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Award Accounts

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Development of Polyethylene Copolymers Manufacturing Technologies and Synthesis of New Functionalized Polyolefins with Designed Catalysts

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Advanced supported metallocene catalysts for commercialization were developed in the consequence of improving catalyst performances and accomplishing industrial tasks. The relationship between molecular structures and physical properties of ethylene and α-olefin copolymers produced with metallocene catalysts was also investigated. Metallocene catalyzed ethylene/α-olefin copolymers have excellent physical properties (high strength, high clarity, good heat sealability) owing to a homogeneous molecular structure that had never been achieved by conventional Ziegler–Natta catalysts. We have also succeeded in producing long chain branched ethylene copolymers with narrow molecular weight distributions but excellent melt properties by the use of the catalyst technologies to control of the branches in a polymer chain. Moreover, we have found the first example of metallocene-catalyzed allyl alcohol or allylamine incorporation having only one CH_2 chain spacer into the nonpolar polymer backbone, using new metallocene and methylaluminoxane with high activity at high temperature. This is the first example of predominant chain end and/or site-selective introduction of polar groups into the polyolefins.

Polyolefins such as polyethylene and polypropylene are the major plastics as regards production and demand, the demand still grows with a higher annual growth rate than other plastics. In the future, this tendency, in other word the replacement of the other materials, will be accelerated because of the ecological and economical reasons, i.e., the safety and the lower prices.

There were four major revolutions in the past that affected industrial polyolefin technologies. The first was the discovery of high pressure polyethylene, the second was the discovery of Ziegler–Natta (Z/N) catalyst to produce polyethylene and polypropylene, the third was the invention of linear low density polyethylene (LLDPE) and the fourth was the discovery of metallocene catalysts by Prof. Kaminsky in 1980.[1]

The metallocene catalyst comprising a zirconium bis(cyclopentadienyl) compound and methylaluminoxane (MAO) showed higher activity than conventional Z/N catalyst and also had a single-site feature that enables the precise control of molecular structure. Therefore, the metallocene catalysts were so called "single-site catalysts (SSC)" and had the capability to produce homogeneous polyolefins unattainable by conventional Z/N catalysts that were the multi-site catalysts (MSC). Thus metallocene catalysts produce different polymers compared to Z/N catalysts, so this technology has been widely applied to produce new polyolefins such as PE, PP, polystyrene (PS), elastomers, and functionalized polyolefins (Fig. 1).

We have succeeded in establishing some new production technologies of polyethylene copolymers, as described below, and also realization of their commercialization.

1. Polyolefins having some property advantages compared to existing MSC catalyzed polyolefins.
2. Polyolefins having controlled branches with a wide range of densities.
3. Polyolefins having polar groups at a chain end and/or a inner site of a polymer chain with a wide range of densities.

1. Ethylene and α-Olefin Copolymers

1-1 Catalyst Development. Homogeneous metallocene single-site catalysts produce various types of polyolefins in extremely high yields, although their direct utilization for industrial olefin polymerization processes has encountered various difficulties. The major disadvantages of the homogeneous catalysts are the lack of polymer morphology control and reactor fouling. A supported catalyst allows control of morphology in a economical gas-phase process and permits the use of less aluminum compounds as the activator while still offering simple control of polymer properties by ligand variation.

The solid supported metallocene catalyst particles generate polymer coherent grains, instead of the polymer dust produced by a dissolved homogeneous metallocene catalyst. Metallocene catalysts that are heterogenised, e.g., on a silica gel support, can thus be readily used in existing Ziegler–Natta production facilities, for slurry or gas-phase reaction systems.

