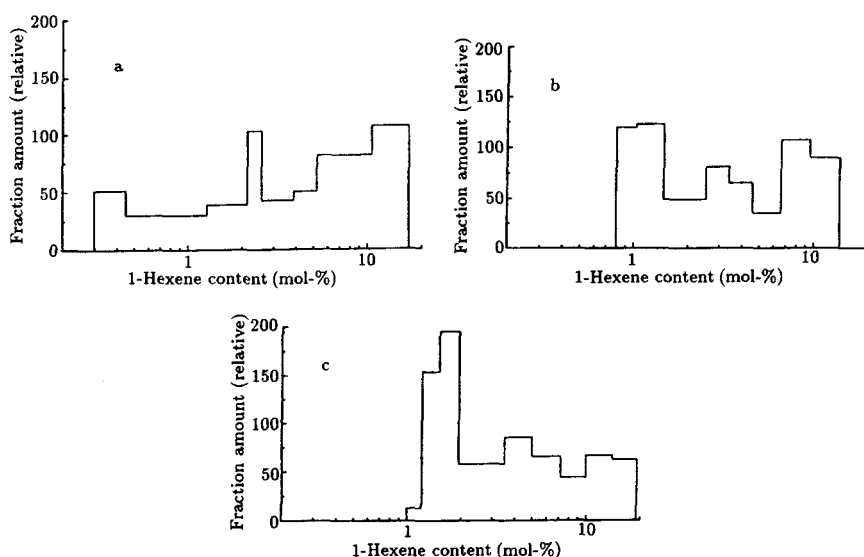


Fig.2 Composition distributions of the propene/1-hexene copolymers synthesized by catalysts with: a, no external donor; b, PTES as external donor; c, TBMS as external donor

(1) All the three copolymers show quite broad composition distribution. The CD diagrams can be divided into three main parts according to hexene content, that is, three parts with low, medium and high hexene content, respectively.

(2) External donor can sensibly increase the part of copolymer with the lowest hexene content and decrease the part with the highest hexene content, with TBMS showing the strongest effect.

(3) The overall distribution range decrease as external donors are introduced into the catalytic system. Considering that CD of copolymer produced on a "single-site" catalyst or initiator under constant polymerization conditions will be quite narrow^[13], the very broad and uneven CD shown in Fig.2 is in fact a reflection of the active center distributions.

Isotacticity distribution

In the previous work it has been found that the microisotacticity of propene segments increases as the hexene content in copolymer decreases^[12]. This result holds true for all three copolymers. Therefore the differential isotacticity distribution (ID) diagram (Fig.3) can also be made by treating the curve of cumulative weight fraction vs. microisotacticity (expressed as $-\log_{10}(1-[mm])$), in which $[mm]$ is the fraction of isotactic triad of propene determined by ^{13}C NMR). In Fig.3 it is clearly observed that: (1) the external donors exerted much stronger effects on ID than on CD. Especially when TBMS is used as external donor, the ID becomes much narrower; (2) when TBMS is the external donor, the higher isotactic part of the copoly-

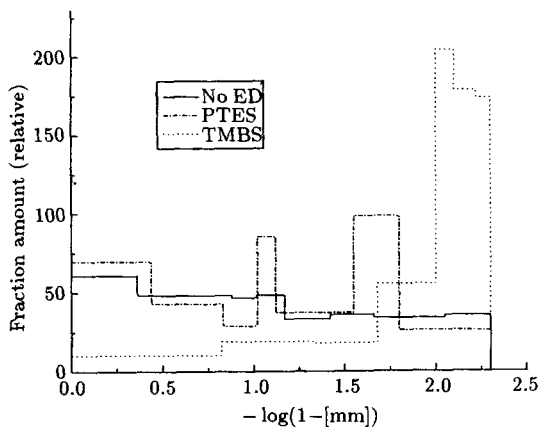


Fig.3 Isotacticity distribution curves

mer, namely the part with $-\log_{10}(1-[mm]) > 2$ or $[mm] > 0.99$ corresponds to the 1-hexene content range of 1–5 mol-% in CD diagram. According to Fig.2(c) these fractions might have been produced on more than one group of active centers. Therefore, in this system there are at least two types of highly isospecific active centers which show different copolymerization reactivities. On the other hand, the high isotacticity part of the copolymer produced without external donor has a relatively narrow composition range. This may mean that some non-stereospecific active sites have been converted to isospecific ones by TBMS.

