Microtacticity of Polypropylene Fractions Produced by Different Active Sites of Heterogeneous Ziegler–Natta Catalyst

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SYNOPSIS

Polypropylene (PP) prepared with the $MgCl_2/TiCl_4$–$AlEt_3/Ph_2Si(OMe)_2$ catalyst system was fractionated by a preparative temperature rising elution fractionation (TREF) technique in the wide temperature range of room temperature to 130°C. The results of fractionation showed that there were plural active sites in this heterogeneous catalyst. Some key fractions were selected for characterization of ^1H- and ^{13}C-NMR. ^1H-NMR results suggested that the fractionation takes place according to tacticity. Based on analysis of ^{13}C-NMR, it was concluded that the polymerization mechanism proceeding on highly stereospecific active sites was active site-controlled and nonstereospecific active sites were able to convert into syndiotactic active sites during the polymerization, which led to the formation of a syndiotactic block. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Heterogeneous Ziegler–Natta catalysts are now widely used in industry, but the nature of the catalytic sites is still ambiguous to us. The main difficulty is that there are plural active sites in a heterogeneous catalyst. The complexity of active sites prevents people from studying them very well, and this problem has attracted many people.[1-3] So far, it is impossible to isolate different active sites. One possible and useful method is investigating the polymers produced by them. From the polymers, the information of the active sites is indirectly obtained and the polymerization mechanism can be inferred also.[4]

To separate the polymers produced by different active sites, a number of methods have been employed including solvent-extraction,[5] consecutive extraction with different solvents,[6] fractionation with a solvent/nonsolvent pair,[7] consecutive extraction with monosolvent at different temperatures,[8] and temperature rising elution fractionation (TREF).[9] Preparative TREF provides a more powerful tool than do other methods, because the temperature for fractionation can be freely chosen in a certain range. Moreover, it fractionates polymer based on crystallinity, and the TREF data directly reflect the tacticity of polypropylene (PP). For PP, tacticity is the only main variable which influences the crystallinity.

Kioka et al. already conducted TREF of PP prepared with a $MgCl_2$-supported Ti catalyst and found that a broad tacticity distribution.[9] Kakugo et al. also fractionated a highly isotactic part of PP with TREF. They suggested that two types of isospecific sites are present in a heterogeneous catalyst.[10] But detailed microstructures of fractions were not studied up to now. In the present study, PP prepared with a heterogeneous catalyst was fractionated with preparative TREF, and our emphasis will be placed on the relationship of the microstructures of fractions and the polymerization mechanism of related catalytic active sites.

EXPERIMENTAL

Preparation of the Catalyst

To obtain a sufficient amount of various fractions for the NMR experiment, a wide tacticity distri-

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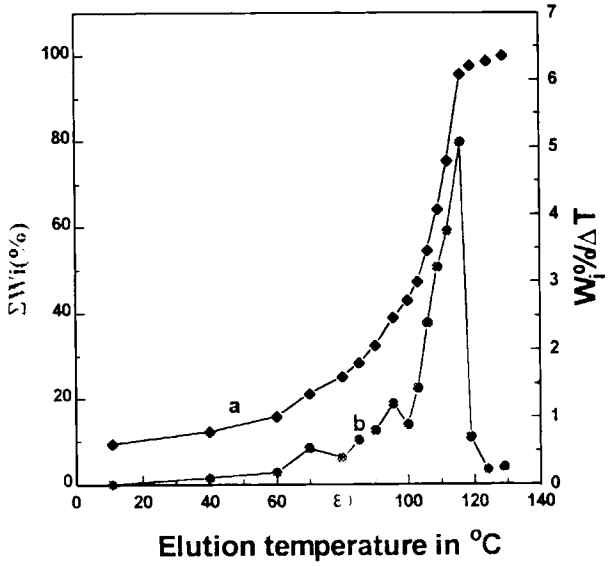

Figure 1 (a) Cumulative weight curve and (b) *Wi* %/ ΔT-T curve of PP fractionated with the TREF method.

bution is the favorite. So, only one kind of electron donor was added the catalyst system. For convenience, a $MgCl_2$-supported catalyst without an internal electron donor was selected. This catalyst was prepared in the following way under the condition of a N_2 atmosphere: One gram of anhydrous $MgCl_2$ and 6 mL BuOH were added to 50 mL *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 $TiCl_4$ was introduced. Subsequently, the resulting solid product was separated by filtration and washed with *n*-octane. $TiCl_4$, 50 mL was added again, and the operations of filtration and washing were repeated. The Ti content in the final catalyst obtained was 2.68%.