Supported catalysts have been obtained by pretreatment of silica gel with methylaluminoxane (MAO), followed by reaction of the formed SiO_2–$[Al(Me)O]_n$ with metallocene complexes of various symmetry, giving solids that might be activat-

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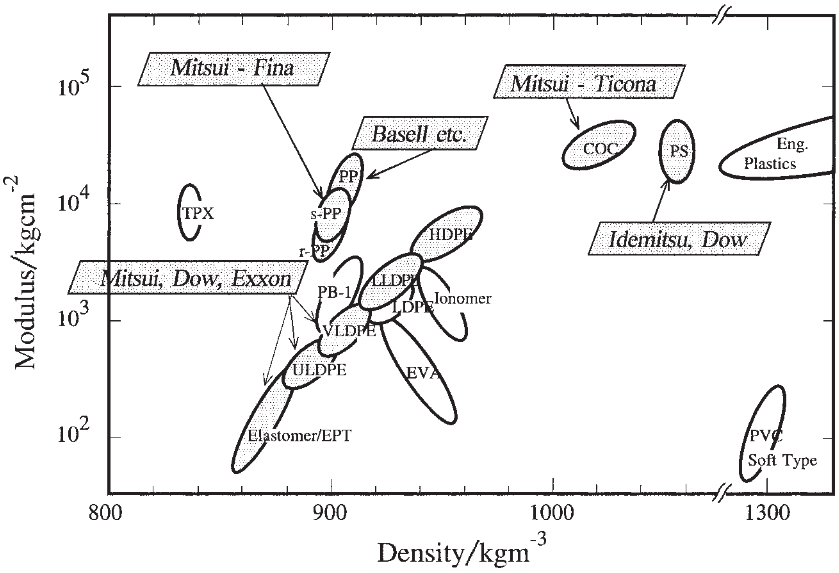
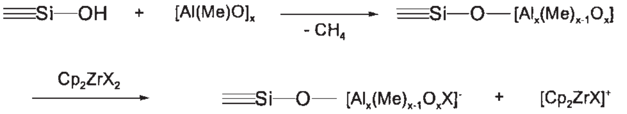


Fig. 1. Polymers expected to apply metallocene technology (shaded polymers in the figure), and active companies to develop this technology.



Scheme 1. Presumable reaction pathway in immobilized metallocene catalyst.

ed with common alkylaluminums.[2–9] Although some important aspects concerning the nature of metallocene-supported catalysts are not clear at the present stage, presumably the metallocene is immobilized by an ionic interaction (Scheme 1). Therefore, it is obvious that catalyst precursors formed can be easily activated with common alkylaluminums, as described before.

There were many factors to control the supported catalyst performances, e.g., ligand variation of metallocenes, preparation methods of MAO, selection of supports, and suppression of static electricity. Our advanced catalyst for commercialization is a comprehensive compilation of settling these factors. Additionally, another important factor was the development of a two-stage polymerization process to control molecular weight distribution (MWD) and composition distribution (CD); these affect the quality and the processability of polymers.

1-2 Molecular Structure. The tested samples were mainly ethylene and 1-hexene copolymers produced in gas phase reactor with metallocene catalyst. The comonomer content of ethylene copolymers produced by conventional MSC varies according to the length of the main-chain of the polymer. The low molecular weight polymers tend to contain more comonomers than the high molecular weight polymers do (Fig. 2).

These low molecular weight polymers are undesirable fractions that cause low performance such as high blocking characteristics of the film and low clarity of the film. In the case of SSC's LLDPE, MWD and CD are very narrow compared with MSC's LLDPE (Figs. 3, 4), and therefore it contains a low amount of *n*-decane solubles (Fig. 5).

1-3 Crystalline Structure. The MSC-based LLDPE contains high-molecular-weight tails having few comonomer