Effects of external donors on the reactivity ratio product

Reactivity ratios are important parameters reflecting the copolymerization behaviors of the comonomers. But there appears a problem in determining the reactivity ratio product r_1r_2 according to the relationship^[14]:

$$r_1r_2 = 4[PP] \cdot [HH]/[PH]^2 \quad (1)$$

Because 1-hexene content in the copolymer has been limited to a rather low level (< 5 mol-%) to ensure effective fractionation, the ^{13}C NMR signal of the main chain CH_2 in HH sequence which is usually used in such calculation becomes too weak to be detected (see Fig.4). To solve this problem, two methods were adopted:

(1) In the NMR spectra of many fractions, a peak at 33.27 ppm (HMDS scale) which has been assigned as the branch $\gamma\text{-CH}_2$ signal of two triads HHP and HHH^[15] can still be clearly measured when the signal of HH at 39.06 ppm become undetectable (Fig.4). This means that the peak at 33.27 ppm is more detectable than the peak at 39.06 ppm. Considering the fact that at very low hexene content [HHH] will be negligible as compared to [HHP], the following approximation should be acceptable:

$$[HH] = 1/2[HHP] + [HHH] \approx 1/2([HHP] + [HHH]) \quad (2)$$

In fact, according to the results of spectra fitting by the first-order Markovian probabilities as described below, the values $[HHH]/[HHP]$ of all the fractions fall in the range of 0.01—0.16 (typically 0.02—0.08). Therefore the theoretical error induced by this approximation should be lower than 5% in most cases, which is lower than the experimental error of such weak peak. Then on this basis we can use the 33.27 ppm peak for the term [HH] in the calculation of r_1r_2 .

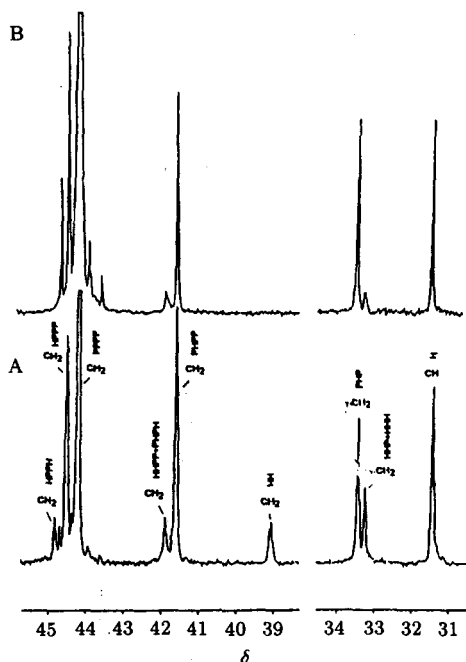


Fig.4 ^{13}C NMR spectra of copolymer fractions with 1-hexene content 13.9 (A) and 2.5 (B) (in mol-%)

(2) The theoretical basis of equation (1) is the first-order Markovian statistics, therefore the intensities of all the peaks can also be fitted by the first-order Markovian probabilities^[16]. A computer program using the SIMPLEX algorithm was made to do such fitting, and the results agree well with experimental data (Table 1). In the following discussions the r_1r_2 values based on the approximated experimental data will be used if available.

In Fig.5 the r_1r_2 of three typical fractions from each copolymer are compared. These fractions (collected at 20, 80 and 110° C, respectively) correspond to the three main parts in the CD diagrams of each copolymer (see Fig.2). It is clearly seen that the external donors can greatly lower r_1r_2 of the fractions with medium and low hexene content, while keep the r_1r_2 of the fractions with the highest hexene content. Combining with the changes of 1-hexene content and microisotacticity [mm] (see Table 1), the effects of external donor may be discussed as follows:

