Characterization of Polypropylenes Prepared with Bis-Indenyl Type Metallocene and $MgCl_2$-Supported $TiCl_4$ Catalyst Systems

Norio Kashiwa*, Jun-ici Imuta, Toshiyuki Tsutsui, Shun-ichi Hama, Shin-ichi Kojoh

Organo-metal Complexes Catalization Laboratory, Mitsui Chemicals, Inc.,
580-32 Nagaura, Sodegaura-City, Chiba 299-0265, Japan

SUMMARY: The homo-polypropylene: m-PP, prepared with *rac*-$Me_2Si[2\text{-}n\text{-}Pr\text{-}4\text{-}(9\text{-}Phenanthryl)\text{-}Ind]_2ZrCl_2$, showed 99.6 % of [mmmm] and 162.8 °C of melting temperature (Tm). This polymer was compared by TREF analysis with the homo-polypropylene: Ti-PP, which was produced by our latest $MgCl_2$-supported $TiCl_4$ catalyst system and showed 99.0 % of [mmmm] and 165.7 °C of Tm. It was indicated that m-PP has narrower stereoregurality distribution than Ti-PP and Tm of the fraction eluted from m-PP at the highest temperature range is 163.6 °C, while that from Ti-PP reaches to 167.3 °C. The characters and advantages of each polymer are discussed on the basis of these results. In addition, an advantage of this metallocene was made clear by characterization of polypropylenes copolymerized with ethylene.

Introduction

Since the discovery of stereospecific polymerization of propylene with the C_2-symmetrical metallocene catalyst$^{1)}$, much effort has been invested for the molecular design of its ligands$^{2,3)}$ and the optimization of the polymerization conditions$^{3,4)}$ in order to enhance the stereospecificity. Consequently, the stereospecificities of the developed metallocene catalyst systems$^{2,3)}$ have reached to a level comparative to the commercial $MgCl_2$-supported $TiCl_4$ catalyst systems. These catalyst systems have contributed to the enhancement of the regiospecificity as well as the stereospecificity, but their regiospecificities are still lower than those of the commercial $MgCl_2$-supported $TiCl_4$ catalyst systems which forbid chain-propagation reaction after regioirregular insertion of propylene monomer by the formation of dormant sites$^{5)}$. Therefore, further investigations have been continuing without a break.

CCC 1022-1360/00/$ 17.50+.50/0

On the other hand, further improvement of the stereospecificities of the commercial $MgCl_2$-supported $TiCl_4$ catalyst systems is desired for the application of polypropylene (PP) to the automobile industry.

Under the circumstances, a comparison of the latest metallocene catalyst system with the latest $MgCl_2$-supported $TiCl_4$ catalyst system would be significant as a step toward an ideal catalyst system for the PP without any defects. The TREF analysis is an useful method for such a comparison6). Besides, there have been a number of reports where the TREF analysis gave a clear relation between the characteristics of the obtained PP and the natures of active sites of the $MgCl_2$-supported $TiCl_4$ catalyst system7-10).

In this paper, the TREF analysis is carried out to compare homo-PPs produced by the latest metallocene and $MgCl_2$-supported $TiCl_4$ catalyst systems. In addition, PPs copolymerized with minor amount of ethylene (random-PPs) by these catalyst systems are characterized in order to discuss the differences in the natures of these catalyst systems.

Experimental

Catalyst

rac-$Me_2Si[2$-*n*-Pr-4-(9-Phenanthryl)$Ind]_2ZrCl_2$ (metallocene-A) was used as the latest metallocene catalyst because it shows the highest stereospecificity among the enormous examined metallocene catalysts in our laboratory. The structure of metallocene-A is shown in Fig.1.

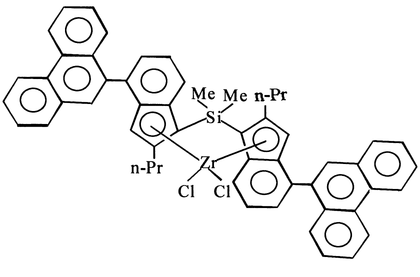

Fig. 1: Structure of metallocene-A (*rac*-$Me_2Si[2$-*n*-Pr-4-(9-Phenanthryl)$Ind]_2ZrCl_2$).

The latest $MgCl_2$-supported $TiCl_4$ catalyst system (Mg/Ti-A), which has been developed in our laboratory and shows higher stereospecificity than any commercially available $MgCl_2$-supported $TiCl_4$ catalyst systems, was used for the polymerizations.