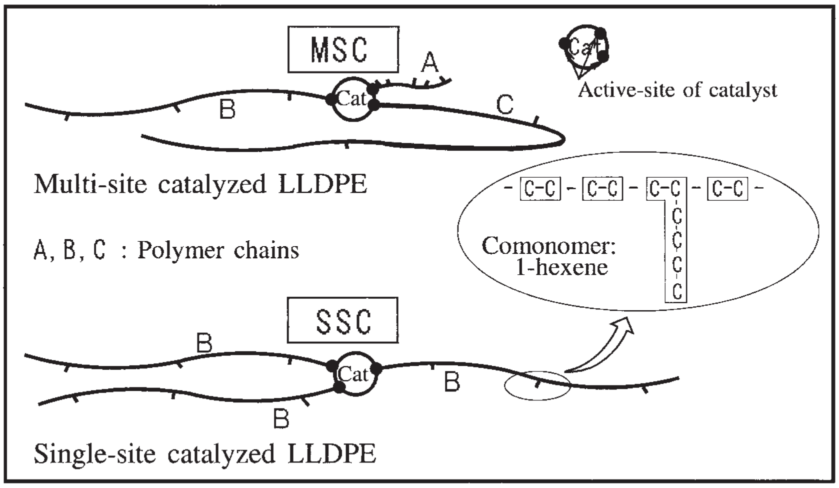


Fig. 2. Differences between multi-site and single-site catalysts.

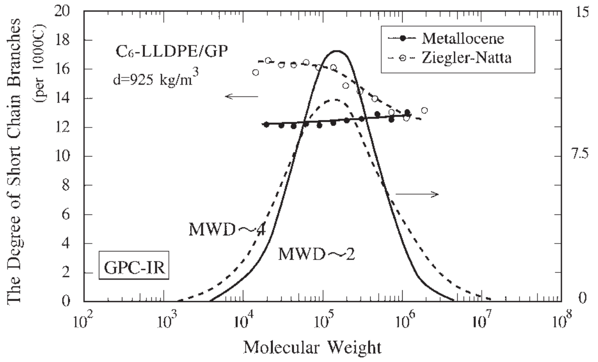


Fig. 3. GPC-IR curves of LLDPEs produced by SSC and MSC.

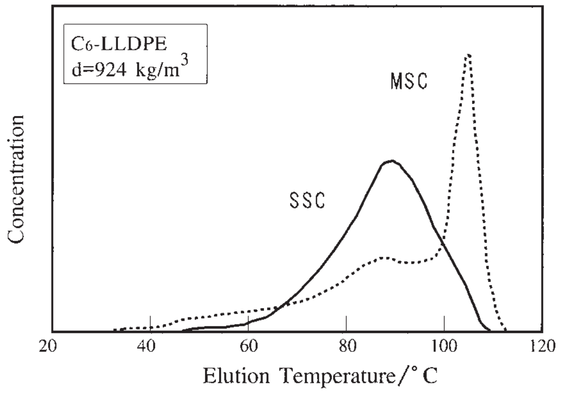


Fig. 4. Comparison of composition distribution by means of temperature rising elution fractionation (TREF) method.

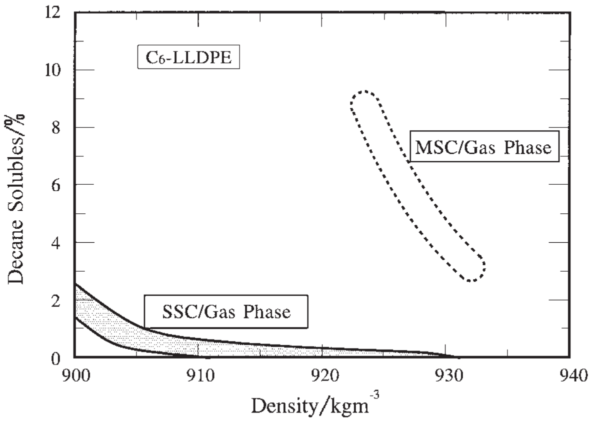


Fig. 5. Decane solubles comparison between SSC and MSC.

branches; this portion tends to nucleate faster than the low molecular chains, so it forms thick lamellae (high T_m). On the other hand, CD of SSC's LLDPE is very narrow and the nucleation speed among chains may be almost the same, so it is conceivable that homogeneous nucleation occurs. Therefore one would expect that the lamellar thickness of SSC's LLDPE would be thinner (lower T_m) than that of MSC's LLDPE (Fig. 6).

