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INVITED REVIEW

Development of low isotactic polyolefin

Yutaka Minami[1], Tomoaki Takebe[1], Masami Kanamaru[2] and Takuji Okamoto[1]

Polymeric material development has made great progress owing to the innovations in catalyst technology for polymerization. In recent years, the use of polyolefins has been expected to expand to various applications as substitutions for materials such as metal, paper and wood. Therefore, metallocene catalysts are a key technology for producing high-performance polyolefins specifically designed for a given application. In this report, we present a novel polypropylene (low modulus polypropylene: LMPP) with low isotacticity and high molecular weight, and which is synthesized using specific C_2-symmetric doubly bridged metallocene complexes. LMPP possesses some isotactic sequences in stereorandom order, and its tacticity can be precisely controlled through the design of the metallocene catalysts. LMPP can be provided as pellets and be applicable to hot melt adhesives, elastic fibers, nonwoven fabrics and so on, because of its unique elastomeric properties and excellent compatibility with isotactic polypropylene.
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INTRODUCTION

Olefin polymerization was originally obtained from the synthesis of high-density polyethylene at ordinary temperature and normal pressure by Ziegler, and of isotactic polypropylene (IPP) by Natta. Olefin polymerization catalysts such as Cr or Ti supported on $MgCl_2$ were then developed in sequence. The progress in technology innovation for these catalysts and the development of materials using polyolefins as a substitution for paper, glass and metal led to advances in polyolefin research. Now, polyolefin is the representative of synthetic polymers and used for many products.

After the development of a metallocene catalyst by Kaminsky *et al.*,[1] homopolymerization of α-olefin and copolymerization with long chain α-olefin were achieved with high activity, comparable with conventional polyethylene or polypropylene. In addition, the coordination polymerization of a wide variety of monomers has been possible to yield novel high-performance materials; for example, the polymerization of cyclic olefin such as norbornene or dicyclopentadiene, regiospecific polymerization of acetylene derivatives, dienes such as butadiene or isoprene, monomers containing polar groups, and stereospecific polymerization of styrene. In particular, it was the epoch-making development in propylene polymerization that made the control of stereoregularity possible, in addition to the control of composition and molecular weight. High-performance materials such as syndiotactic polypropylene or perfectly atactic polypropylene, which have physical properties unlike commercially available polypropylene, cannot be synthesized using conventional catalysts. However, their synthesis became possible through the use of metallocene catalysts.[2]

There are several methods for the production of soft polypropylene (soft PP). Through the innovations in catalyst technology and the progress in material development, high crystalline and high rigid polypropylene have been developed and are currently used as mentioned above. Examples of methods to produce soft PP are as follows (Figure 1):

1. Copolymerization of ethylene or other α-olefin with propylene. (random PP) (Figure 1b).
2. Adding an elastomeric component such as rubber (block PP) (Figure 1c).
3. Lowering the stereoregularity (lowmodulus polypropylene: LMPP) (Figure 1d).

All three methods were commercialized using Ziegler-Natta catalysts. However, there were problems in the generated materials, which were caused by limitations in the performance of the Ziegler-Natta catalysts. For example, the transparency of the molded articles was not adequate and the surface of the material was sticky. These problems were caused by the low-molecular-weight component of the polymer and another component of the crystallinity. These problems were noticeably occurring in the production of soft PP. Soft PP has been actively investigated since the development of new catalysts such as metallocene. Copolymerization of propylene with α-olefin using metallocene enabled the production of soft PP with comparatively narrow molecular weight and composition distributions. However, there were still problems caused by the softening of the polypropylene, such as the drop in the glass transition temperature and the drop in the compatibility to polypropylene due to a decrease in propylene content. These problems in the properties of the synthesized soft PP led to difficulties in their practical use and difficulty in processing in several applications.

[1]Performance Materials Laboratories, Idemitsu Kosan Co., Ltd., Ichihara, Chiba, Japan and [2]Advanced Technology Research Laboratories, Idemitsu Kosan Co., Ltd., Ichihara, Chiba, Japan
Correspondence: Y Minami, Performance Materials Laboratories, Idemitsu Kosan Co., Ltd., 1-1 Anesaki-Kaigan, Ichihara, Chiba 299-0193, Japan.
E-mail: yutaka.minami@idemitsu.com
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SYNTHESIS AND STRUCTURE OF DOUBLY BRIDGED ZIRCONIUM COMPLEXES

Structure of catalysts and polymers

The modification of the metallocene catalysts for the polymerization of α-olefin has been performed to increase the stereoregularity and molecular weight. Following those efforts, IPP with high stereospecificity and high molecular weight have been obtained by polymerization of propylene using C_2 symmetric silylene bridged bis(indenyl) zirconium with substituents at the 2- and 4-positions of the indenyl ligand. Regarding the mechanism that accounts for the performance, it is speculated that the introduction of steric hindrance to the ligand has a large influence on the control of the monomers coordination direction and the propagation direction of polymer chains while restricting the β-H elimination reaction. Many polyolefin manufacturers have been developing various metallocene catalysts. As a result, IPP, in which [mmmm] is 99%< with a melting point (161 °C) equal to conventional polypropylene from a Ziegler-Natta catalyst has been obtained (Figure 2).[2]

