Tacticity distribution of polypropylene prepared by $MgCl_2$-supported titanium catalyst

Mamoru Kioka*, Haruyuki Makio, Akira Mizuno and Norio Kashiwa
Iwakuni Polymer Research Laboratories, Mitsui Petrochemical Industries Ltd, Waki-cho, Kuga-gun, Yamaguchi-ken, 740 Japan
(Received 11 May 1993)

Polypropylenes (PP) prepared with $MgCl_2/TiCl_4$–Et_3Al and $MgCl_2/TiCl_4$/bis(2-ethylhexyl)phthalate–$Et_3Al/Ph_2Si(OMe)_2$ catalyst systems were fractionated by the temperature-rising elution fractionation method in the wide temperature range of −65 to 140°C. The fractionations were proved to take place mainly on the basis of isotacticity from the analyses of key fractions by ^{13}C nuclear magnetic resonance, gel permeation chromatography, differential scanning calorimetry and X-ray diffraction. PP was shown to have a broad and continuous distribution of tacticity, ranging from nearly atactic to highly isotactic structures in the case of no electron donor system. The addition of electron donor, however, drastically reduced the amount of atactic and low isotactic PP, resulting in a very sharp tacticity distribution.

(Keywords: tacticity distribution; polypropylene; fractionation)

INTRODUCTION

It is generally accepted that a heterogeneous titanium catalyst has plural active species. One of the reasons was based on the fact that polypropylene (PP) prepared with the catalyst systems was composed of polymers with different tacticities, which were analysed by successive Soxhlet extraction using various solvents[1–3]. This extraction method, however, gives information on only a discrete distribution of tacticity.

Temperature-rising elution fractionation (t.r.e.f.) provides a more effective method than successive Soxhlet extraction, because the temperature for fractionation can be freely chosen in a certain range. More importantly, the interpretation of t.r.e.f. data is more straightforward, for temperature is the only main variable during the fractionation.

Kakugo *et al.* have already conducted t.r.e.f. of PP prepared with $MgCl_2$-supported Ti catalysts with and without an electron donor[4,5]. They pointed out that there existed a bimodal tacticity distribution between 93% and 98% in the pentad level in fractions eluted above 100°C for the polymer with the catalyst system having an electron donor, suggesting that at least two types of active species are present in the system. However, their analysis using t.r.e.f. was focused on the highly isotactic part, and there have been no reports on the t.r.e.f. analysis of the whole PP including low isotactic and amorphous parts.

In the present study, therefore, we will report the tacticity distributions of the PPs by using t.r.e.f. in a wide temperature range (−65 to 140°C). These distributions are assumed to reflect directly the properties of the active species. The key fractions obtained by t.r.e.f. are fully characterized by ^{13}C n.m.r., g.p.c., d.s.c. and x.r.d.

EXPERIMENTAL

Preparation of the catalysts

The $MgCl_2$-supported catalyst without the electron donor (Cat A) was prepared in the following way. Twenty grams of $MgCl_2$ were milled in a vibration ball mill for 8 h at room temperature under a dry nitrogen atmosphere. The milled product was heated with 200 ml of $TiCl_4$ at 100°C for 2 h, stirring vigorously. Subsequently, the resulting solid product was separated by filtration and washed with n-decane. The catalyst with the electron donor (Cat B) was prepared in the same manner as stated above except that $MgCl_2$ was milled in the presence of 12 ml of bis(2-ethylhexyl)phthalate (BEHP).

Polymerization of propylene

Polymerizations were performed in a 2 litre autoclave at 70°C for 2 h. Partial pressure of propylene in the autoclave was kept at 7 $kg\,cm^{-1}$ by supplying gaseous propylene monomer. Polymerization was started by adding the catalyst components to n-hexane saturated by propylene monomer and after a given time was terminated by stopping the monomer supply. The polymers are denoted PP-A and PP-B. The concentrations of catalyst components in the polymerization systems were as follows: $[Ti] = 0.03$ mM (Cat A), $[Et_3Al] = 5.0$ mM for PP-A; and $[Ti] = 0.02$ mM (Cat B), $[Et_3Al] = 5.0$ mM, $[Ph_2Si(OMe)_2] = 5.0$ mM for PP-B. Three hundred millilitres of hydrogen at standard pressure were introduced into the system for Cat B to adjust the molecular weight. The products were poured into a large amount of methanol containing HCl, washed with methanol and vacuum-dried at 80°C.