The melting point (T_m) of SSC's LLDPE decreased with decreasing of density, and on the contrary the T_m of MSC's LLDPE decreased very little according to the expectated crystallization mechanism (Fig. 7).

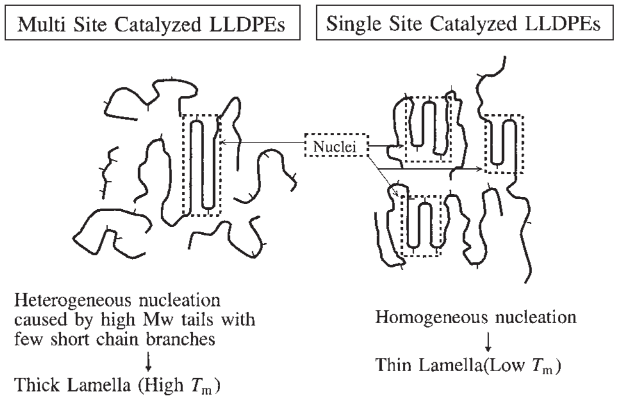


Fig. 6. Crystallization mechanism of MSC and SSC LLDPE.

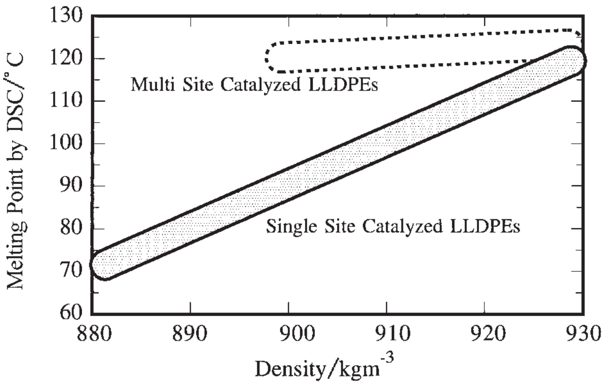


Fig. 7. Melting point versus density.

Table 1. Solid Structure of SSC and MSC LLDPE

	Single Site Catalyzed LLDPE	Multi Site Catalyzed LLDPE
Density/kg m^{-3}	923	922
MFR/g (10 min)$^{-1}$	1.1	1.0
DSC T_m/°C	117	123
Crystallinity/%	55.5	54.7
Long period/A	235	278
Probability for forming tie molecules/×100	3	1

The dependence of density on comonomer contents is also different for SSC and for MSC. MSC's LLDPE needs more comonomers than SSC's LLDPE does at the same density. Characterization results of solid structures of SSC- and MSC-based LLDPEs are shown in Table 1. The probabilities for forming tie molecules of SSC's LLDPE estimated by Brown's method[10] was higher than that of MSC's LLDPE, because the lamellar thickness is thinner.

The solid structures and properties of LLDPE are affected by the kind of α-olefin as used comonomers. Hosoda[11] reported the differences in the probabilities of branches included in the lamellar crystal for various LLDPE. He pointed out that the probability of short chain branches being included in a crystal lamellae was decreasing with the length of the branch. For example, the probability of a methyl branch being included in the crystal was almost triple that of butyl branch inclusion and the case of ethyl branch was twice of that. Presumably, the completeness of crystals is increasing with the length of short chain branches. So, the density of LLDPE depends on comonomer contents but also the kind of short chain branch. As shown in Fig. 8, higher comonomer contents are necessary with shorter comonomer, when we want to produce the same density of ethylene and α-olefin copolymer.

