Influence of Electron Donors on the Tacticity and the Composition Distribution of Propylene−Butene Copolymers Produced by Supported Ziegler−Natta Catalysts

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ABSTRACT: Four copolymer samples of propylene with a small amount of butene were prepared by different $MgCl_2$-supported Ziegler−Natta catalysts and were fractionated by using the preparative temperature rising elution fractionation (TREF) technique. Some selected fractions were characterized by ^{13}C NMR. The data obtained suggest that the fractionation is mainly conducted according to tacticity. The influence of electron donors on the tacticity distribution and the composition distribution was investigated. It is found that both internal and external donors increase the isotacticity and narrow the tacticity distribution of copolymers but do not narrow the composition distribution of copolymers, though the butene content is reduced. ^{13}C-NMR results show that electron donors have a larger effect on the composition of the fractions of highest and lowest isotacticity, leading to a different dependence of composition on elution temperature from that of tacticity. This further confirms the supposition proposed in our previous work that electron donors can be present in the environment of both aspecific and isospecific active sites. The differences between internal and external donors were also compared. It is observed that internal and external donors change the proportion of fractions differently and that an external donor decreases the butene content of fractions more effectively.

Introduction

It is generally believed that there exists more than one kind of active site in heterogeneous Ziegler−Natta catalysts.[1−3] The plurality of active sites leads to a broad tacticity distribution and intermolecular heterogeneity of polypropylene. For the copolymer, the heterogeneity of active sites also results in a broad composition distribution and sequence distribution. The composition distribution is the distribution of comonomer over different polymer chains. The sequence distribution is the distribution of monomers' arrangement in a polymer chain.

The tacticity distribution and microstructure of the polymer can provide some useful information of the active sites, and this has been widely studied by many authors.[4−6] From this point of view, more information can be obtained from copolymers of propylene with other α-olefins, since the composition and the sequence distribution must also be considered for copolymers besides the tacticity distribution.[7−9] The tacticity, the composition, the sequence distribution and the relationships among them may throw light on the complicated nature of the active site in the Ziegler−Natta catalyst.[10−13]

The frequently used method for obtaining propylene homo- and copolymer fractions with different isotacticities and compositions is extraction with different solvents[14] or consecutive extraction with monosolvent at different temperatures.[10] Recently, a powerful tool, temperature rising elution fractionation (TREF), was developed.[4,15−16] Kakugo investigated the composition heterogeneity of propylene−ethylene and propylene−butene copolymers prepared with $TiCl_3{\cdot}{}^1/_3AlCl_3{-}AlEt_3$ catalyst by using the TREF method, and a relatively homogeneous composition was observed for the fractions of propylene−butene copolymer.

Electron donors are important components in $MgCl_2$-supported catalysts for propylene polymerization, and the roles of them are complicated. Electron donors have a great influence on the tacticity distribution and composition distribution of polymers. Sacchi et al. fractionated the copolymer of propylene with butene by means of extraction. They found that internal donors mainly selectively poisoned the least stereospecific sites, while the cooperation of internal and external donors might produce a new active site that was more selective in the choice of the incoming monomer.[11] The influence of different silane compounds as external donor on the isotacticity and composition of copolymers of propylene with butene or hexene was also investigated.[10,12]

In this paper, a small amount of butene was introduced in the polypropylene chains so that sequence distribution needs not to be considered. Four copolymer samples were prepared with different supported Ziegler−Natta catalysts and were fractionated with the preparative TREF technique. The influence of internal and external donors on the tacticity and composition distribution was examined.

Experimental Section

Preparation of Catalysts. By using di-*n*-butyl phthalate (DNBP) and diphenyl dimethoxysilane (DPDMS) as internal and external electron donor, respectively, four supported catalysts were prepared according to published procedures:[17,18] $MgCl_2/TiCl_4{-}AlEt_3$ (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).