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 a cocatalyst and diphenyl dimethoxylsilane was employed as the external electron donor. Typical polymerization conditions were 100 mL of *n*-heptane, 30 mg 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 filtrated, then dried *in vacuo* at 80°C overnight.

Preparative TREF

A preparative TREF apparatus was used to collect large fractions of fractionated polymer. One gram polymer and 3% antioxidant were added in a 1000 mL flask containing 250 mL xylene. The polymer was dissolved at 130°C. Clean and dry sea sand, 500 g, was heated to the same temperature. Then, the sand was added to the flask and maintained at 130°C for 2 h. The mixture was cooled to room temperature at a rate of 1.5°C/h. The cooled sand wrapped with the polymer was transferred into a steel column with a temperature-controlling unit. The sand was heated in incremental steps of temperature and eluted with xylene. The polymer was recovered by evaporating the xylene solvent and drying in a vacuum oven. Because a small amount of antioxidant is added, the recovery of the polymer is 105% or so.

NMR Analysis

^1H- and quantitative ^{13}C-NMR spectra were recorded at 370 K on a Bruker AMX-400 spectrometer operating at 400 MHz for ^1H-NMR and 100.7 MHz for ^{13}C-NMR. The polymer solutions were prepared by dissolving ca. 50 mg polymer at 130°C in 0.5 mL $C_6D_4Cl_2$. Hexamethyldisiloxane, 1%, was added as the internal standard. The pulse angle was 90°; the pulse repetition, 10 s; the spectral width, 5000 Hz; the number of scans, 2000; and the data points, 32 K.

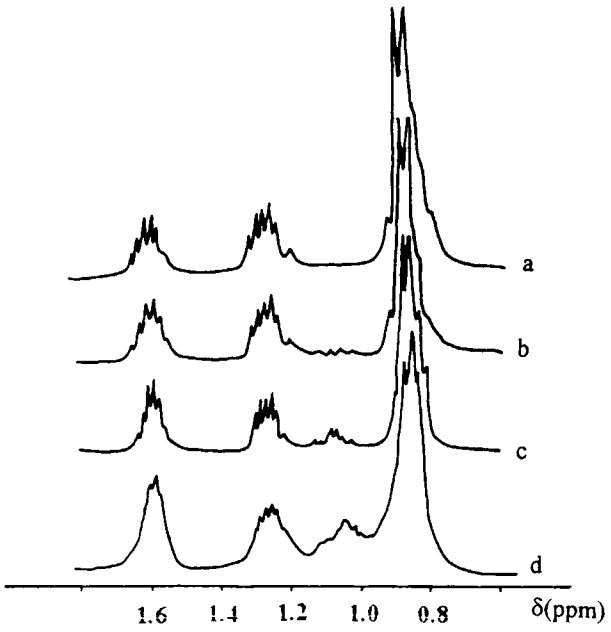

Figure 2 High-resolution ^1H-NMR spectra of fraction (a) A14, (b) A8, (c) A5, and (d) A1.

Table I Assignments of ^{1}H-NMR of PP

	Chemical Shift (ppm)			
	δ = 0.87	δ = 1.03	δ = 1.27	δ = 1.57
Assignments	CH_3 + syn, m-CH_2	r-CH_2	anti, m-CH_2	CH

RESULTS AND DISCUSSION

Temperature Rising Elution Fractionation

The preparative TREF was applied to PP prepared with a $MgCl_2/TiCl_4$-$AlEt_3/Ph_2Si(OMe)_2$ catalyst. The whole polymer was fractionated into 17 fractions in the range of room temperature to 130°C. Some key fractions were characterized by ^{1}H-NMR and ^{13}C-NMR. The TREF curves of $\sum Wi\ \%-T$ and $Wi\ \%/\Delta T-T$ are shown in Figure 1. It is found that the polymer prepared with this catalyst has a broad isotacticity distribution. Multiple peaks appear in the $Wi\ \%/\Delta T-T$ curve. It means that they are produced by different active sites. There is also a considerable part of the polymer eluted at room temperature. It is generally considered to be generated by aspecific active sites.

NMR Analysis

The fraction eluted at room temperature (A1) and the fractions near maximum of $Wi\ \%/\Delta T$ (A5, A8, A14) were selected for analysis of NMR. Their ^{1}H-NMR spectra are demonstrated in Figure 2 and the assignments of ^{1}H-NMR are summarized in Table I.[11]

From A8 to A1, the intensity of the peak contributed by r units increases gradually. It means that the amount of racemic units increases when the eluted temperature decreases. Therefore, the tacticity of fractions increases with the elution temperature. This confirmed that TREF fractionates PP according to the tacticity. This can also be seen from the variation of average sequence length with the elution temperature. An average sequence length of meso (n_1) and racemic (n_2) was defined as[12]

$$n_1 = \frac{[mm] + \frac{1}{2}[mr]}{\frac{1}{2}[mr]} \quad (1)$$

$$n_2 = \frac{[rr] + \frac{1}{2}[mr]}{\frac{1}{2}[mr]} \quad (2)$$

The values of n_1 and n_2 of these four fractions are reported in Table II. It is found that n_1 increases drastically with the elution temperature, while n_2 is nearly constant in all the fractions except A14. This also shows that the tacticity increases with the elution temperature.