1-4 Solid Properties. SSC-based LLDPE showed excellent properties: high impact strength (Fig. 9), high stress crack resistance, high clarity (Fig. 10), and good heat sealability (Fig. 11), because of the homogeneous crystal structure that is due to narrow CD. The impact strength of SSC's LLDPE film is about three times that of MSC's LLDPE at the density of around 923 kg/m^3, and it corresponds to a calculation of the probabilities for forming tie molecules. The heat seal plateau temperature was the lowest temperature at which the heat seal strength reaches its maximum level as a function of heat seal temperature as shown in Fig. 11. And at this plateau temperature, failure mode changes from interfacial delamination to cohesive failure. The heat seal temperature of SSC-based LLDPE was lower than that of MSC-based LLDPE.

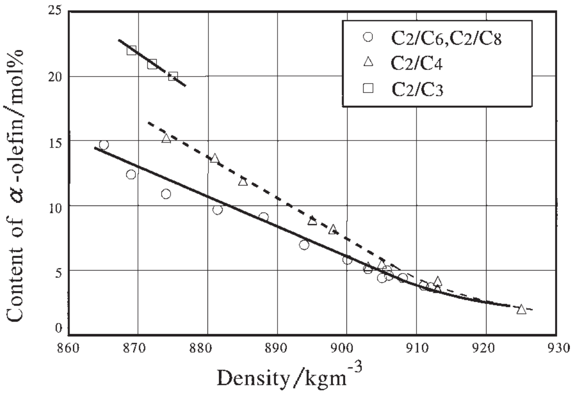


Fig. 8. The density dependence of the content of α-olefin of various ethylene copolymers.

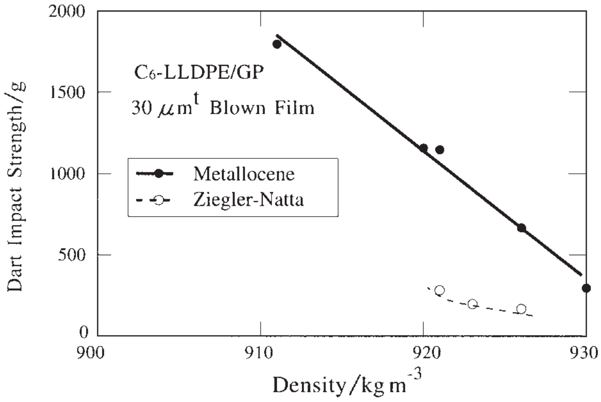


Fig. 9. Impact strength versus density.

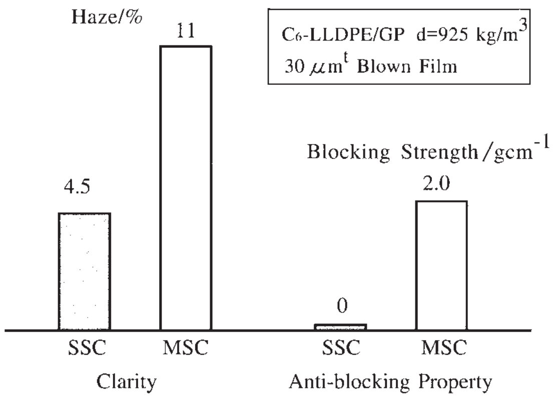


Fig. 10. The clarity and anti-blocking property of blown films of SSC and MSC catalyzed LLDPE.

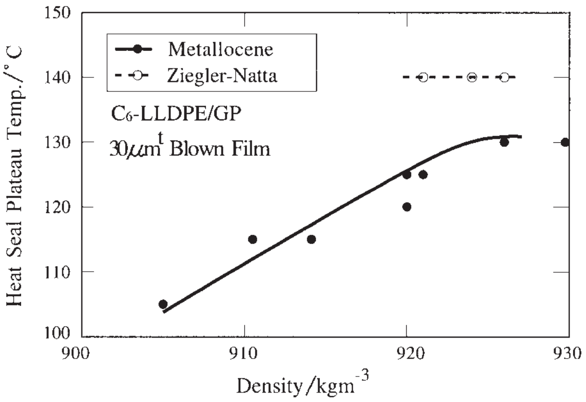


Fig. 11. The comparison of heat seal property between SSC and MSC catalyzed LLDPE's blown films.