Copolymerization. Copolymerization of propylene and butene was carried out in slurry at atmospheric pressure for 1 h. Propylene and butene gas were rapidly bubbled through the stirred *n*-heptane solvent in a reactor at a constant feed

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Table 1. Some Basic Data of Original Samples and Catalysts

sample	A	B	C	D
catalyst[a]	no	IED	EED	IED and EED
activity (kg of polymer/g of Ti·h)	10.2	6.9	7.3	5.8
M_w ($\times 10^{-4}$)	20.6	24.3	25.1	27.4
M_w/M_n	13.5	12.3	11.8	10.7
m %	70.4	85.6	87.8	97.0
butene (mol %)	3.1	2.6	2.0	1.4
T_m (°C)	92	138	143	154

[a] IED, internal electron donor; EED, external electron donor.

ratio. $AlEt_3$ was used as cocatalyst, and DPDMS was employed as external electron donor. Typical polymerization conditions were as follows: 100 mL of *n*-heptane, 30 mg of each catalyst, $[AlEt_3]/[Ti] = 100$, $[Si]/[Al] = 0.04$, 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 propylene−butene copolymer samples (A, B, C, D) were prepared with corresponding catalysts.

Preparative TREF. A preparative TREF apparatus was used to collect large amounts 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 has been added, the total recovery of polymer was around 105%.

^{13}C NMR Analysis. ^{13}C NMR spectra (100.7 MHz) were recorded on a Bruker AMX-400 spectrometer at 370 K in a pulsed Fourier transformation model. The polymer solutions were prepared by dissolving ca. 50 mg of polymer at 130 °C in 0.5 mL of $C_6D_4Cl_2$. Hexamethyldisiloxane (1%) was added as internal standard. The pulse angle was 90°, the pulse repetition was 10 s, the spectral width was 5000 Hz, the number of scans was 2000, and there were 32K data points. Since BB (continuous units) sequences did not appear in the copolymers, the butene content was defined as[9]

$$\text{butene (mol \%)} = \frac{{}^1/_2 S\alpha\alpha(\text{PB})}{S\alpha\alpha(\text{PP}) + S\alpha\alpha(\text{PB})} \times 100\% \qquad (1)$$

Results and Discussion

Original Samples and Fractionation Results. Some basic data of the unfractionated samples are summarized in Table 1, and the pentad distributions of them and their fractions are listed in Table 2. Only a small amount of butene was introduced in the polypropylene chains for two reasons: (1) to ensure that the copolymers are crystallizable and (2) to simplify the structure of the copolymers. In such copolymers, only isolated butene units are present in the polypropylene chains and the sequence distribution may not be taken into account.

The data in Table 1 show that electron donors have different influences on various parameters. The catalytic activity and incorporation of butene are reduced after addition of electron donors in the catalyst, but the isotacticity of copolymers is enhanced drastically. Electron donors also increase the molecular weight and narrow the molecular weight distribution slightly.

The fractionation data of the curves the four copolymer samples produced by different catalysts are listed in Table 3−6, and Figure 1 shows the TREF curves. The Wi%/ΔT−T curve in Figure 1 approximates the differential curve of the cumulative weight curve. The fractions near the maximal Wi%/ΔT values and the fractions eluted at room temperature were selected for ^{13}C NMR analysis. The data of the pentad distributions and butene contents of these fractions are summarized in Table 2. When the isotacticity of the fractions eluted at the same temperature is examined, no considerable difference in tacticity is found. On the other hand, for all four samples, the mean isotactic sequence length and the [*mmmm*] content of fractions increase with increasing elution temperatures. This is the same behavior as that for the fractionation of PP homopolymer.[19]

In the fractionation of PP homopolymer, there exist three peaks near 80, 103, and 115 °C in the Wi%/ΔT−T curves of TREF.[19,21] Similarly, three peaks near 70, 94, and 104 °C appear in the fractionation of copolymer samples. The large difference in tacticity and multiple peaks in Wi%/ΔT−T curves indicates the existence of plural active sites in heterogeneous Ziegler−Natta catalysts. On the other hand, there exist also many differences in comparison with PP homopolymers. Firstly, the amount of the fractions eluted at room temperature becomes larger and the elution temperatures, to which the peaks correspond, are lower for copolymers. This results from the incorporation of butene into the polymer chain, which decreases the crystallinity of the polymer. Secondly, the Wi%/ΔT values of the largest peaks (115 and 104 °C for homopolymer and copolymer, respectively) in copolymers are smaller, while the peaks near 70 and 94 °C become more pronounced and broader compared with the corresponding peaks in PP homopolymers (near 80 and 103 °C). Thus the intermolecular heterogeneity of the copolymers is more serious than that of homopolymers. This is understandable, since both tacticity and composition heterogeneity are present in copolymers.

