

Supported Metallocene Catalyst for Long Chain Branched Polypropylene

*Iku Kozai¹⁾, Masaaki Ito¹⁾, Sachio Hotta¹⁾ and Kuninori Takahashi¹⁾
Takehiro Sagae²⁾, Shinichi Kitade²⁾ and Takao Tayano²⁾*

1) Japan Polypropylene Corporation, 1-1-1, Marunouchi, Chiyoda-ku, Tokyo 100-8251 Japan

2) R&D Division, Japan Polychem Corporation, 1 Toho-cho, Yokkaichi, Mie 510-0848 Japan

Abstract

Japan Polypropylene Corporation (JPP) and Japan Polychem Corporation (JPC) have developed a new metallocene catalyst for long chain branched polypropylene (LCB-PP). LCB structure [1] is useful for improving melt strength of linear polyolefins like polyethylene (PE) and polypropylene (PP). However it has not been sufficiently solved by catalyst technology to introduce LCB into PP main chains because selective synthesis of active vinyl macromers and following incorporation at active sites for PP main chains were very difficult. JPP and JPC successfully solved the problem by their unique metallocene complex and clay mineral technologies and launched high melt strength (HMS) PP under the brand name of WAYMAX. Rheological properties and some application examples will be also reported.

Introduction

LCB PP is one of the most interesting targets for PP manufacturers because melt-strength of general linear PP is too low for foaming application. In order to install LCB structure into PP, mainly post reactor modification technologies have been developed. Peroxide [2] or electron beam radiation [3] is usually used. However post reactor modification has some disadvantages such as poor appearance by gels, coloring by residual radicals, limited suitability for repeated extrusion and so on. In case of PE, catalytic introduction of LCB has been achieved. For example, constrained geometry complex (CGC) is widely used. On the contrary, there was no commercialized catalyst technology for LCB-PP. It might be because of essential difference in structural properties, that is, secondary carbon atoms at methyl substituents of polymer chains. Therefore new catalyst technology for selective and effective LCB installation has been desired.

JPP and JPC have developed a new catalyst system for LCB-PP based on their unique metallocene technology including clay mineral support and launched a new product lineup under the brand name of WAYMAX. Some technical features will be discussed.

Requirements and Architecture

Requirements for LCB-PP catalyst are summarized in the following three points.

1. Selective synthesis of active vinyl macromers
2. Effective incorporation of synthesized macromers
3. Overall melt flow rate (MFR) control for extrusion foaming application

Macromer synthesis reaction needs very specific catalyst behavior and decreases molecular weight of polymer chains because it accelerates elimination reaction. So if we use only the complex suitable for macromer synthesis for catalyst preparation, overall MFR of the product PP doesn't reach to necessary values for extrusion foaming. Therefore we selected the architecture for LCB-PP catalyst shown in Figure 1.

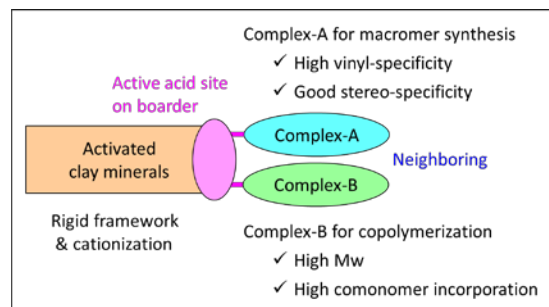


Figure 1. Architecture for LCB-PP catalyst

In-situ Macromer Synthesis

General olefin polymerization catalysts are active only for α -olefins which have a terminal double bond and inactive for internal olefins such as vinylidene compounds. In case of CGC for LCB-PE, active macromers are synthesized by β -elimination reaction at the connecting metal-carbon bond. Because PE has essentially no substituents on polymer chains, all reactions provide only active macromers. However in case of PP, there is a methyl substituent at β -position of metal-carbon bond. In addition, hydrogen extraction is much faster than methyl extraction in β -elimination reaction. Then major

products are inactive vinylidene macromers generally (Figure 2). Therefore we need to develop a very specific catalyst which promotes thermally less preferred β -methyl extraction.