In addition, a low stereospecific polypropylene obtained using a metallocene catalyst has been reported. Ewen *et al.*[3] prepared a mixture of IPP and atactic polypropylene by polymerizing propylene at low temperature using a bis(cyclopentadienyl)titanium complex. Chien *et al.*,[4] Collins *et al.*[5] and Rieger *et al.*[6] prepared stereoblock polypropylenes consisting of different stereospecific block chains by using a bridged metallocene catalyst with C_1 symmetry (Figure 3a: ***2-a*** ~ ***2-c***), which have an asymmetry steric environment. As propylene repeats coordination and insertion in two basically asymmetric coordination sites, hemi-isotactic polymerization of propylene progresses. However, depending on the polymerization conditions, it is reported that low IPP is obtained because coordination and insertion deviates to one coordination site by isomerization of the coordination site (back-skip). Waymouth *et al.*[7] prepared stereoblock polypropylene with an atactic polypropylene-IPP block using 2-(substituted phenyl) indenyl complexes (Figure 3b: ***3***). These authors reported that these complexes changed into a complex with different stereocontrol ability by taking plural conformations because they have no bridge structure.

In this paper, we report that crystalline polypropylene, poly(1-butene) and poly(higher α-olefin) can be obtained with high activity by using a catalyst prepared from silylene doubly bridged bis(indenyl) complexes. The obtained crystalline polypropylene, poly(1-butene) and poly(higher α-olefin), showed a controlled 'stereo-random' microstructure in which stereospecific disorder is distributed evenly in the polymer chain.[8,9]

First, we evaluated a C_2 symmetric structure that connected the indenyl ring by 'two bridging' as a basic frame with the intent to control stereoregularity of polypropylene to a low level. Because the

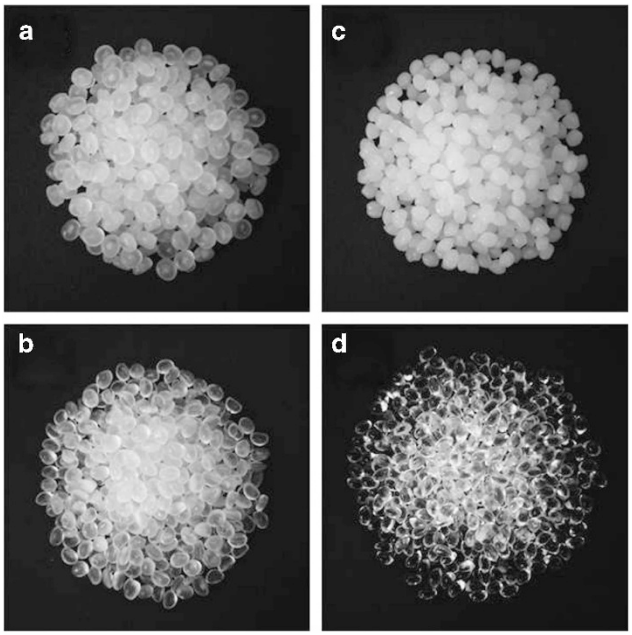


Figure 1 Polypropylene (PP) pellets. (**a**) High isotactic, high crystalline and high stiffness PP, (**b**) propylene–ethylene random PP, (**c**) propylene–ethylene block PP, (**d**) low isotactic, low crystalline and soft PP.

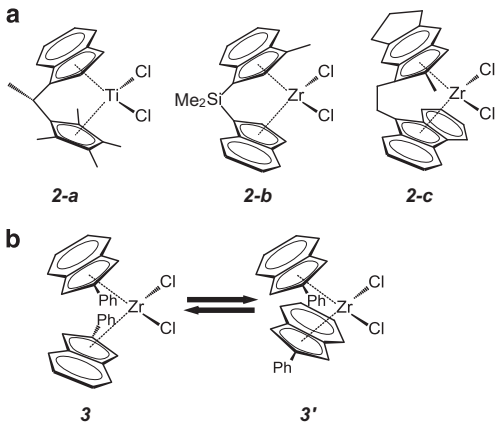
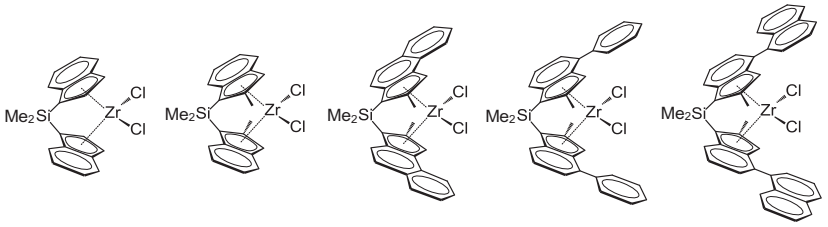


Figure 3 (**a**) Asymmetric single bridged metallocene catalyst and (**b**) oscillating metallocene catalyst between chiral and achiral geometries.