Polymerization

Homo-polymerization of propylene with metallocene-A was carried out as follows. In a 2 L glass autoclave, 1 L of toluene was added and the system was charged with propylene. After cooling to 0 °C, a toluene solution dissolving 1.0 μmol of metallocene-A and 0.9 mmol of i-Bu_3Al was further added. Finally, 2.0 μmol of $Ph_3CB(C_6F_5)_4$ was added and the polymerization was carried out under atmospheric pressure for 30 min. During the polymerization, propylene and hydrogen were supplied continuously at the rates of 150 L h^{-1} and 3 L h^{-1}, respectively. At the end of the polymerization, the feed of propylene was stopped and a small amount of methanol was added. The whole product was then poured into 4 L of methanol containing a small amount of HCl. The obtained polymer was filtered, washed with excess amount of methanol and vacuum-dried at 80 °C for 12 h.

Homo-polymerization of propylene with Mg/Ti-A as follows. Into a 1 L stainless-steel autoclave, 400 mL of heptane was added and the system was charged with propylene. Then 0.4 mmol of Et_3Al, 0.4 mmol of an external donor and 8.0 μmol in terms of Ti (8.0 μmol-Ti) of Mg/Ti-A were added in this order at 60 °C. Next, 100 mL of hydrogen was added, and the system was pressurized to 0.49 MPa by propylene and heated to 70 °C. The polymerization was carried out at 70 °C for 1 h and propylene was fed continuously to keep 0.49 MPa. After the polymerization, the resulting slurry was filtered to separate into a powder and a liquid phase portion. The powder was washed with hexane and vacuum-dried at 80 °C for 12 h. The liquid phase portion was concentrated to obtain the heptane-soluble polymer.

The production of random-PP with metallocene-A was carried out as follows. Metallocene-A was supported on SiO_2 with methylaluminoxane (MAO) by pre-polymerization of propylene. The supported catalyst was fed into a sequential reactor at 0.035 mmol-Zr h^{-1} with MAO supplied at 10 mmol-Al h^{-1}. Propylene, ethylene and hydrogen were fed at the rates of 18 kg h^{-1}, 0.8 kg h^{-1} and 3.5 L h^{-1}, respectively. Polymerization was carried out at 60 °C for 2 h.

The production of random-PP with Mg/Ti-A was carried out as follows. Into a 2 L stainless-steel autoclave, 400 g of propylene, 4 L of ethylene and 4.5 L of hydrogen were added. Then 0.3 mmol of Et_3Al, 0.3 mmol of an external donor and 1.5 μmol-Ti of Mg/Ti-A were added in this order at 60 °C. The system was heated to 70 °C and the polymerization was carried out at that temperature for 30 min.

Polymer Characterization

The TREF analysis was carried out as follows. A stainless-steel column (21.5 mm in diameter and 150 mm in length) was packed with glass beads of 100 μm in diameters and maintained at 145 °C. Then 7.5 mL of *o*-dichlorobenzene (ODCB) solution dissolving 37.5 mg of the polymer sample at 145 °C was injected into the column. The cooling step was performed at 10 °C h^{-1} from 145 °C to 25 °C and the subsequent elution step was carried out by pumping ODCB at 1.0 mL min^{-1} and raising the temperature at 15 °C h^{-1} from 25 °C to 145 °C. The amount of eluted polymer was monitored for every 2.5 min by a Mercury Cadmium Telluride detector on a Nicolet FT-IR Magna-550. The whole solution was fractionated into 4 fractions and they were poured into five times volume of methanol. The precipitated polymer was collected by filtration and washed with methanol, followed by vacuum-dry.

The ^{13}C NMR, the gel permeation chromatograph (GPC) and the differential scanning calorimeter (DSC) analyses were performed according to our previous paper$^{5)}$.

The portion which is soluble in decane at 23 °C (C10 Sol) was measured as follows. Into a 1 L flask, 3 g of the polymer sample was added with 20 mg of 2,6-di-*t*-butyl-4-methylphenol and 500 ml of decane. The mixture was heated to 150 °C in order to dissolve the polymer sample completely. The obtained solution was cooled to 23 °C during 8 h and kept at that temperature for 8 h. The resulting slurry was filtered and the liquid phase portion was vacuum-dried until it reached constant weight. The percentage of thus-obtained constant weight in the weight of the polymer sample is C10 Sol.