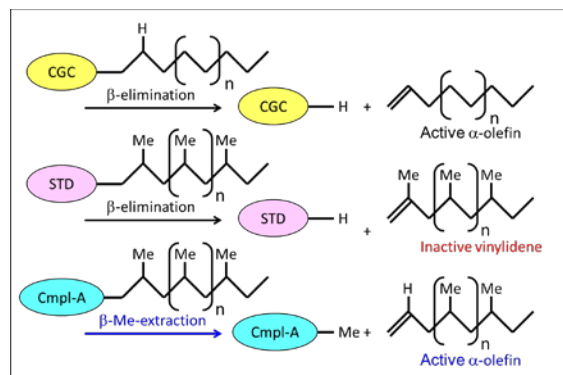


Figure 2. Difference in structure and specificity

We tried a lot of types of metallocene and found that certain complex framework worked well.

Complex		A-1	A-2	A-3
Stereo/Regio [mol%]	mm	97.6	98.0	97.8
	2-1	0.08	0.07	0.09
	1-3	0.18	0.16	0.18
Unsaturated terminal [unit/1,000unit]	1-Propenyl	0.79	0.72	0.88
	Vinylidene	N.D.	N.D.	N.D.
	1-Butenyl	N.D.	N.D.	N.D.
	<i>i</i> -Butenyl	N.D.	N.D.	N.D.
Saturated terminal [unit/1,000unit]	<i>i</i> -Butyl	1.23	1.17	1.21
	<i>n</i> -Propyl	N.D.	N.D.	N.D.
	<i>n</i> -Butyl	N.D.	N.D.	N.D.
	Et	N.D.	N.D.	N.D.

Table 1. ^{13}C -NMR analyses of PP obtained by complexes in the same category

Table 1 shows microstructures of PP obtained by some complexes in the same category supported on activated clay mineral. Polymerization was conducted without hydrogen addition. Stereospecificity is not so high but acceptable. Regiospecificity is high. Therefore we can estimate that β -elimination reaction will usually happen after regular 1-2 insertion. The most important point is unsaturated terminal structure. It is noted that only 1-propenyl structure was observed for all complexes. Hydrogen and methyl extraction at the metal-carbon bond after regular 1-2 insertion provides *i*-butenyl and 1-propenyl structure respectively. The above experimental

findings mean that only methyl substituent is extracted. Specificity of extraction is perfect. Similarly saturated terminal structure is interesting. Active sites after β -hydrogen elimination have a metal-hydrogen bond. Then regular 1-2 insertion after the reaction provides *n*-propyl terminal structure. However no *n*-propyl was observed in all samples. Observed *i*-Butyl terminal corresponds to regular 1-2 insertion after methyl extraction. As a conclusion, saturated terminal structure also shows that specificity of extraction is perfect. We selected this type of complex for LCB-PP catalyst as a potential macromer preparation site.

Macromer Incorporation

The second point is macromer incorporation. Even though macromers have an active terminal carbon-carbon double bond, only the limited conformation toward an active site is necessary for incorporation into active polymer chain. Indeed solution polymerization is relatively easier for analysis and understanding. However, we are afraid that it is not suitable for effective synthesis of LCB-PP. One of well-known advantages of solid catalysts is to accelerate reaction by concentrating substrate on its surface. If we support a pair of metallocene complexes, complex-A for macromer synthesis and complex-B for incorporation, within the close distance, macromer incorporation will be enhanced. Then we selected supported catalyst instead of solution polymerization.

Fortunately JPP and JPC had developed their original supported metallocene catalysts for propylene random copolymerization when we started this study. The fundamental framework was applied to LCB-PP catalyst. The following Figure 3 is a typical analysis result of prepared LCB-PP with the LCB-PP catalyst-I comprising complex-A, complex-B and clay mineral support according to the typical preparation recipe.

Gel permeation chromatography combined with light scattering and viscometer detectors (GPC-MALLS-V) was employed to detect LCB structure. Branching frequency is evaluated by the following equation (1):

$$g' = [\eta]_{\text{br}} / [\eta]_{\text{lin}} \quad (1)$$

where g' is a branching index, $[\eta]_{\text{br}}$ and $[\eta]_{\text{lin}}$ are intrinsic viscosity of the measured sample and reference linear PP.