---

* To whom correspondence should be addressed

0032-3861/94/030580-04

Temperature-rising elution fractionation (t.r.e.f.)

Coating methods. Six hundred milligrams of the polymer, 120 g of glass beads and 120 ml of n-decane were added to a 200 ml flask. The mixture was heated to 145°C, maintained at this temperature for 1.25 h and then cooled to room temperature at a rate of 9.6°C h^{-1}. The system was rotated through these procedures for uniform coating. The liquid part, containing soluble polymer in n-decane at room temperature ($C_{10\text{sol.}}$ part), was separated by filtration from the glass beads and recovered by evaporating n-decane in vacuum. The obtained $C_{10\text{sol.}}$ part was again dissolved in 38 ml of n-heptane and mixed with the glass beads separated by the previous filtration. The mixture was heated to 70°C, kept at this temperature for 0.5 h and cooled slowly to 30°C under rotation. The n-heptane was evaporated very slowly under reduced pressure. After complete removal of n-heptane, 120 ml of methanol was poured into the flask. Thus, methanol slurry, containing glass beads coated with whole polymer, was obtained.

As to PP-B, the glass beads merely coated with $C_{10\text{sol.}}$ part were additionally prepared with 600 mg of $C_{10\text{sol.}}$ part and 120 g of glass beads according to the latter part of the above procedure.

Fractionation. A fractionation was carried out by a double-tubed glass column (20 mm in diameter and 270 mm in length) with a temperature controlling unit described in our previous work[6]. The methanol slurry obtained in the manner above was packed into the column. The first fraction was obtained at low temperature (−65 or −30°C) by dropping 250 ml of n-hexane into the column over 2.5 h. In this procedure, all methanol had flowed out from the column before ca. 100 ml of n-hexane was added. The temperature was then raised stepwise and a series of fractions were obtained by adding 100 ml of n-hexane (fractionation below 30°C) or n-decane (above 30°C) over 1 h. Hardly any difference was observed in the amount of polymer fraction eluted around 30°C between n-hexane and n-decane. The polymer fractions in n-hexane were recovered by evaporating the solvent at reduced pressure and those in n-decane were precipitated by pouring the eluate into a mixture of 0.6 litres of acetone and 1.8 litres of methanol, recovered by filtration and dried in vacuum.

Polymer analyses

^{13}C n.m.r. spectra were recorded at 120°C on a JEOL GSX-270 spectrometer operating at 67.8 MHz with proton decoupling. The polymer solutions were prepared by dissolving ca. 50 mg of polymers at 120°C in a mixture of 0.5 ml hexachlorobutadiene and 0.1 ml of deuteriobenzene. The pulse angle was 45°, the pulse repetition was 5.0 s, the spectral width was 5000 Hz, the number of scans was 10 000–20 000, and the data points were 64k. The molecular weight of polymers was measured by a Millipore Waters 150C gel permeation chromatograph equipped with a refractive index (r.i.) detector, using a TSK mixed polystyrene gel column (G3000–G7000, exclusion limits 400 000 000 for polystyrene *MW*) and *o*-dichlorobenzene as solvent at 140°C. The number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) were calculated on the basis of a polystyrene standard calibration. Thermograms were recorded at a heating rate of 10°C min^{-1} in order to measure melting temperatures for the samples on a Perkin–Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated by measurements of the melting points of indium and lead. The X-ray diffraction pattern of the polymer, which was deposited on a glass plate, was measured in a reflection mode using a Rigaku RU-300 X-ray diffractometer. Instrumental conditions were as follows: Ni-filtered Cu Kα radiation, 50 kV, 300 mA; divergence slit 1/2°; receiving slit 0.15 mm; scatter slit 1/2°; scanning speed 2° min^{-1}; measurement angle 5–35°.