	1-a	*1-b*	*1-c*	*1-d*	*1-e*
[mmmm]	0.817	0.885	0.887	0.952	0.991
Tm (°C)	137	145	146	157	161
Mw (× 10^4)	3.6	19.7	33.0	72.9	92.0

Figure 2 Representative C_2-symmetric *ansa*-metallocene catalyst for isoselective propylene polymerization.

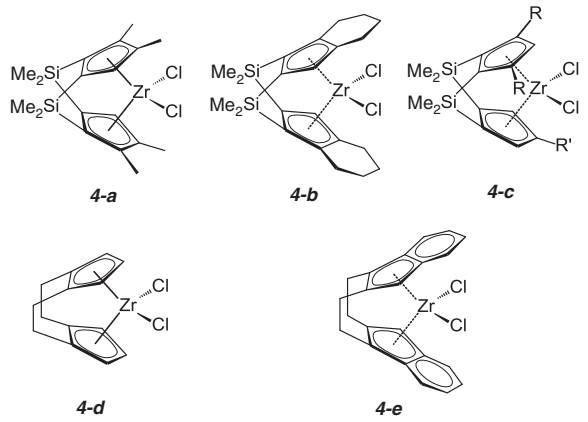


Figure 4 Doubly dimethylsilylene bridged bis(cyclopentadienyl) metallocene complexes and doubly ethylene bridged metallocene complexes.

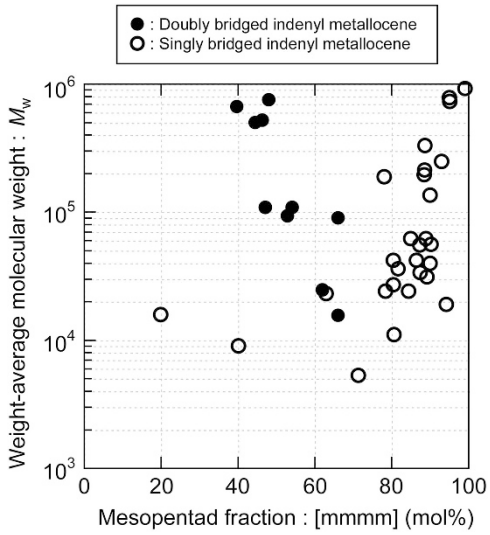
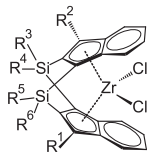


Figure 5 Relationship between mesopentad fraction and weight-average molecular weight for polypropylene polymerized by various catalysts.

positional relations of the indenyl ring with the coordination site in doubly bridged metallocene are markedly different from those in singly bridged metallocene, doubly bridged metallocenes are thought to have a structure that can decrease stereoregularity. Several doubly bridged metallocene complexes have been reported (Figure 4). A chiral Me_2Si-doubly bridged zirconocene was reported by Brintzinger *et al.*[10] (***4-a***, ***4-b***). A C_s symmetric doubly bridged zirconocene was reported by Bercaw *et al.*[11] (***4-c***). A doubly ethylene bridged bis(cyclopentadienyl) zirconocene was reported by Brintzinger *et al.*[12] and Hafner *et al.*[13] (***4-d***). A doubly ethylene bridged bis(indenyl) zirconocene was reported by Halterman *et al.*[14] (***4-e***). Most of these doubly bridged metallocene complexes have two cyclopentadienyl rings with two bridges, and their catalytic performance in propylene polymerization is not sufficient in terms of activity and the molecular weight of the polymer. In this report, we are the first to succeed in the synthesis of doubly Me_2Si-bridged bis(indenyl) zirconocene with a C_2 symmetric structure.

Regarding doubly bridged metallocenes, control of stereoregularity with high catalytic activity and high molecular weight would become possible in propylene polymerization, presumably because the



5-1 ~ 5-8

	R^1	R^2	R^3	R^4	R^5	R^6
5-1	H	H	Me	Me	Me	Me
5-2	Me	Me	Me	Me	Me	Me
5-3	n-Bu	n-Bu	Me	Me	Me	Me
5-4	CH_2SiMe_3	CH_2SiMe_3	Me	Me	Me	Me
5-5	CH_2SiMe_3	H	Me	Me	Me	Me
5-6	CH_2SiMe_3	CH_2SiMe_3	Me	Ph	Ph	Me
5-7	CH_2SiMe_3	CH_2SiMe_3	Me	Ph	Me	Ph
5-8	CH_2SiMe_3	CH_2SiMe_3	Me	Me	Ph	Ph

Figure 6 Doubly dimethylsilylene bridged bis(indenyl) zirconocene complexes used in this study.

stereospecific coordination site for monomer opens widely. Figure 5 shows the relationship between mesopentad ([mmmm]) and the molecular weight (M_w) of polypropylene with singly bridged and doubly bridged bis(indenyl) metallocene. In the case of singly bridged bis(indenyl) metallocene catalyst, when [mmmm] decrease, M_w also decreases. However, low [mmmm] with high M_w polypropylenes were obtained using doubly bridged bis(indenyl) metallocene.