It is noted that there is clear g' drop at high molecular weight region which means that the corresponding high molecular weight PP chains contain LCB considerably. Therefore our selection of supporting instead of solution was effective.

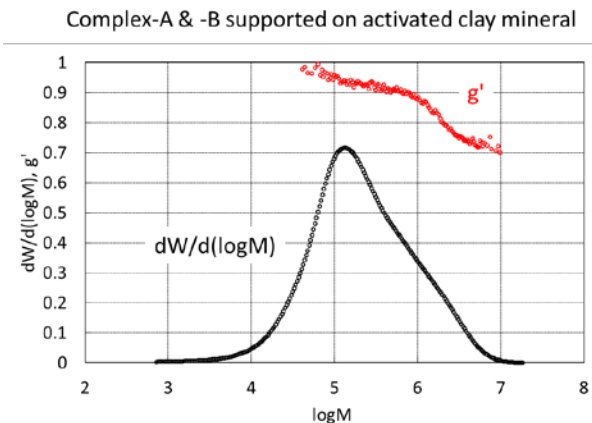


Figure 3. GPC-MALLS-V profile of LCB-PP prepared with the catalyst-I comprising complex-A, complex-B and clay mineral support.

Then we investigated influence of solid components. If we employ different types of solid activation materials, active site surroundings of supported two complexes might be different. For the purpose, we prepared the model catalyst-II supported on MAO-SiO₂ using the same mixing ratio of complex-A and complex-B as the above catalyst-I. Analysis result is shown in the following Figure 4.

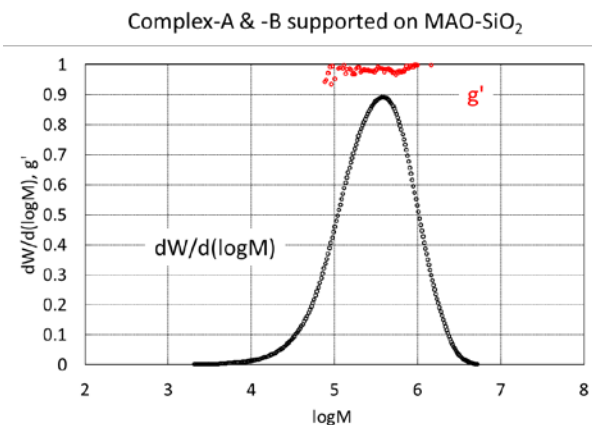


Figure 4. GPC-MALLS-V profile of the PP sample prepared with the catalyst-II comprising complex-A, complex-B and MAO-SiO₂.

Even though the same mixing ratio was employed, the PP sample doesn't contain any recognizable LCB. Therefore supported surroundings of metallocene might strongly influence on LCB preparation reaction. The authors believe that activated complex-A and -B will be located within the closer distance in the catalyst-I than in the case of catalyst-II because acid sites which cationize metallocene on activated clay minerals are concentrated

on the border [4]. The following Figure 5 is a typical AFM image of activated clay mineral. The border gets thicker than the original through some atom extraction by acid treatment. Clay minerals are not capable of activating metallocene without acid treatment in advance. Then it is rational to consider that only the chemically and physically modified part has activation ability. Therefore activated metallocene complexes are located within only the limited part, which might increase probability of preferable distance between complex-A and complex-B.

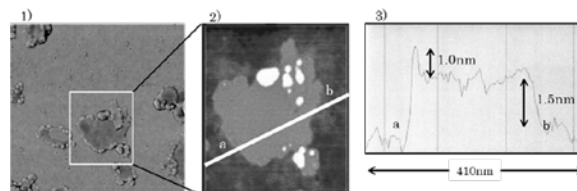


Figure 5. Typical AFM image of clay mineral platelets after acid treatment

Properties of LCB-PP

Various kinds of LCB-PP samples were prepared with the LCB catalyst described above and their rheological properties were investigated. Finally we found a good proportion of complex-A and complex-B for foaming application. Then we launched WAYMAX grades whose rheological properties are shown in the following figures.