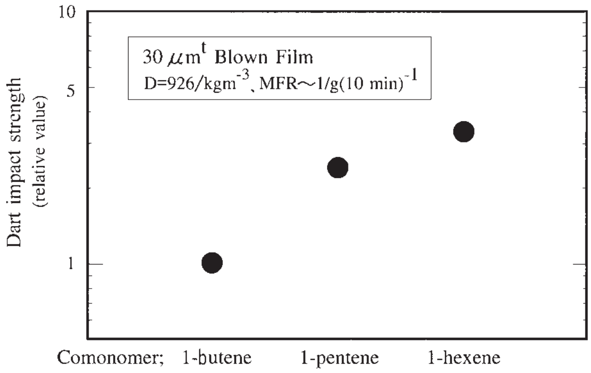


Fig. 12. Comonomer dependence on impact strength.

The anti-blocking characteristics of SSC-based LLDPE were also excellent because the material contained very few low molecular chains that cause blocking of the film (Fig. 10).
The kind of comonomer also affects the mechanical properties, e.g., the dart impact strength was shown as a function of comonomer type (Fig. 12). The impact strength of the ethylene/1-hexene copolymer was about four times that of ethylene/1-butene copolymer.

Figure 13 shows the density dependence of the tensile stress of various ethylene/α-olefin copolymers. It was found that the strength of ethylene copolymer was increasing with the length of short chain branch and that it leveled off at the butyl branch. The long chain branch (LCB) also affects the strength of ethylene copolymer. The strength of ethylene/1-octene copolymer with LCB decreases and becomes almost same level of the strength of ethylene/1-butene copolymer without LCB. This phenomenon arises from a decrease of the lamellar crystal perfection by LCB.

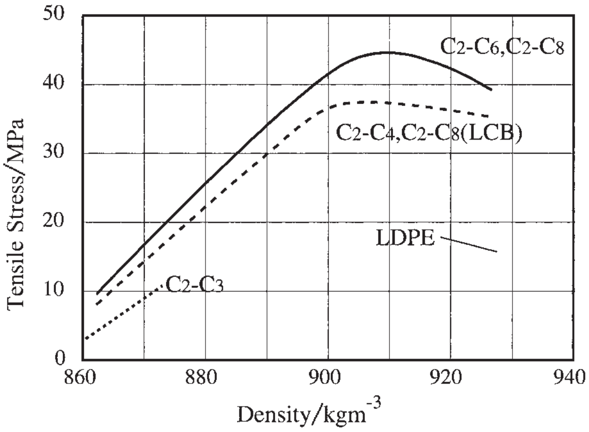


Fig. 13. Comonomer dependence on tensile strength of various copolymers composed of ethylene and α-olefin.

2. Long Chain Branched Copolymers

Another important factor for use in commercial scale is processabilities of copolymers. When molded into articles such as film, copolymers of ethylene and α-olefins of 3 to 20 carbon atoms are desired to have excellent mechanical strength such as tensile strength, tear strength, or impact strength and also excellent heat resistance, stress crack resistance, optical characteristics and heat-sealing properties in comparison with conventional high-pressure low density polyethylenes. They are known as materials that are particularly useful for the preparation of inflation film or the like.

If the ethylene copolymers have such excellent characteristics, then when such copolymers come to be narrower in molecular weight distribution represented by the ratio (M_w/M_n) of weight average molecular weight (M_w) to number average molecular weight (M_n), the molded articles obtained therefrom, such as film, are found to be less tacky. However, when these ethylene copolymers having a narrow molecular weight distribution are melted, there were some drawbacks. For example, their flowability represented by the ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg as measured at 190 °C was small, with the result that they become poor in moldability.