The doubly bridged bis(indenyl) metallocene mentioned in this article is shown in Figure 6. The synthetic route is shown in Figure 7. Coupling reaction of dimethyl(2-indenyl)dichlorosilane generated a doubly bridged bis(indenyl) ligand with a 30% yield. A variety of substituents were introduced to the 3-position of the indenyl ring.

The molecular structures of complexes ***5-1*** and ***5-4*** were determined using single crystal X-ray analysis. The ORTEP drawings of ***5-1*** are illustrated in Figure 8. Selected bond lengths and angles, determined by X-ray crystallography, are summarized in Table 1. In complexes ***5-1*** and ***5-4***, the Cp(c)-Zr-Cp(c) angles (121.04°,121.7°) were smaller than those in the singly bridged bis(indenyl)zirconium dichloride complex ***1-a***. The interplaner angle between the two indenyl planes (77.52°) of ***5-4*** was considerably larger than that in the singly bridged bis(indenyl)complexes. That larger angle between the two indenyl ligands indicates that the coordination site in ***5-4*** opens widely. The angle was also larger than that in the doubly bridged bis(tetrahydroindenyl)zirconium complex ***4-b***.[15] By contrast, the CR(1)-Zr-CR(1′) angle in ***5-1*** and ***5-4*** was smaller than that in other complexes. These structural characteristics for these doubly bridged bis(indenyl) complexes indicate that high catalytic activity would be due to the open coordination site.

Polymerization behavior

Batch propylene polymerizations by activation with methylaluminoxane (MAO) using various doubly bridged metallocenes were conducted in heptane at 50 °C. The results are shown in Table 2. With complex ***5-1*** having no substituents on the indenyl ligand, [mmmm] of polypropylene was 0.66. The complexes ***5-2*** ~ ***5-5*** with the substituent on the 3-position of the indenyl ligand yielded low [mmmm] (0.4-0.5). By contrast, the 0.014 of mis-insertion was observed complex ***5-1***, but in complex ***5-2*** ~ ***5-4*** it was not detected. The substituent on the 3-position of the indenyl ligand is thought to sterically prevent the 2,1-insertion of propylene. When the monosubstituted complex ***5-5*** is used in polymerization, [mmmm] was slightly larger than the bis-substituted indenyl complex. Higher molecular weight of polypropylene was obtained with complex ***5-4*** than with complex ***5-1***. As shown in Table 2, [mmmm] of polypropylene decreased by introducing a substituent on the 3-position of the ligand. In the case of 3-trimethylsilylmethyl as a substituent ***5-4***, the [mmmm] of polypropylene was the smallest.

The addition of hydrogen during polymerization caused a significant increase in catalytic activity. Complex ***5-1*** showed higher activity

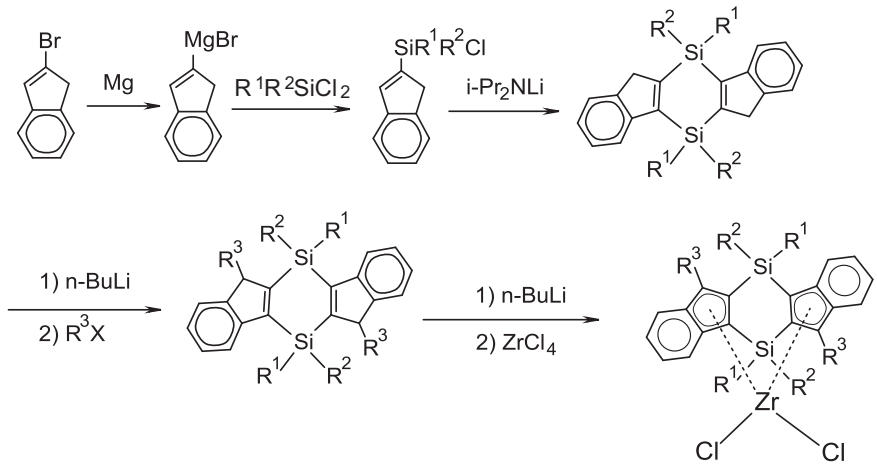


Figure 7 Synthetic route of doubly bridged bis(indenyl) metallocene.

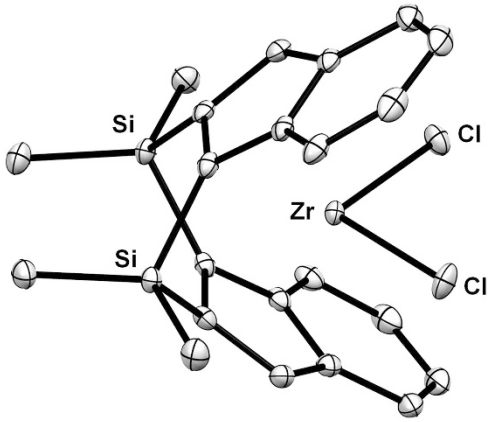


Figure 8 Molecular structure of complex ***5-1*** with 50% probability thermal ellipsoids depicted and H atoms removed for clarity.

upon adding hydrogen. This was most likely due to the reactivation of the active site's dormant state.