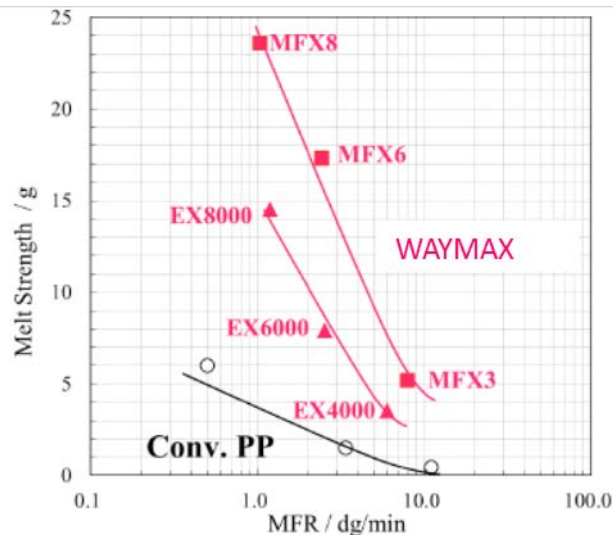


Figure 6. Melt strength of WAYMAX and conventional PP

Figure 6 shows melt strength (MS) of WAYMAX. MFR was measured according to ISO 1133 standard. CAPIROGRAPH (TOYO SEIKI SEISAKU-SHO, Ltd.) was used for MS measurement under the following conditions: capillary size: diameter: 2 mm, length: 40 mm, piston speed: 20 mm/min, barrel temperature: 230 °C. It is noted that MS is drastically enhanced compared with the conventional linear PP (a commercial grade produced with ZN catalyst) even though any post reactor reaction was employed.

Elongation viscosity shown in Figure 7 was measured with ARES rheometer combined with extensional viscosity fixture tools (TA instruments) at 180 °C and strain rate of 0.1 sec⁻¹. We can see clear "strain-hardening" which is generally required for foaming application.

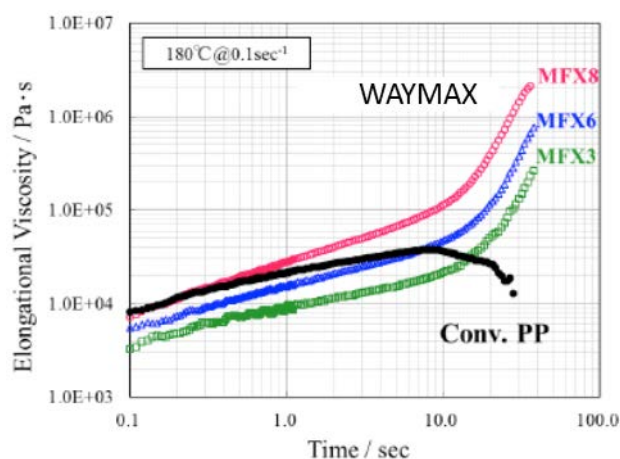


Figure 7. Elongation viscosity of WAYMAX and conventional PP

Conclusion

JPP and JPC have developed unique LCB-PP catalyst utilizing their experience and knowledge on metallocene catalyst. The architecture comprising three components, complex-A for macromer synthesis, complex-B for macromer incorporation and clay mineral support for accelerating necessary reactions, was used for catalyst development. Certain kind of complex has high specificity for active macromer synthesis. Some complexes show almost perfect specificity for thermally unfavorable β -methyl extraction reaction instead of hydrogen extraction. Clay mineral support contributes to high branching efficiency which is clearly different from unsuccessful result with MAO-SiO₂. It might be because of activation site surroundings mainly prepared on the border. The developed catalyst system is used for commercial production of HMS-PP under the brand name of

WAYMAX whose rheological properties are far different from conventional PP.

References

1. R.P. Legendijk et al., *Polymer*, **42**, 10035 (2001)
2. Japanese patent application, Hei10-330436
3. US patent 4916198.
4. T. Tayano et al., *J. Mol. Catal. A: Chem.*, **420**, 228 (2016)