Separation Mechanism. It can be seen from Table 2 that, the higher the elution temperature, the higher the isotacticity of the fraction is. The large difference in tacticity of the fractions eluted at different temperatures shows that these copolymers have a broad tacticity distribution. As to the butene content of the fractions, not in all samples does it decrease monotonously with increasing elution temperature and there isn't a common tendency for them. This means that copolymers may not be fractionated on the basis of composition. A possible reason is that the butene content in the copolymer is too small and composition is not the main factor influencing the crystallinity of the copolymer. In addition, in our other work, a set of molecular weight and molecular weight distribution data for the fractions of sample C was also reported.[20] The molecular weights of C1 (room temperature), C6 (85.5 °C), C8 (94 °C), C10 (100.5 °C), and C14 (116 °C) are 2.39×10^4, 13.48×10^4, 24.74×10^4, 45.39×10^4 and 46.07×10^4, respectively, and the molecular weight distributions are 8.20, 6.09, 5.17, 4.44, and 8.01 for these five fractions (Figure 2). Therefore it seems impossible that the fractionation is mainly based on molecular weight, since the fractions have a broad molecular weight distribution and C10 and C14 have close molecular weights. The increase of the molecular weight of the fractions with elution temperature may be due to the coincidence between molecular weight and tacticity.[19] These results indicate that the fractionation of these four copolymer samples is mainly conducted according to tacticity and that the TREF curves largely reflect the tacticity distribution of copolymers.

Table 2. Pentad Distributions and Butene Contents of Original Samples and Some Selected Fractions

elution temp	fraction	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mrmm* + *rrmr*	*mrmr*	*rrrr*	*rrrm*	*mrrm*	butene (mol %)	$\bar{n}_m$[a]	$\bar{n}_r$[a]	T_m (°C)
rt	1/A	24.6	12.4	3.7	14.1	13.4	4.4	9.9	9.2	8.2	4.10	3.5	2.7	n.d.[b]
	1/B	27.7	12.5	2.9	14.5	11.7	3.3	10.5	8.0	8.9	2.39	3.9	2.9	n.d.
	1/C	25.8	12.1	4.4	12.4	12.8	5.1	10.2	8.0	9.2	1.89	3.8	2.8	n.d.
	1/D	25.5	11.1	2.9	12.8	14.4	3.5	11.5	9.3	9.0	1.54	3.6	2.9	n.d.
70 °C	5/A	74.8	8.8	0	6.4	3.5	0	1.7	1.6	3.2	3.72	17.9	2.3	124
	4/B	76.5	7.7	0	7.2	3.0	0	2.0	0	3.5	3.51	17.5	2.1	127
	4/C	77.2	8.0	0	6.3	3.5	0	1.6	0	3.4	2.63	18.4	2.0	136
	4/D	77.3	8.4	0	6.4	3.6	0	1.8	0	2.6	2.19	18.1	1.9	140
94°C	10/A	90.8	4.0	0	3.4	0	0	0	0	1.8	3.46	56.7	2.1	143
	8/B	92.5	4.0	0	2.4	0	0	0	0	1.1	3.30	81.7	1.9	146
	8/C	92.0	2.7	0	3.8	0	0	0	0	1.5	2.17	50.8	1.8	150
	8/D	92.5	2.8	0	3.0	0	0	0	0	1.7	1.51	64.5	2.2	152
104 °C	13/A	95.3	3.7	0	0	0	0	0	0	1.0	2.70			157
	11/B	95.5	3.5	0	0	0	0	0	0	1.0	1.85			159
	11/C	95.4	3.6	0	0	0	0	0	0	1.0	1.74			159
	11/D	95.6	3.1	0	0	0	0	0	0	1.3	1.17			160
	unfractionated A	48.5	10.2	1.9	11.5	10.9	2.5	4.5	2.1	6.7	3.1	5.8	2.1	92
	unfractionated B	68.1	9.3	1.0	7.9	4.5	1.7	2.2	1.5	3.8	2.6	12.1	2.1	138
	unfractionated C	73.0	8.4	0.6	6.9	3.2	1.5	1.9	0.8	3.7	2.0	15.1	2.1	143
	unfractionated D	92.3	3.0	0	2.2	0.7	0	0.4	0.2	1.2	1.4	66.7	2.2	154