Therefore, if ethylene copolymers which are small in value of M_w/M_n and narrow in molecular weight distribution, while having large values of MFR_{10}/MFR_2 and excellent flowability, come to be obtained, such ethylene copolymers will certainly be of great commercial value. We have studied under such circumstances as mentioned above. As a result, we have found that, by the use of a metallocene **1** (Chart 1) wherein hafnium ion is bound to the ethylene bis-indenyl group, an olefin (co)polymer of high molecular weight can be prepared with large values of MFR_{10}/MFR_2 and thus an olefin copolymer of much higher comonomer content can be obtained.[12]

Brintzinger[13] and Ewen[14] have succeeded to prepare *ansa*-metallocenes and they have produced highly isotactic and syndiotactic polypropylene, respectively, by use of Zr catalyst as we mentioned in introduction. After these works, a high molecular weight isotactic polypropylene was obtained by polymerization of propene in the presence of a catalyst system comprising 1,1′-ethylenebis(indenyl)hafnium dichloride **1** and aluminoxane; this isotactic polypropylene having a narrow molecular weight (M_w/M_n) of 2.1–2.4.[15] These results clearly show that filled 4f orbitals in Hf catalyst provides a useful advantage in olefin polymerization. We applied this catalyst system to the production of ethylene copolymers, aiming at obtaining high molecular weight copolymers with high polymerization activities. We examined ethylene/propene or ethylene/octene copolymerization at 40–90 °C under atmospheric pressure.

The results of polymerization obtained with this catalyst system comprising 1,1′-ethylenebis(indenyl)hafnium dichloride **1** and aluminoxane is summarized in Table 2. The indenyl derivative **1** produced higher molecular weight and low density copolymers. This result suggests that metallocene **1** and aluminoxane is one of the catalyst candidates for ethylene copolymers.

Our first attempt to produce high molecular weight copolymers was gratifyingly successful. To explain producing such high molecular weight copolymers, we suggest that shorter ligand–metal distances result in lower Lewis acidities for hafnium metallocene relative to zirconium analogues, which will suppress the chain transfer by α-hydride elimination. Another interesting feature of metallocene **1** is the nature of the relatively high comonomer conversion, as exemplified by producing lower density copolymers. It is suggestive that the filled 4f orbitals providing a useful advantage in a catalytic reaction.

It is required for the ethylene copolymers to be small in value of M_w/M_n and be large in value of MFR_{10}/MFR_2 as regards properties and processability. We have obtained ethylene copolymers with various densities using the catalyst system com-

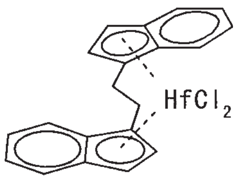


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Chart 1.

Table 2. Ethylene/α-Olefin Polymerization Using Catalyst **1**/MAO Catalyst System

Run	Metal	Comonomer		Total	d	$[\eta]$	MFR_2	MFR_{10}	M_w/M_n
		Species	Amount/mL	volume/mL	g cm^{-3}	dL g^{-1}	g (10 min)$^{-1}$	/MFR_2	
1	Hf	Octene	28	1000	0.868	1.80	0.87	—	2.27
2	Hf	Octene	5	500	0.901	1.45	1.80	9.2	2.35
3	Hf	Octene	3	500	0.915	1.67	0.70	11.8	2.53
4	Hf	Octene	4	500	0.907	1.49	1.48	8.7	2.22
5	Hf	Propene	4	1000	0.887	1.50	0.80	12.7	2.50

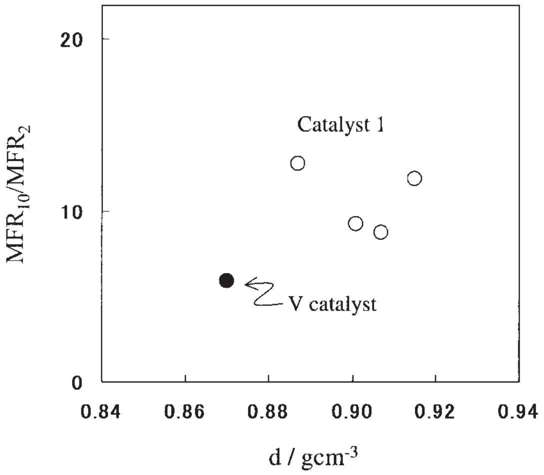

Fig. 14. Differences of flowability between catalyst **1** and V catalyst.