Propylene polymerization results with borate: $[PhNMe_2H][B(C_6F_5)_4]$ and triisobutylaluminium are shown in Table 3.

Owing to the steric hindrance of the substituent on the 3-position of the indenyl ring, β-H abstraction from the propagating polymer chain would be restricted to yield high-molecular-weight polymer. The reason that stereoregularity decreased by introduction of a substituent on the 3-position of the indenyl group would be the steric hindrance in the propagating polymer chain. As a result, the control of stereoregularity became possible with high activity (Figure 9).

CHARACTERISTICS OF LMPP

Melting behavior

Crystallization of polypropylene is controlled by structural regularity. Figure 10 shows the relationship between the enthalpy of fusion ΔH and the melting point T_m, and the mesopentad fraction [mmmm] of polypropylene. Both ΔH and T_m monotonically decrease with the lowering [mmmm] and disappear at less than 30 mole% of [mmmm]. The structural irregularity caused the melting point depression, and the crystallinity was completely destroyed when the number of irregular units became large.

The component causing the melting point depression may be a constituent of the polymer itself. If a copolymer consists of A units that crystallize and B units that do not, then the equation that expresses the melting point depression in a random copolymer is as follows:[16]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln x_A \quad (1)$$

where T_m^0 and T_m are the melting temperature of the homopolymer and copolymer, respectively, ΔH_u is the enthalpy of fusion per repeating chain unit and x_A is the mole fraction of monomer A.

In low IPP, assuming that stereoregular sequences correspond to the crystallizable unit and stereo-irregular sequences correspond to the non-crystallizable one, the fraction of mesopentad [mmmm] can be used instead of fraction A; so, equation (1) is changed as follows:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln[\mathrm{mmmm}] \quad (2)$$

Figure 11 shows the plot of $1/T_m - 1/T_m^0$ against $\ln[mmmm]$. Because a good linearity was obtained from this plot, it was found that the melting point depression follows the above relationship. From the plot in Figure 11, we can calculate $\Delta H_u = 2.6$ kcal mol^{-1} in close agreement to the literature values of 1.8–2.4 kcal mol^{-1}.[17]

Table 1 Selected bond lengths and angles for bridged metallocene complexes

	5-1	*5-4*	*1-a*[15]	*4-b*[10]
Zr(1)-CR(1) (Å)	2.217	2.260	2.241	—
Zr(1)-Cl(1) (Å)	2.422	2.427	2.431	2.435
Cl(1)-Zr(1)-Cl(1') (deg)	99.96	100.06	98.76	99.7
CR(1)-Zr(1)-CR(1') (deg)[a]	121.04	121.7	127.81	122.5
E1-E2 (deg)[b]	68.92	77.52	61.94	72.9

[a]CR: Center of the five-membered rings of the indenyl ligands.
[b]Interplaner angle between the two indenyl ligands.

Crystallization kinetics

Figure 12 shows the typical time evolution of wide-angle X-ray diffraction profiles $I(2\theta, t)$ during isothermal crystallization at room temperature after rapidly dropping the temperature from 150 °C. It was observed that the diffraction peaks appear because of crystallization and that the diffraction peak intensities increase with lapse of time and cease to change at time $t >$ ca. 10 min. This indicates that

Table 2 Polymerization of propylene by *5-1* ~ *5-5* complexes with MAO[a]

Complex (μmol)	*Temp. (°C)*	*Yield (g)*	*Activity (kgPP/gZrh)*	M_w[b]	*[η] (dl g^{-1})*	*[mmmm]* [c]	*2,1-, 1,3-bond*
5-1 (1)	50	10.0	110	90 000	0.75	0.661	0.014
5-1 (0.5)[d]	60	52.6	2305	—	0.27	0.686	0.018
5-2 (1)	50	28.7	315	753 000	4.37	0.481	0
5-3 (1)	50	19.5	214	499 000	3.18	0.445	0
5-4 (0.5)	50	70.1	1537	664 000	3.39	0.398	0
5-5 (1)	50	38.8	425	521 000	2.71	0.464	0.011

[a]Reaction conditions: C3 0.65MPa, [Zr]/[MAO] = 1/1000, 60 min.
[b]Determined by GPC.
[c]Determined by 13C NMR spectroscopy.
[d]Reaction conditions: C3 0.77MPa, H2 0.03 MPa, [Zr]/[MAO] = 1/1000, 30 min.

Table 3 Polymerization of propylene by *5-1* ~ *5-8* with borate and alkylaluminium[a]

Complex (μmol)	*Temp. (°C)*	*Yield (g)*	*Activity (kgPP/gZrh)*	M_w[b]	*[η] (dl g^{-1})*	*[mmmm]* [c]
5-1 (0.2)	60	7	406	15 600	0.18	0.661
5-2 (0.2)	60	66	3612	108 500	0.82	0.542
5-3 (0.2)	60	69	3766	93 400	0.73	0.529
5-4 (0.2)	60	233	12760	108 300	0.82	0.472
5-5 (0.2)	60	94	5169	24 600	0.26	0.620
5-6 (0.2)	60	45	2466	—	0.86	0.424
5-7 (0.2)	60	70	3837	—	0.59	0.261
5-8 (0.2)	60	128	7011	—	0.53	0.276

[a]Reaction conditions: C3 0.65 MPa, H2 0.05 MPa, [Zr]/[B] = 1/4.
[b]Determined by GPC.
[c]Determined by ^{13}C NMR spectroscopy.