[a] $\bar{n}_m = ([mm] + {}^1/_2[mr])/{}^1/_2[mr]$, $\bar{n}_r = ([rr] + {}^1/_2[mr])/{}^1/_2[mr]$. [b] Melting peak was not detected.

Table 3. TREF Data of Sample A

no.	*T* (°C)	Wi%	ΣWi%	Wi%/Δ*T*
1	12	32.14	32.14	
2	39	5.18	37.32	0.192
3	60	6.50	43.82	0.309
4	70.5	5.52	49.34	0.526
5	75.5	3.54	52.88	0.708
6	81	2.80	55.68	0.509
7	83.5	2.34	58.02	0.934
8	87.5	2.61	60.63	0.652
9	91	2.84	63.47	0.812
10	94	3.35	66.82	1.115
11	97	3.07	69.89	1.025
12	100	5.60	75.49	1.868
13	105	14.28	89.77	2.856
14	108	6.15	95.92	2.049
15	111	1.01	96.93	0.337
16	115.5	1.67	98.60	0.372
17	118	1.40	100.0	0.560

Table 4. TREF Data of Sample B

no.	*T* (°C)	Wi%	ΣWi%	Wi%/Δ*T*
1	5	30.87	30.87	
2	40	4.66	35.53	0.133
3	61	4.38	39.91	0.209
4	71	7.80	47.71	0.780
5	81	6.47	54.18	0.647
6	86	6.91	61.09	1.383
7	91	8.56	69.65	1.712
8	94	5.51	75.16	1.835
9	97	4.30	79.46	1.434
10	101	5.26	84.72	1.316
11	104.5	10.05	94.77	2.870
12	108	1.77	96.54	0.505
13	113	1.85	98.39	0.370
14	117.5	0.88	99.27	0.196
15	122	0.72	99.99	0.161

Table 5. TREF Data of Sample C

no.	*T* (°C)	Wi%	ΣWi%	Wi%/Δ*T*
1	12	21.57	21.57	
2	40.5	3.09	24.66	0.109
3	61	4.96	29.62	0.242
4	70	4.02	33.64	0.447
5	80	2.88	36.52	0.288
6	85.5	7.98	44.50	1.451
7	90.5	6.69	51.19	1.337
8	94	8.77	59.96	2.489
9	97	7.04	67.00	2.348
10	100.5	13.51	80.51	3.861
11	104	8.34	88.85	2.383
12	107	3.52	92.37	1.174
13	111	1.87	94.24	0.467
14	116	3.16	97.40	0.633
15	123	2.59	99.99	0.370

Table 6. TREF Data of Sample D

no.	*T* (°C)	Wi%	ΣWi%	Wi%/Δ*T*
1	16	18.31	18.31	
2	41.5	3.15	21.46	0.124
3	60	4.25	25.71	0.230
4	70	4.25	29.96	0.425
5	79.5	4.87	34.83	0.512
6	86	3.27	38.10	0.503
7	91	5.55	43.65	1.109
8	94	9.50	53.15	3.166
9	98	12.84	65.99	3.210
10	101	12.31	78.30	4.103
11	104	12.31	90.61	4.103
12	107	7.07	97.67	2.356
13	110	0.61	98.28	0.203
14	113	0.30	98.58	0.101
15	116.5	0.46	99.04	0.130
16	121	0.46	99.50	0.101

Since TREF fractionates PP mainly according to crystallinity, and therefore according to lamellar thickness, lamellar thickness depends on isotactic sequence length. The longest sequences form the thickest lamellae that are dissolved and eluted at the highest temperatures. The comonomer units shorten isotactic sequences in the same way as other structural defects. The melting temperatures of fractions (see Table 2) show a similar variation tendency to that for isotacticity instead of butene content. This also indicates that fractionation is mainly based on isotacticity.