RESULTS AND DISCUSSION

First of all, t.r.e.f. was applied to PP prepared by $MgCl_2$-supported titanium catalyst without electron donor (PP-A). The whole polymer was fractionated into 11 fractions in the range of −65 to 130°C and the key fractions were analysed by d.s.c., ^{13}C n.m.r., x.r.d. and g.p.c. All the analytical data are summarized in *Table 1*. The thermograms measured by d.s.c. show that the melting temperature (T_m) of each fraction increases from 71.9 to 158.0°C as the elution temperature is raised from 0 to 130°C. The fraction eluted at −45°C, however, shows no T_m above room temperature. The mm triad content and the crystallinity determined by ^{13}C n.m.r. and x.r.d. also increase with the elution temperature, as expected from the d.s.c. results. The fraction at −65°C is considered to be nearly atactic from the mm value (26.8%) and the amorphous property (crystallinity = 0%). Furthermore, the weight-average molecular weight ($\bar{M}_w$) of each fraction measured by g.p.c. also tends to increase gradually with the elution temperature. The molecular-weight distribution ($\bar{M}_w/\bar{M}_n$) is still large (4.5–7.1) even after the fractionation. If the fractionation operates on the molecular-weight basis, the change of $\bar{M}_w$ is expected to be much larger (because the whole sample has a broad $\bar{M}_w/\bar{M}_n$) and $\bar{M}_w/\bar{M}_n$ of each fraction to be much smaller, ideally equal to 1. When we used anisole as elution solvent, in fact, the $\bar{M}_w$ of the fraction eluted at the highest temperature was more than 10^2 times as high as that at the lowest one, and the $\bar{M}_w/\bar{M}_n$ values of all fractions were less than 2. From these results, the fractionation using n-alkane as elution solvent is mainly subjected to the crystallinity derived from isotactic sequences, while anisole induced the fractionation on a molecular-weight basis.

In order to investigate the effect of electron donor, PP produced by $MgCl_2$-supported titanium catalyst with electron donor (PP-B) was also fractionated and analysed in the same manner. All the data are listed in *Table 2*. In the temperature range between −30 and 140°C, the mm content of the fraction increases with the elution temperature except for the one eluted at 30°C, while T_m monotonically increases with the elution temperature. The reason for the isotacticity decrease in the fraction at 30°C will be discussed later in this section. The analytical data listed in *Table 2* reveal the following features: (i) $\bar{M}_w/\bar{M}_n$ of the fractions above 110°C, which cover ca. 90 wt% of the whole polymer, is relatively small (2.2–2.7), unlike the corresponding ones from PP-A (5.4–6.0); (ii) the rr value (65.7%) of the fraction at 30°C indicates that the main component of this fraction has a somewhat syndiotactic structure (see *Figure 1b*).

It has been pointed out that the polymer with high isotacticity and high molecular weight is newly formed by the addition of external donor[3,7]. Observation (i)

Table 1 Characterization data of PP prepared by $MgCl_2/TiCl_4$–Et_3Al

No.	Temp. (°C)	$P(w)^a$ (wt%)	$I(w)^b$ (wt%)	$\bar{M}_w$ (10^5)	$\bar{M}_w/\bar{M}_n$	mm (%)	T_m (°C)	Crystallinity (%)
1	−65	17.2	17.2	0.69	7.06	27	–	0.0
2	−45	0.9	18.1	1.11	4.46	–	n.d.	0.4
3	−30	2.4	20.5	1.18	5.38	–	–	–
4	−15	3.9	24.4	1.22	5.04	38	–	6.6
5	0	4.1	28.5	1.20	5.30	45	71.9	10.8
6	30	11.6	40.1	1.98	5.88	53	83.5	17.2
7	70	12.5	52.6	1.70	5.93	–	111.5/120.5	–
8	90	8.8	61.4	2.72	5.87	–	130.6/137.7	–
9	100	5.1	66.5	2.61	5.29	–	141.9/149.5	–
10	110	9.7	76.2	3.57	5.42	–	149.3/155.1	–
11	130	20.9	97.1	8.35	6.04	98	158.0	–
Whole		–	–	2.89	8.43	67	147.1/155.6	–

[a] Weight fraction of eluted polymer
[b] Cumulative fraction of eluted polymer

Table 2 Characterization data of PP prepared by $MgCl_2/TiCl_4$/BEHP–$Et_3Al/Ph_2Si(OMe)_2$