The ethylene content was measured according to the literature[11)] and the melt flow ratio (MFR) was measured according to ASTM D1238.

Results and Discussion

The ^{13}C NMR analysis was carried out for the overall homo-PP: m-PP, prepared with metallocene-A, and the overall homo-PP: Ti-PP, prepared with Mg/Ti-A. The [mmmm] of m-PP reached to 99.6 %, while that of Ti-PP was 99.0 %. Then 0.10 mol% of 2,1-inversion was detected in m-PP in contrast with no detection in Ti-PP. It would interpret the lower Tm of m-PP than the expectation from the [mmmm] as shown in Table. 1.

The TREF analysis for m-PP and Ti-PP was carried out to discuss the differences in their characteristics. The varying amount of polymer eluted from each sample as a function of elution temperature is shown in Figure 2. While m-PP was eluted in the temperature range of 105 - 135 °C, Ti-PP was in the range of 110 - 140 °C. In both cases, the elution of polymer was negligible at temperatures below their characteristic

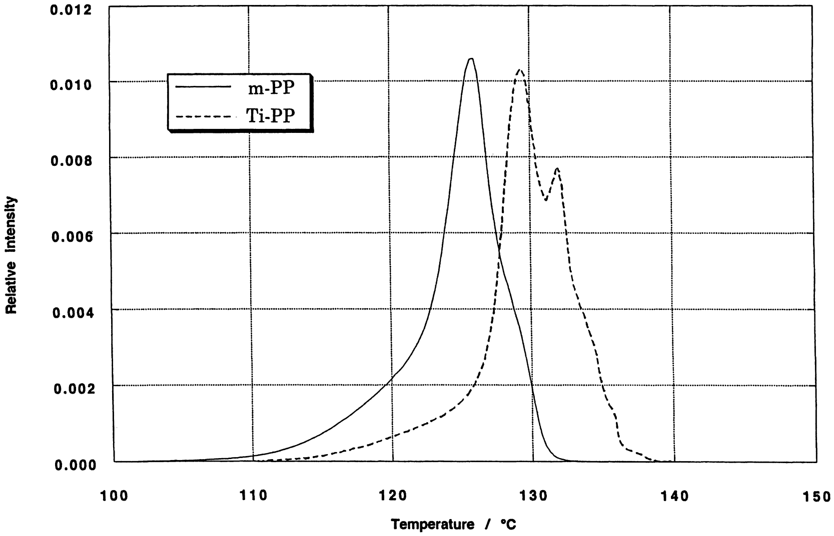

Fig. 2: TREF profiles of m-PP and Ti-PP; m-PP: homo-PP prepared with metallocene-A, Ti-PP: homo-PP prepared with Mg/Ti-A.

temperature ranges, indicating that the yield of atactic PP is too small to detect. Figure 2 shows that the elution curve of Ti-PP has two peaks at least in contrast to a single peak of m-PP. This suggests that the Mg/Ti-A and the metallocene-B would involve heterogeneous and homogeneous active sites, respectively.

In the measurement of TREF, both samples were fractionated into 4 fractions in order to analyze with DSC and GPC, and the results are shown in Table 1. Both the Tm and Mw of each fraction increased with raising the elution temperature, in which the extent of the increase for Ti-PP was much greater than that for m-PP. It is likely that the higher stereospecific active sites produce homo-PP of the higher molecular weight, especially in the use of Mg/Ti-A. Comparing fractions eluted at lower temperature (Fr.3) and higher temperature (Fr.4), the Tm increased from 166.4 °C to 167.3 °C and the Mw increased from 440,000 to 700,000 in the case of Ti-PP, while the Tm (from 163.3 °C to 163.6 °C) and the Mw (from 140,000 to 180,000) changes occurred to smaller extent in the case of m-PP. Thus, the microstructures of Fr. 3 and Fr. 4 from Ti-PP would be significantly different, while those from m-PP would be substantially the same. It is

Table 1. TREF, DSC and GPC analyses of m-PP (homo-PP with metallocene-A) and Ti-PP (homo-PP with Mg/Ti-A).