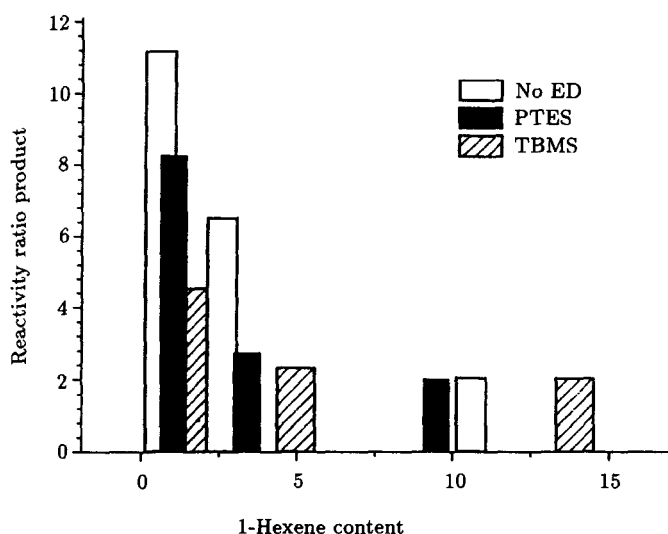


Fig.5 Reactivity ratio product of the typical fractions with different 1-hexene content

(1) For the fractions extracted at 20° C, the external donor PTES basically does not affect the hexene content, [mm] and r_1r_2 values, while TBMS raise both hexene content and [mm]. Therefore with PTES as external donor some non-stereospecific active centers may remain unchanged, only their number is decreased. But when TBMS is used, most of the non-stereospecific sites are converted into more stereospecific ones, remaining very few sites with quite open space to accommodate the bulky 1-hexene. As the microisotacticity of the fraction is also increased by TBMS, it is possible that the external donor is present in the vicinity of this group of active

centers.

Table 1 Reactivity ratios measured by NMR and by fitting NMR with the first-order Markovian probabilities^{a)}

Catalyst used ^{b)}	Extraction temp. in °C	1-Hexene content in mol-%	[mm] ^{c)}	Expl. data ^{d)}			Data by fitting		
				r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
No ED	22	10.6	0.56	3.46	0.60	2.07	—	—	—
	80	2.59	0.93	15.5	0.42	6.53	14.2	0.23	3.25
	110	0.45	0.99	51.7	—	—	49.6	0.23	11.2
PTES	20	9.48	0.63	3.62	0.56	2.03	4.34	0.70	3.03
	80	3.40	0.92	11.0	0.25	2.75	11.6	0.26	2.99
	110	1.03	0.98	41.7	0.20	8.27	42.3	0.23	9.86
TBMS	22	13.9	0.85	2.78	0.74	2.06	2.86	0.83	2.37
	80	4.96	0.99	8.07	0.29	2.35	8.20	0.31	2.54
	110	1.50	0.99	29.0	0.16	4.55	26.1	0.23	5.88

a) The data for three typical fractions of each copolymer have been listed.

b) In this column only the type of external donor used for polymerization is indicated.

c) Molar fraction of the isotactic triad calculated from the NMR spectrum.

d) The r_1 values were calculated according to the relationship $r_1 = 2[PP]/[PH]/x$ where $[PP]/[PH]$ is measured by the peaks of the PP and PH sequences ($\alpha\alpha\text{-CH}_2$). The r_2 values were calculated according to the relationship $r_2 = 2x[HH]/[PH]$ where $[HH]$ is the averaged intensities of the peak at 39.06 ppm ($\alpha\alpha\text{-CH}_2$ of HH) and the peak at 33.27 ppm (HHP+HHH), or the intensity of the peak at 33.27 ppm if the peak at 41.05 ppm can not be detected.

(2) For the fractions with medium and low hexene content, the external donors sensibly lower the $r_1 r_2$ values, or in other words, the chain-end effects in copolymerization are weakened by the external donors. At the same time 1-hexene content in the fractions is also increased by the external donors, especially when TBMS is used. As mentioned in the previous paper^[12], monomers bulkier than propene should preferentially approach the active sites located at more exposed positions of the catalyst surface. Therefore, when external donor is used, the fractions with medium and low hexene content might be mainly produced on those relatively more exposed active sites. In the author's opinion, the external donor affects the stereospecificity of active sites in a greater extent while only slightly affects the 1-hexene reactivity and $r_1 r_2$ of the same sites. In this case the external donor might coordinate with the relatively more exposed active sites and make them more stereospecific, and increase their productivity by increasing their k_p or their number. Those originally stereospecific active sites on unexposed positions may become unimportant when external donor is used, because they produce only a small fraction of copolymer now. Other explanations might also hold for these results. For example, it may be considered that the stereospecificity, 1-hexene reactivity and chain-end effects of the

active sites are simultaneously affected by the external donor. But such explanation seems to be too complicated and provides less information for understanding the problem.