No.	Temp. (°C)	$P(w)^a$ (wt%)	$I(w)^b$ (wt%)	$\bar{M}_w$ (10^5)	$\bar{M}_w/\bar{M}_n$	mm (%)	T_m (°C)
1	−30	1.3	1.3	0.26	10.46	31	–
2	−15	0.3	1.6	–	–	50	–
3	0	0.3	1.9	0.48	11.99	52	81.3/91.5
4	30	0.1	2.0	0.91	8.78	17	91.1/110.5
5	70	2.0	4.0	0.32	5.17	–	–
6	90	2.5	6.5	–	–	87	–
7	100	2.5	9.0	–	–	–	–
8	105	1.9	10.9	–	–	–	–
9	110	1.8	12.7	0.45	2.71	–	–
10	112.5	2.5	15.2	–	–	–	–
11	115	4.1	19.3	–	–	–	–
12	117.5	5.8	25.1	–	–	–	–
13	120	4.6	29.7	0.86	2.15	98	160.9
14	122	7.7	37.4	–	–	–	–
15	124	6.4	43.8	–	–	–	–
16	126	8.0	51.8	–	–	–	–
17	130	36.3	88.1	3.02	2.49	99	163.1
18	134	3.1	91.2	–	–	–	–
19	136	1.1	92.3	–	–	–	–
20	140	2.3	94.6	–	–	–	164.5
Whole		–	–	2.05	4.94	98	160.4

[a] Weight fraction of eluted polymer
[b] Cumulative fraction of eluted polymer

suggests that this newly formed polymer has a narrow $\bar{M}_w/\bar{M}_n$. Syndiotactic PP was fractionated by Kakugo *et al.* from the polymer prepared by the $TiCl_3$–Et_2AlCl system[8]. The fraction at 30°C in our present work also shows similar syndiotacticity (observation (ii); rrrr = 50%). The spectrum of the fraction at 30°C even without electron donor gives a large rrrr pentad signal as shown in *Figure 1a*, showing the existence of syndiotactic sequences. From these results, we believe that both fractions at 30°C with and without the electron donor are a mixture of syndiotactic PP and low isotactic PP. So the production of a small amount of syndiotactic PP is assumed to be a general feature in heterogeneous Ti catalyst systems. The addition of an electron donor is supposed to be less effective to reduce syndiotactic PP than the low isotactic PP, with the result that the weight ratio of both polymers in these fractions is reversed.

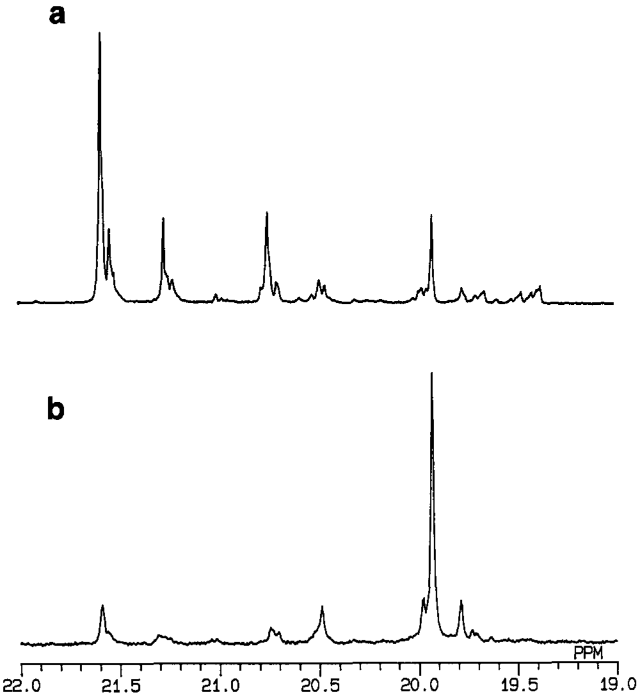

Figure 1 Expanded ^{13}C n.m.r. spectra of methyl regions of the fractions eluted at 30°C: (a) PP-A, (b) PP-B

Figure 2 shows histograms of weight fraction vs. elution temperature of PPs in the present study. These figures clearly show that PP-B is eluted at higher and narrower temperature range than PP-A. We believe that these histograms reflect a qualitative isotacticity distribution, because isotacticity monotonically (almost linearly) increases vs. the elution temperature. From this viewpoint, PP prepared without the electron donor was experimentally shown to be composed of fractions with different tacticities, ranging from atactic structure to highly isotactic one, meaning a broad and continuous property distribution of active species. Moreover, the *p*-xylene-soluble part at room temperature, which was considered to be atactic PP, may correspond to the fractions below room temperature in this experiment. In