Tacticity Distribution. As shown in Tables 1 and 2, both internal and external donors enhance the isotacticity and [*mmmm*] content of the whole copolymers, and sample D has the highest isotacticity. Accordingly, the electron donors decrease the amount of atactic fractions (Table 3−6). Comparing the TREF curves of these four samples in Figure 1, one can see that internal and external electron donors have great but different influences on the tacticity distribution of copolymers. Judging from Table 2, the fractions eluted below 80 °C can be considered as fractions of low isotacticity and the fractions eluted above 80 °C are highly isotactic. The weight percentage of fractions in

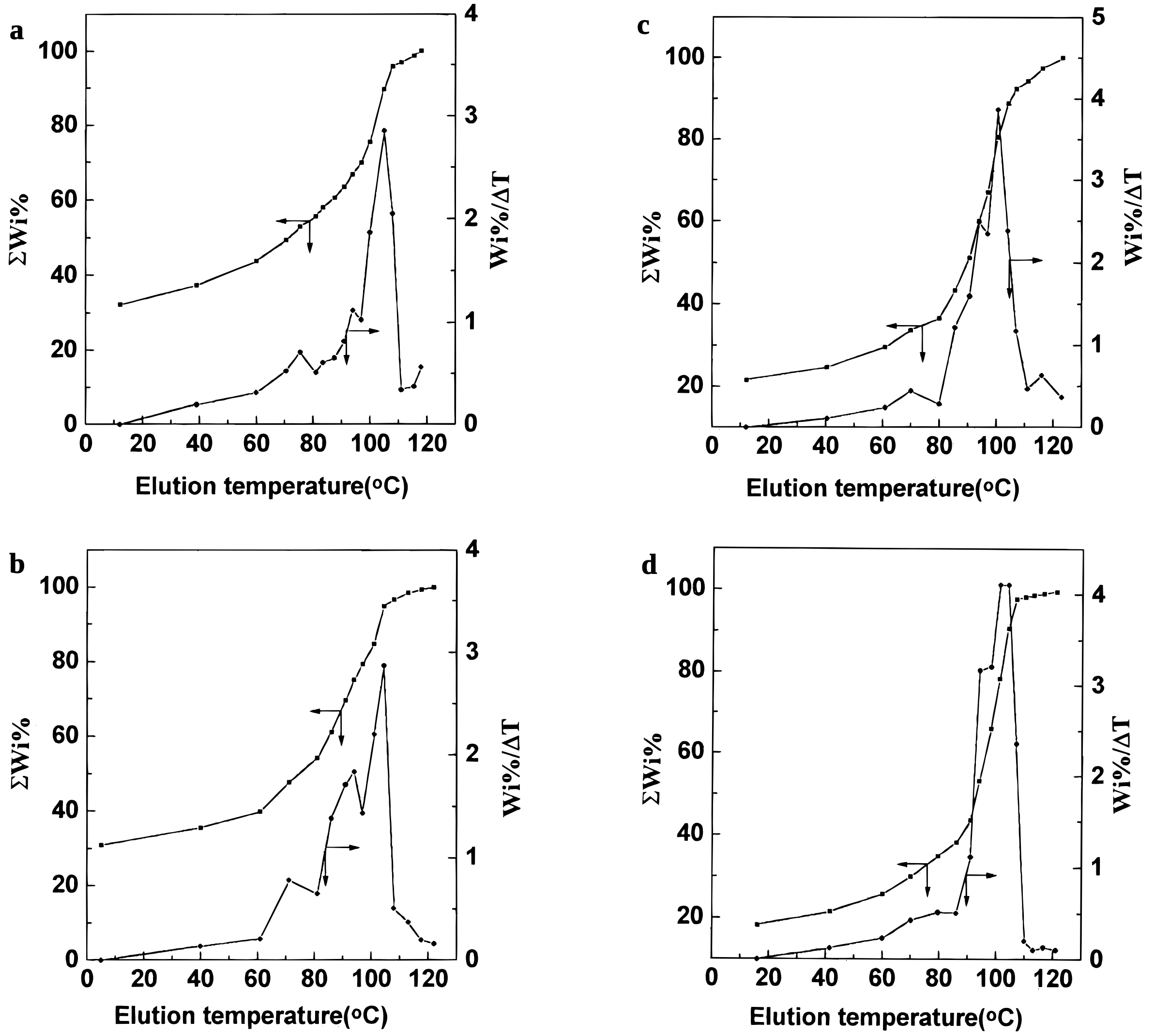

Figure 1. TREF curves of (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

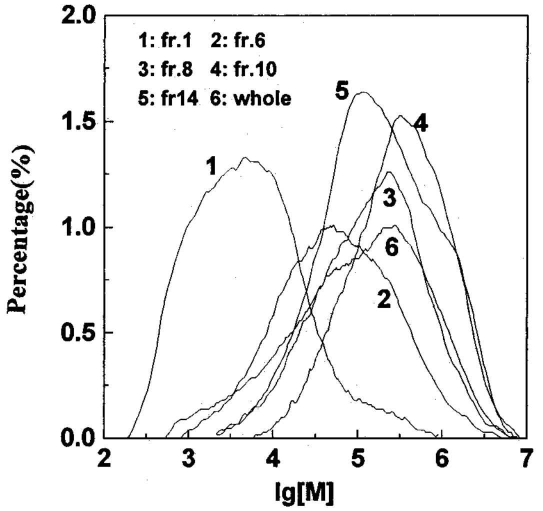

Figure 2. GPC curves for some fractions of sample C.

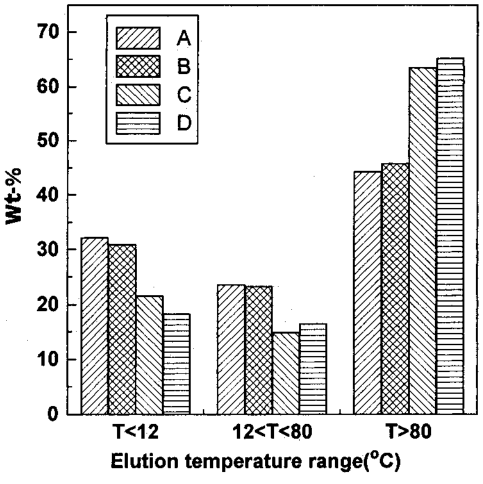

Figure 3. Weight percentage of fractions in different elution temperature ranges.

different elution temperature ranges is illustrated in Figure 3. The amount of the fractions with low isotacticity is smaller for samples C and D, indicating that external donors can decrease these fractions more effectively than internal electron donors. Nevertheless, internal electron donors evidently increase the proportion of the fractions eluted near 94 °C, which are produced by isospecific active sites of less stereospecificity. These results show that the effects of internal and external electron donors are different to some extent. Therefore, the cooperation of internal and external donors is necessary for the production of relatively homogeneous polymers. In fact, examining the maximal value of Wi%/ΔT and the widths of peaks, one can find that sample D has a narrower tacticity distribution than those of the other three samples. Additionally, it should be noted that internal and