As mentioned in our previous work^[12], the evident differences between the behaviors of PTES and TBMS come from their difference in coordination capacity. The results in this work further support this point. In Fig.5 it is clearly seen that TBMS shows much stronger effects on hexene content, $[mm]$ and r_1r_2 than PTES in all the three typical fractions. It may be said that TBMS is able to make active sites located on more exposed positions into isospecific active centers, while in the PTES system the most isotactic fractions are still produced mainly on certain unexposed active centers with high r_1r_2 . Seeing that TBMS can evidently increase the polymerization efficiency^[12], it is highly probable that in this system most of the copolymer is produced on active centers which have been formed by the coordination of TBMS on some very exposed active sites. Those less exposed sites may be unimportant in this case. Therefore TBMS can coordinate a wider range of active centers and influence them in a greater extent than PTES. The less bulkier methoxy groups in TBMS is the reason for its high coordination capacity, and the very bulky tert-butyl has strengthened its capacity in enhancing the stereospecificity of active centers.

In conclusion, the active center distribution may be effectively elucidated by fractionating a copolymer and characterizing the microstructures of the fractions. In the studied systems, three groups of active centers which produce copolymer of different comonomer content are tentatively distinguished. The external donor sensibly change composition distribution, isotacticity distribution and the reactivity ratio product of the copolymer, showing the formation of relatively more exposed and highly stereospecific active centers by coordination of the donor, and therefore the active center distribution can be extensively changed by the external donor.

Acknowledgement Thanks are due to Mr. Giulio Zannoni for making NMR analysis.

Keywords:

Supported Ziegler-Natta catalyst; Propene/1-hexene copolymer; External donor; Active center distribution

REFERENCES

- [1] Locatelli, P.; Sacchi, M.C. and Tritto, I., *Macromolecules*, **1986**, 19(2): 305.

- [2] Kissin, Y.V., *Makromol. Chem., Macromol. Symp.*, **1993**, 66: 83.
- [3] Sacchi, M.C.; Fan, Z.Q.; Forlini, F.; Tritto, I. and Locatelli, P., *Macromol. Chem. Phys.*, **1994**, 195: 2805.
- [4] Fan Z.Q.; Feng, L.X. and Yang, S.L., *Acta Polymerica Sinica* (in Chinese), **1993**, (6): 691.
- [5] Fan, Z.Q.; Feng, L.X. and Yang, S.L., *Chem. J. Chinese Univ.*, **1991**, 12(12): 1681.
- [6] Busico, V.; Corradini, P. and De Biasio, R., *Macromolecules*, **1994**, 27: 4521.
- [7] Kakugo, M.; Miyotake, T. and Naito, Y., *Macromolecules*, **1988**, 21: 314.
- [8] Paukkeri, R.; Iiskola, E. and Lehtinen, A., *Polymer*, **1994**, 35(12): 2636.
- [9] Cheng, H.N. and Kakugo, M., *Macromolecules*, **1991**, 24(8): 1724.
- [10] Fan, Z.Q.; Feng, L.X. and Yang, S.L., *Chem. J. Chinese Univ.*, **1992**, 13(1): 137.
- [11] Fan, Z.Q.; Feng, L.X. and Yang, S.L., *J. Polym. Sci., Part A: Polym. Chem.*, **1996**, 34: 3329.
- [12] Fan, Z.Q.; Forlini, F.; Tritto, I.; Locatelli, P. and Sacchi, M.C., *Macromol. Chem. Phys.*, **1994**, 195: 3889.
- [13] Cheng, H.N.; Tam, S.B. and Kasehagen, L.J., *Macromolecules*, **1992**, 25: 3779.
- [14] Randall, J.C., *Macromolecules*, **1978**, 11: 592.
- [15] Kissin, Y.V. and Brandolini, A.J., *Macromolecules*, **1991**, 24: 2632.
- [16] Cheng, H.N., *Polym. Mater. Sci. Eng.*, **1992**, 67: 35.