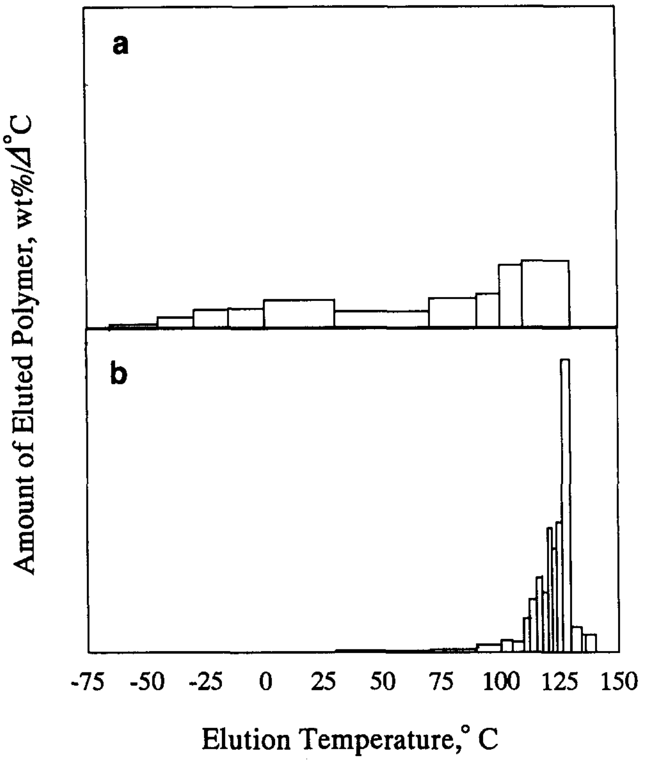

Figure 2 Plots of the elution temperature vs. weight fraction of (a) PP-A and (b) PP-B. Δ°C on the *Y* axis means the temperature range of each elution. The area of each bar corresponds to the weight fraction. The lowest-temperature fractions of each polymer are not drawn in the histograms. The *Y* axis of graph (a) is magnified by 2 times

the present work, we found that this fraction contained not only almost atactic polymer but also low isotactic one. On the other hand, the isotactic part of PP-B shows higher tacticity and a narrower tacticity distribution than the corresponding part of PP-A. It is noticeable that $\bar{M}_w/\bar{M}_n$ of this part is also narrow (2.2–2.7), as stated earlier in this section. This fact suggests that the addition of the electron donor makes the distribution of the active catalyst species extremely narrow. We are convinced that the suitable selection of an electron donor may open up a new route to control the active catalyst species and to produce a single-site catalyst even in heterogeneous Ti systems.

REFERENCES

1 Kashiwa, N., Yoshitake, J. and Toyota, A. *Polym. Bull.* 1988, **19**, 333
2 Kashiwa, N., Kawasaki, M. and Yoshitake, J. 'Catalytic Polymerization of Olefins' (Eds T. Keii and K. Soga), Kodansha, Tokyo, 1990, p. 43
3 Soga, K., Shiono, T. and Doi, Y. *Makromol. Chem.* 1988, **189**, 1531
4 Kakugo, M., Miyatake, T., Naito, Y. and Mizunuma, K. *Macromolecules* 1989, **21**, 314
5 Miyatake, T., Mizunuma, K. and Kakugo, M. 'Catalytic Olefin Polymerization' (Eds T. Keii and K. Soga), Kodansha, Tokyo, 1986, p. 155
6 Mizuno, A., Abiru, T., Motooka, M., Kioka, M. and Onda, M. *J. Appl. Sci., Appl. Polym. Symp.* to be published
7 Kashiwa, N. 'Transition Metal Catalyzed Polymerization–Alkenes and Dienes, Part A' (Ed. R. P. Quirk), Harwood Academic, New York, 1981, p. 379
8 Kakugo, M., Miyatake, T., Naito, Y. and Mizunuma, K. *Makromol. Chem.* 1989, **190**, 505