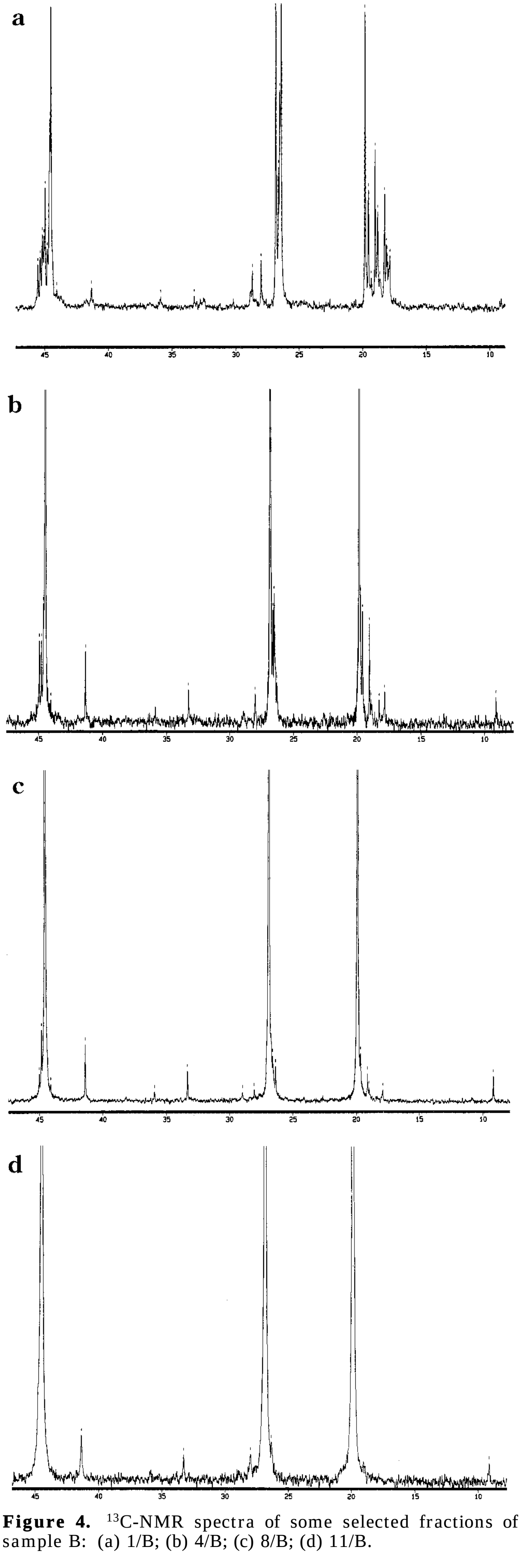

Figure 4. ^{13}C-NMR spectra of some selected fractions of sample B: (a) 1/B; (b) 4/B; (c) 8/B; (d) 11/B.

external donors do not show such a large difference in the fractionation of PP homopolymers.[21] The propylene homopolymers produced by Cat-B and Cat-C have a similar weight percentage of the fraction eluted at room temperature. Internal donors increase the proportion of the fraction eluted at 103 °C a little, while external donors have a reversed effect on it, which is similar to the case of copolymer. But compared with the case for copolymer, the variation is much less. Consequently, copolymerization may amplify the differences between internal and external donors. This is advantageous for elucidating the roles of electron donors.

Composition Distribution. It is found from Table 2 that the butene contents of the fractions eluted at various temperatures are different, indicating that composition heterogeneity also to some extent exists in the copolymers besides tacticity heterogeneity. The data in Table 1 show that the butene content of the whole copolymers is reduced by both internal and external donors. Accordingly, the butene content of fractions is also decreased. However, the degree of declination varies with fractions. One can see that the butene content of the first fractions and the fractions at 104 °C is decreased more than that of the other two fractions. These two fractions are produced by the most aspecific and isospecific active sites, respectively; thus, these two kinds of active sites are influenced by electron donor more seriously. The different effects of electron donors on different fractions lead to a distinct dependence of composition on elution temperature from that of tacticity. In sample A, which is produced by the catalyst containing neither internal nor external electron donors, butene content decreases monotonously with the increase of elution temperature. The same result was obtained by Kakugo in the temperature rising elution fractionation of propylene−butene and ethylene−propylene copolymers prepared with the conventional Ziegler−Natta catalyst $TiCl_3{\cdot}{}^1/_3AlCl_3{-}AlEt_3$,[13] whereas, for the other three samples produced by the catalysts containing electron donors, the variation of composition with elution temperature shows a different tendency. As shown in Table 2, it is not the first fraction but the fraction eluted near 70 °C that contains the most butene. This can also be seen from Figure 4, which shows the ^{13}C NMR spectra of the four fractions of sample B. In the methyl resonance region of Figure 4a, all pentads appear, and the peaks attributed to butene units are very weak. In contrast, the fraction eluted at 70 °C is of higher isotacticity than the first fraction, since in Figure 4b only five pentads appear and the relative intensity of the *mmmm* pentad is high. Meanwhile, the resonances originating from butene units are strong, suggesting that this fraction contains more butene. It is quite likely that these results are related with electron donors. In our previous work we proposed a supposition that electron donors may be present in the environments of both isospecific and aspecific active sites.[18,21] By using different compounds as internal donor, it proved that the internal donor was able to convert aspecific active sites into isospecific ones.[18,22] The presence of an electron donor in isospecific active sites makes them more bulky and results in the decrease of incoming comonomer. On the other hand, the chemically inverted structure was observed in the first fraction of PP produced by the catalyst employing bis-(2-ethylhexyl) phthalate as internal electron donor, while, in the case of other internal electron donors, such a structure did not appear.[21] In addition, it was found that electron donors had a large influence on the length of the stereoblock in the first fraction, suggesting electron donors may also be present in aspecific active sites.[23] The results obtained in the present work further confirm the supposition that electron donors participate in both isospecific and aspecific active sites. As to the reason that electron donors are present in aspecific active sites, we believe that there exists a series of different aspecific active sites and that the interactions of the electron donor with them may be different. Electron donors convert some of them into isospecific active sites, while others may remain aspecific after interaction and electron donors. The different interactions between electron donors and aspecific active sites can also reasonably explain the fact that electron donors decrease the isotacticity of the first fractions of propylene homopolymers.[21]