Sample		Elution Temp. / °C	Proportion / wt %	Tm / °C	Mw / 10^5	Mw/Mn
m-PP	whole	-	100	162.8	1.4	2.1
	Fr.1	105 - 115	3.3	-	-	-
	Fr.2	115 - 123	24.3	162.0	0.7	1.7
	Fr.3	123 - 127	49.6	163.3	1.4	1.7
	Fr.4	127 - 135	22.8	163.6	1.8	1.7
Ti-PP	whole	-	100	165.7	4.9	4.0
	Fr.1	110 - 123	7.2	160.4	-	-
	Fr.2	123 - 128	17.8	164.1	1.7	2.1
	Fr.3	128 - 131	40.3	166.4	4.4	2.5
	Fr.4	131 - 140	34.7	167.3	7.0	2.3

noteworthy that the Tm of Fr. 4 from Ti-PP is obviously higher than that of the whole sample which shows 99.0 % of [mmmm] and no regioirregularity. Although the [mmmm] of this fraction was not less than 99.7 %, the value could not be determined precisely with our current accuracy of ^{13}C NMR analysis.

The results of characterization of random-PPs prepared with metallocene-A and Mg/Ti-A were summarized in Table 2. Commonly, the portion which is soluble in decane at 23 °C (C10 Sol) is considered as the polymer containing much more ethylene comonomer than the overall polymer. Therefore, the higher value of C10 Sol of the random-PP with Mg/Ti-A at the almost same Tm as metallocene-A would show the broader distribution of ethylene content in the resulting polymer than metallocene-A. Besides, the higher ethylene content of the random-PP with Mg/Ti-A at the almost same Tm as metallocene-A would indicate that metallocene-A is more effective than Mg/Ti-A for lowering Tm of the resulting random-PP by the copolymerized ethylene unit.

Table 2. Results of characterization of random-PPs prepared with metallocene-A and Mg/Ti-A.

Catalyst	Tm / °C	C10 Sol / wt%	ethylene content / mol%	MFR / dg min^{-1}
metallocene-A	132	1.4	3.2	8.8
Mg/Ti-A	131	6.7	5.5	3.6

Conclusions

The TREF analysis indicated that the homo-PP prepared with metallocene-A had narrower distribution of stereoregularity than Mg/Ti-A. While the Tm of the homo-PP eluted at the highest temperature range in the case of metallocene-A was 163.6 °C, that of corresponding fraction with Mg/Ti-A reached up to 167.3 °C. Those would show each advantage of metallocene-A and Mg/Ti-A, namely homogeneity and regiospecificity, respectively. The characterization of the random-PPs with both the catalyst systems made an advantage of metallocene-A clear. This catalyst could lower the Tm of the random-PP by the smaller amounts of the ethylene content and C10 Sol than Mg/Ti-A. In view of these evidences, there may be two approaches to the development of an ideal catalyst. One is the enhancement of the regiospecificity of metallocene-A and another is to unify the plural active sites of Mg/Ti-A into the highly stereospecific active site that can produce such a PP eluted as Fr. 4 from Ti-PP.

References

1. W. Kaminsky, K. Kulper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem., Int. Ed. Engl.* **24**, 507 (1985)
2. W. Spalek, F. Kuber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E. F. Paulus, *Organometallics* **13**, 954 (1994)
3. H. Deng, H. Winkelbach, K. Taeji, W. Kaminsky, K. Soga, *Macromolecules* **29**, 6371 (1996)
4. A. Toyota, T. Tsutsui, N. Kashiwa, *J. Mol. Catal.* **56**, 237 (1989)
5. S. Kojoh, M. Kioka, N. Kashiwa, M. Itoh, A. Mizuno, *Polymer* **36**, 5015 (1995)
6. A. Mizuno, T. Abiru, M. Motowoka, M. Kioka, M. Onda, *J. Appl. Polym. Sci: Appl. Polym. Symp.* **52**, 159 (1993)
7. M. Kakugo, T. Miyatake, Y. Naito, K. Mizunuma, *Macromolecules* **21**, 314 (1988)
8. M. Kioka, H. Makio, A. Mizuno, N. Kashiwa, *Polymer* **35**, 580 (1994)
9. J. Xu, F. Feng, S. Yang, Y. Yang, X. Kong, *Polym. J.* **29**, 713 (1997)
10. I. Mingozzi, G. Cecchin, G. Morini, *Int. J. Polym. Anal. & Charact.* **3**, 293 (1997)
11. M. Kakugo, T. Naito, K. Mizunuma, T. Miyatake, *Macromolecules* **15**, 1150 (1982)