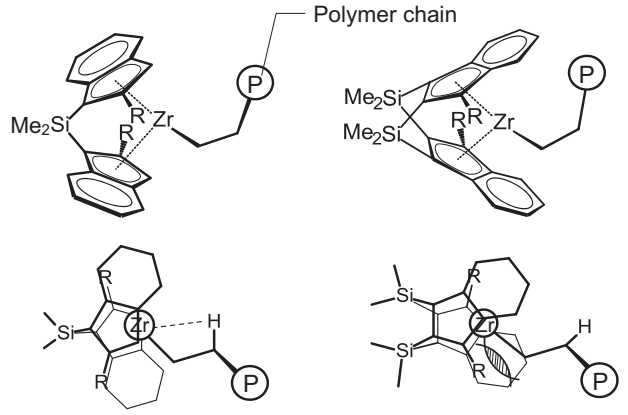


Figure 9 Steric differences between singly bridged and doubly bridged metallocene ligand.

spherulitic growth has occurred and then terminated because of the impinging of spherulites. Thus, we conveniently evaluated the crystallization rate by using the time evolution of the diffraction peak. The diffraction peaks are attributed to the α-crystal form of polypropylene.[18] Figure 13 shows the change in intensities with time at $2\theta = 13.5$ degrees at room temperature. We fit the Avrami equation below using the least square method.

$$\frac{I(t)}{I(t_x)} = 1 - \exp[-kt^n] \tag{3}$$

where $I(t)$ and $I(t_x)$ are diffraction intensity at time under spherulite growth and time at cessation of growth, respectively, k is the rate

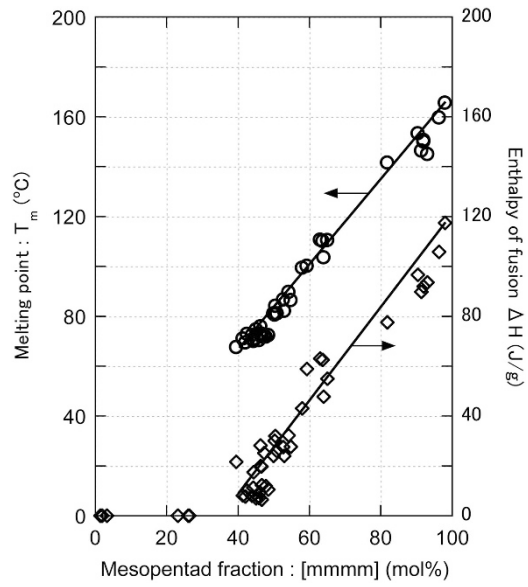


Figure 10 Relationship between mesopentad fraction and enthalpy of fusion and melting point for polypropylene polymerized by various catalysts.

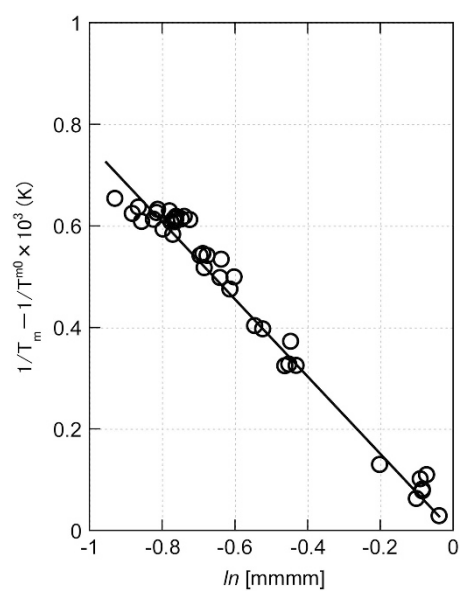


Figure 11 Plot of $1/T_m - 1/T_m^0$ against ln[mmmm] for isotactic polypropylene with various mesopentads.

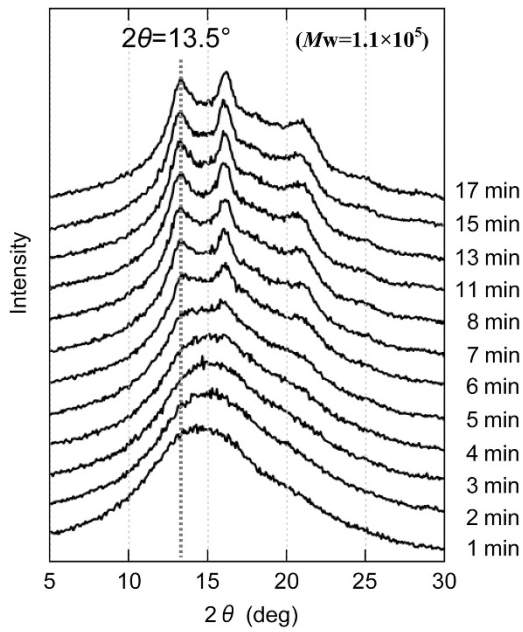


Figure 12 Time evolution of WAXD profiles during the isothermal crystallization at room temperature after rapidly dropping temperature from 150 °C (T-drop). Time after T-drop is shown on the right side of each profile.