From the different dependences of tacticity and butene content on elution temperature, it can be inferred that stereoregularity and insertion of comonomer may be decided by different factors. It is generally accepted that the stereoregularity of a polymer depends on the chirality of active sites.[24] The incorporation of comonomer and regioregularity may be related to the hindrance of active sites. When electron donors are present in aspecific active sites, they become more steric, leading to a lower incorporation of comonomer. Isospecific active sites that are dimerized Ti ions or result from the interaction of electron donors with aspecific active sites are also very steric. The active sites producing the copolymer fractions near 70 °C may have little interaction with electron donors, and this makes them less steric; thus, high butene content is observed in this fraction for the case of catalysts containing electron donors.

The phenomenon that the butene content of the first fraction is not the highest was also observed by Sacchi et al. in the propylene−butene copolymer prepared with $MgCl_2/TiCl_4$/DIBP (diisobutyl phthalate)−$AlEt_3$/PTES (phenyltriethoxylsilane) catalysts.[10] But no more discussion was given, because a linear relationship between comonomer content and $\log(1 - [mm])$ was found for other catalytic systems. The reasons why different dependences of tacticity and composition on elution temperature are observed are the advantages of TREF and the particularity of our copolymer samples. Firstly, the samples are carefully pretreated (isothermal crystallization) before fractionation and the elution temperature can be freely chosen, while, for extraction with solvent, the boiling point of the solvent is a limitation. If the temperature of extraction is too high, the fraction eluted at 70 °C in TREF may be extracted with the first fraction. Secondly, the butene contents in our samples are very low. The effect of the incorporation of comonomer on the crystallinity of the copolymers is small. If the butene content of the copolymers is high, which may decrease the crystallinity of the copolymer drastically, the fraction eluted at 70 °C in our work will also be eluted at room temperature and we cannot distinguish it from the first fraction. In addition, when the butene content is high, composition may become the major factor that influences the crystallinity of the polymer, and the fractionation may be carried out according to composition. Moreover, the incorporation of comonomer decreases the tacticity of the copolymer,[25] which accelerates the decrease of crystallinity of copolymers. This can be seen from the first fraction (A1). The [*mmmm*] content of A1 is 24.6%, while it is 41.7% for the first fraction of PP homopolymer prepared with the same catalyst.[21] Since the butene content of this fraction is the highest, the decrease of the tacticity of it is also the largest. Although the comonomer content in the copolymer samples of Sacchi et al. is also relatively low, it is still higher than that in our samples.[10]

When the butene content of different copolymers is examined, it is found that the composition ranges of fractions for different samples are similar. Judging from this, one can reach the conclusion that electron donors do not narrow the composition distribution of copolymers, though comonomer content is decreased. Additionally, internal and external donors have different effects on the decrease of butene content. External donors reduce the amount of comonomer units in fractions more effectively than internal donors do.

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