From Table III, it can be seen that the molecular weight of fractions also increases with the elution temperature, which shows that there exists a coincidence between molecular weight and tacticity to some extent. However, the molecular weight distribution of each fraction is considerably broad. This indicates that the fractionation of PP with the TREF technique is not mainly according to molecular weight.

The expanded methyl region ^{13}C-NMR spectra of some selected fractions are shown in Figure 3 and the observed pentad distributions are listed in Table III. In the spectrum of A14, there appears only one resonance which is assigned to the *mmmm* pentad. The resonances of other pentads are covered by noise signals and cannot be observed. The characteristic of fraction A14 is high isotacticity and there is nearly no defect in the polymer chain. It is produced by highly stereospecific active sites.

In Figure 3(b), four peaks are present. They correspond to pentads *mmmm*, *mmmr*, *mmrr*, and *mrrm*, respectively. The intensity ratio of *mmmr* : *mmrr* : *mrrm* is near to 2 : 2 : 1. Therefore, the chain structure of this fraction is like that in Figure 4(a).

Table II Triads and Average Sequence Length of Some Selected Fractions

Fraction	*mm*	*mr*	*rr*	n_1	n_2
A1	0.46	0.32	0.22	3.88	2.34
A5	0.85	0.08	0.07	22.3	2.75
A8	0.94	0.04	0.02	48.0	2.00
A14	~ 1.00	0	0	—	0

Table III Observed Pentad Distributions of Some Selected Fractions

Fraction	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mrmm* + *rmrr*	*rmrm*	*rrrr*	*mrrr*	*mrrm*	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$
A1	0.28	0.14	0.04	0.15	0.15	0.02	0.10	0.06	0.06	2.15	8.58
A5	0.77	0.08	0	0.08	0	0	0.04	0	0.03	5.74	7.67
A8	0.90	0.04	0	0.04	0	0	0	0	0.02	7.66	5.60
A14	~ 1.0	0	0	0	0	0	0	0	0	48.99	4.16
Whole	90.7%[a]									22.83	11.84

[a] *n*-Heptane insoluble part obtained from extraction method.

This fraction is also produced by highly stereospecific active sites, but propagation errors accidentally take place during polymerization. From the structure of the polymer chain, the polymerization mechanism is able to be inferred. Because occasional *r* "errors" are corrected, the propagation is under the control of the catalytic active site. When the *r* "error" appears, the active site can restore the absolute relationship of chain to active site. If the chain propagation is controlled by the chain end, the principal regulative force is the chain itself. When an *r* propagation step occurs, the correcting influences provide a new *m* configuration beyond the error, and chain propagation proceeds as before. Then, the chain structure like that in Figure 4(b) is formed and in the ^{13}C-NMR spectrum of the resulting polymer, only three pentads, *mmmm*, *mmmr*, and *mmrm*, will be observed.

Compared with Figure 3(b), in the ^{13}C-NMR spectrum of A5 [Fig. 3(c)], a new resonance of the *rrrr* pentad is present. This fraction may be generated by active sites with lower stereospecificity. The absence of other pentads indicates that there exists a syndiotactic block in the polymer chain. The occurrence of stereoblocks in PP was hypothesized earlier by many authors and was confirmed to some extent with various analyses.[13,14] This is a direct evidence for the presence of a stereoblock, although the amount of syndiotactic block is small. If the polymer is fractionated by solvent extraction, this fraction cannot be separated properly. By using the TREF technique, it is accomplished readily, because the elution temperature is controllable. This is an advantage over other methods.