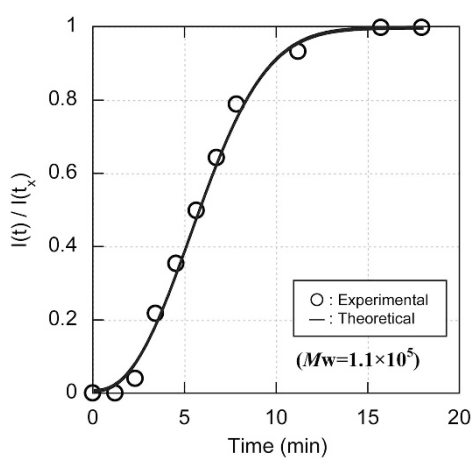


Figure 13 Change of diffraction peak intensity with time at room temperature.

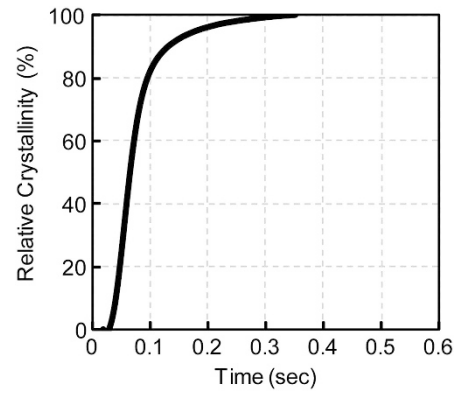


Figure 14 Time change of crystallinity for IPP-STD. Crystallinity was measured using the Flash-DSC method and calculated as $\Delta H/\Delta H_0$, where ΔH is exothermic heat, ΔH_0 is enthalpy of complete PP, i.e., $\Delta H_0 = 209\ \mathrm{J\ g^{-1}}$.

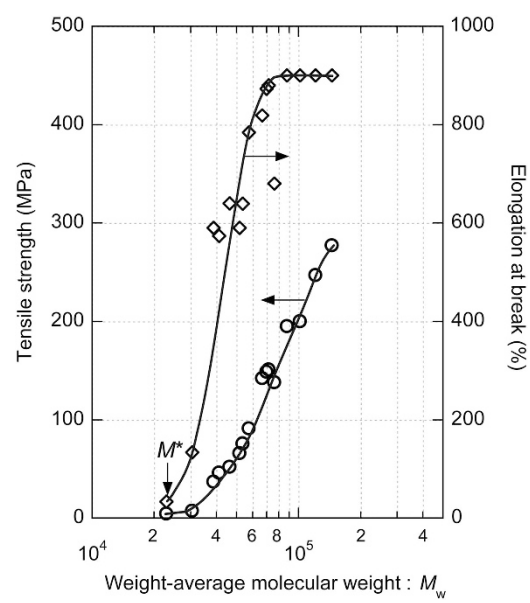


Figure 15 Tensile strength and elongation at break of LMPP as a function of weight-average molecular weight.

constant, and n is the Avrami index. We listed the kinetic parameters determined from the Avrami equation. Using these values of kinetic parameters, one can obtain the half-time for crystallization $\tau_{1/2}$ given by

$$\tau_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{4}$$

Thus, we obtained $\tau_{1/2}$ as 6 min. As shown in Figure 14, the crystallization rate of general IPP (IPP-STD, $T_m = 160$ °C) was measured using the Flash-DSC technique (Flash DSC 1: Mettler Toledo, Tokyo, Japan). After melting at 230 °C and quenching to 25 °C with s rate of 2000 °C min^{-1}, we then recorded the exothermic heat due to crystallization. We evaluated the half-time for crystallization of IPP-STD to be $\tau_{1/2}$ = ca.0.06 s using equations (3) and (4). Comparing the lifetimes of LMPP and IPP-STD shows that the lifetime $\tau_{1/2}$ of LMPP was much longer than that of IPP-STD.

Mechanical properties

From the relationship between mesopentad [mmmm] and enthalpy of fusion ΔH in Figure 10, it was found that the crystallinity of LMPP with [mmmm] = 46% was ca. 15%. This value was highly comparable to that of general polypropylene. LMPP also shows superior softness compared with conventional polypropylene and shows an excellent elasticity due to its low crystallinity. Introducing an elastic behavior in LMPP is a physical crosslink method through crystallization.

It is important to control the molecular weight of LMPP as well as its stereoregularity for the development of elasticity properties.