It is expected that the amount of syndiotactic block will increase in the fractions eluted at lower temperature, but the other pentads will also appear and make it difficult to find the existence of stereoblocks. It is indeed so in fraction A1. This fraction is produced by highly aspecific active sites, for all the pentads are present. To find the stereoblocks, a

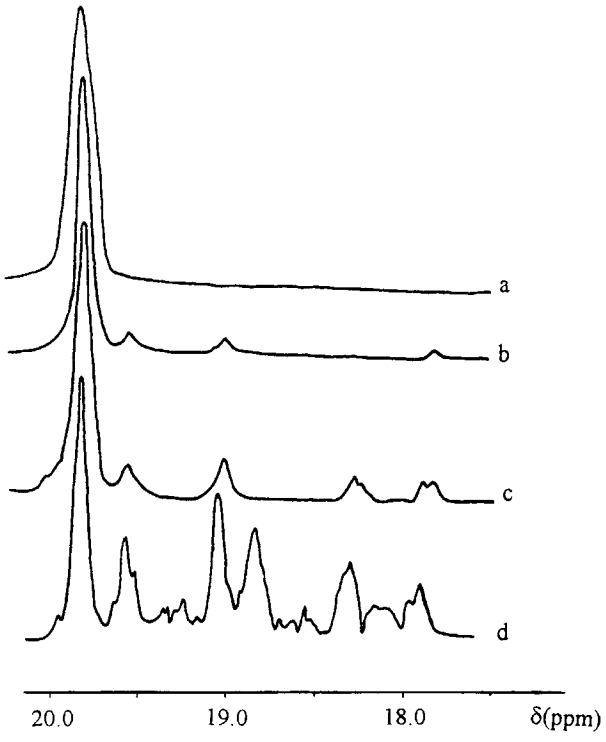

Figure 3 Expanded methyl region ^{13}C-NMR spectra of fraction (a) A14, (b) A8, (c) A5, and (d) A1.

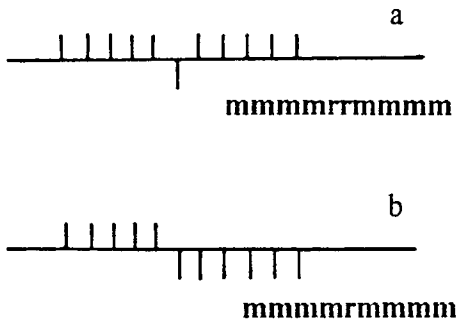

Figure 4 Two possible structures for the defects in isotactic propagation.

model analysis is needed. For simplicity, the first-order Markovian statistical model was applied. PP can be taken as a copolymer of meso and racemic units. The reactivity ratio of meso unit (r_1) and racemic unit (r_2) is calculated on the basis of the relationship

$$r_1 = 2[mmmm]/[mmmr] \quad r_2 = 2[rrr]/[rrrm] \quad (3)$$

or

$$r_1 = 2[mm]/[mr] \quad r_2 = 2[rr]/[mr] \quad (4)$$

The values of r_1 and r_2 calculated from eq. (3) is 4.0 and 3.34, but 2.88 and 1.38 calculated from eq. (4). This disagreement may be due to that fraction A1, which is eluted at room temperature, is still a mixture and a single active site model is inadequate. For long stereoblock sequences, the values of r_1 and r_2 calculated from eq. (3) is more accurate compared with that from eq. (4), because eq. (4) involves short sequences. However, in both cases, the product $r_1 \cdot r_2$ is larger than 1. This implies that stereoblocks tend to be formed. On the other hand, from pentad distributions of A1 (Table III), it can be seen that the amount of *rrrr* is larger than that of *rrrm,* which indicates that there exist some long sequences of racemic. The pentads *rrrm* are the points that long sequences of racemic convert into meso units. If the presence of *mrrrm* is not considered, all the pentads *rrrm* are originated 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 $n = 4$. In A1, [*rrrr*] : [*rrrm*] = 3.34 : 2, so n is equal to 3.34. It means that the average sequence length of racemic is 6.34 in long racemic sequences. When the structure *mrrm* is considered, the amount of *rrrm* resulting from $m(r)_n rrrm$ sequences becomes less; then, the average sequence length of racemic in long racemic sequences should be longer.

Based on the analysis of ^{13}C-NMR, we can conclude that there are two types of stereospecific active sites, which produce fraction A14 and A8, in the heterogeneous catalyst. This agrees with the results of Kakugo et al.[10] The polymerization mechanism of stereospecific active sites is active site-controlled. Also, there exist also two types of active sites with low stereospecificity, which produced A5 and A1. The highly stereospecific active sites are invariant during polymerization, but the nonstereospecific active sites are flexible. They are able to invert their stereospecificity. When they interconvert on a time scale comparable with that of polymer chain growth, stereoblocks are formed.

It is noted that, after this work was completed, Busico et al. also confirmed the existence of stereoblocks in a fraction (hexane-soluble/pentane-insoluble) of PP with a high-resolution ^{13}C-NMR technique.[15] Our work shows that the stereoblock structures are present mainly in the less isotactic part of PP, but not in all fractions.

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