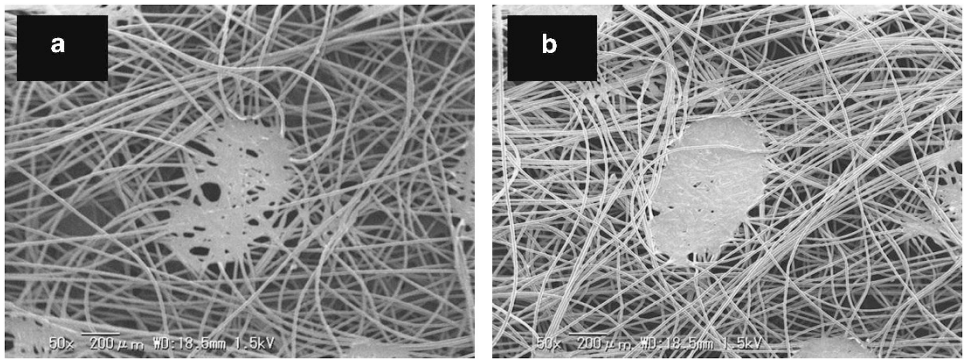


Figure 16 Scanning electron microscope images of spunbond nonwoven fabrics: (**a**) spunbond fibers using only conventional PP (1.7 denier), (**b**) spunbond fibers (1.2 denier) using PP/LMPP (=90 wt% /10 wt%) blend (1.2 denier).

Figure 15 shows the tensile strength and elongation at break as a function of molecular weight as measured using gel permeation chromatography. Although both the tensile strength and elongation were extremely small at low molecular weight, they remarkably increase above a certain molecular weight. We defined the specific molecular weight above which the tensile strength and elongation at break begin to increase as $M^{\star}=2\times10^{4}$ above which the tensile strength and elongation at break begin to increase. Because $M^{\star}$ is very close to the critical molecular weight of entanglement between molecular chains (ca. 1.5×10^{4}),[19] the elasticity of LMPP is thought to be affected by the entanglement in the amorphous phase.

APPLICATIONS OF LMPP

The production process for LMPP can yield a wide range of molecular weights through the precise control of the polymerization temperature, which was previously difficult. Furthermore, LMPP, which has a low melting point and is soft, can be supplied in pellets by establishing a new pelletizing system. Conversely, conventional low-molecular-weight and low modulus poly-α-olefins such as APAO are difficult to supply as pellets because of their tackiness.

LMPP can be applied to hot melt adhesives especially for base polymer for diaper construction, for which stable growth is foreseeable in the future. Furthermore, LMPP is anticipated to be a base polymer for adhesives because of its sprayabilities at low temperature and high adhesion strength, as derived from the modest solidification rate of the homogeneous component of LMPP.

An elastic nonwoven polymer with excellent elasticity was obtained using the elastomeric property of LMPP. A direct use of this polymer can be in the field of nonwoven fabrics. Spunbond nonwoven fabrics with excellent softness are obtained by blending LMPP with conventional polypropylene and by controlling the crystallinity ratio and crystallization rate. Spunbond nonwoven fabrics of fine denier and high strength are obtained by exploiting the stable excellent spinability and high spinning rate, and melt blown nonwoven fabrics with high hydrostatic head were obtained by exploiting the stable processability under ultimate spinning conditions. When fibers of spunbond become finer under the same fabrication conditions, the number of fibers related to adhesion by embossing increases to yield a nonwoven fabric with a higher strength (Figure 16).

Addition of LMPP improved the processability of biaxially oriented film by reducing the uneven film breaking. This reduction of uneven thickness is derived from the reduction of elongation yield under high processing rate conditions.

CONCLUSIONS

Polyolefins are important materials for industrial use. Soft polyolefins possess excellent properties (flexibility and elastomeric property). Therefore, the development of non-sticky and soft polyolefins has long been desired. We have successfully developed a novel polypropylene (LMPP) with low isotacticity and high molecular weight that is synthesized using specific C_2-symmetric doubly bridged metallocene complexes. LMPP has some isotactic sequences in stereorandom order, and its tacticity can be precisely controlled by designing the metallocene catalysts. LMPP can be provided as pellets and be applicable to hot melt adhesives, elastic fibers, nonwoven fabrics and so on. We anticipate that this low IPP will grow to be an important raw material for high-performance materials.

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Yutaka Minami was born in 1968 in Tokyo, Japan. He received his Master degree of Engineering in 1994 from Tokyo University of Agriculture and Technology. He joined Idemitsu Petrochemical Co., Ltd. in 1994.

Tomoaki Takebe was born in 1960 in Niigata, Japan. He received his Master degree in Engineering from Kyoto University in 1985. He joined Idemitsu Petrochemical Co., Ltd in 1988. He obtained his Doctoral degree in Engineering in 1990 from Kyoto University.

Masami Kanamaru was born in 1967 in Yamanashi, Japan. He received his Master degree in Engineering from Tokyo Institute of Technology in 1992. He joined Idemitsu Kosan Co., Ltd in 1992. He obtained his Doctoral degree in Engineering in 1995 from Tokyo Institute of Technology.

Takuji Okamoto was born in 1961 in Osaka, Japan. He received his Master and Doctoral degrees in Science from Osaka University in 1985 and 1988, respectively. He joined Idemitsu Kosan Co., Ltd. in 1988.