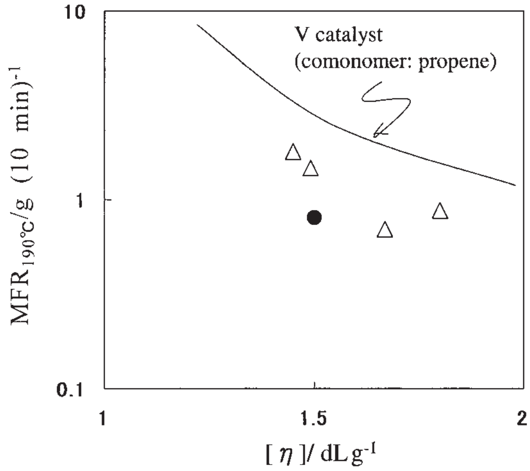

Fig. 15. Relationship between flow (MFR) and viscosity ([η]) of ethylene copolymers (● comonomer: propene; △ comonomer: 1-octene).

prising 1,1′-ethylenebis(indenyl)hafnium dichloride **1** and aluminoxane (Table 2).

This catalyst system is good for keeping MFR_{10}/MFR_2 with a small value of M_w/M_n compared to conventional catalyst composed of $VOCl_3$ and ethylaluminum sesquichloride (Fig. 14).

The success of this finding of our new catalyst system producing ethylene copolymers which are large in value of MFR_{10}/MFR_2 has encouraged us to examine the relationship between flow and viscosity of these copolymers. Especially, we are very interested in the reason why our new catalyst system and the conventional V catalyst system behave differently. Indeed, the relationship between MFR_2 and [η] of these copolymers in our new catalyst system was quite different from the conventional catalyst composed of $VOCl_3$ and aluminum ethyl sesquichloride (Fig. 15).

To explain the different behavior in flow and viscosity of these two catalysts, we suggest that a long chain branch is easily formed with a new catalyst system by the insertion of β-hydride eliminated polymer as a macromer whose chain end is a vinyl group. In order to demonstrate this hypothesis, the best way to determine the chemical structure of ethylene copolymers produced by the catalyst system comprising 1,1′-ethylenebis(indenyl)hafnium dichloride **1** and aluminoxane using ^{13}C NMR technique. However, it is difficult to determine the correct length of long chain branch more than six carbons at this stage. The possible structure of this copolymer is now under evaluation.

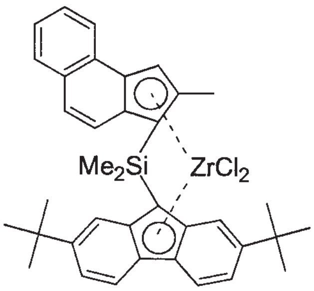

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Chart 2.

3. Functionalized Copolymers Containing Polar Groups

The incorporation of polar groups, especially ones having highly reactive hydrogen such as OH or NH_2, into an otherwise non-polar material is desired as a way for modifying the properties of polyolefins to broaden the polyolefin applications.[16] Promising catalysts containing group 10 transition metals[17] or organolanthanide[18] have succeeded in the controlled copolymerization of simple olefins with polar monomers. Zirconocene/MAO catalysts were also successfully used in copolymerizing ethylene with 10-undecen-1-ol[19] or other polar monomers[20] that have long CH_2 spacers between polar and vinyl groups, although Ziegler–Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature.[21]

In recent research, we discovered that a novel stereorigid bridged metallocene having an indenyl ligand, a fluorenyl ligand, and a zirconium ion named IFZ catalyst **2** (Chart 2) exhibited unique catalytic performance for olefin polymerization[22] and ethylene/10-undecen-1-ol[23] or allyl alcohol[24] copolymerization.

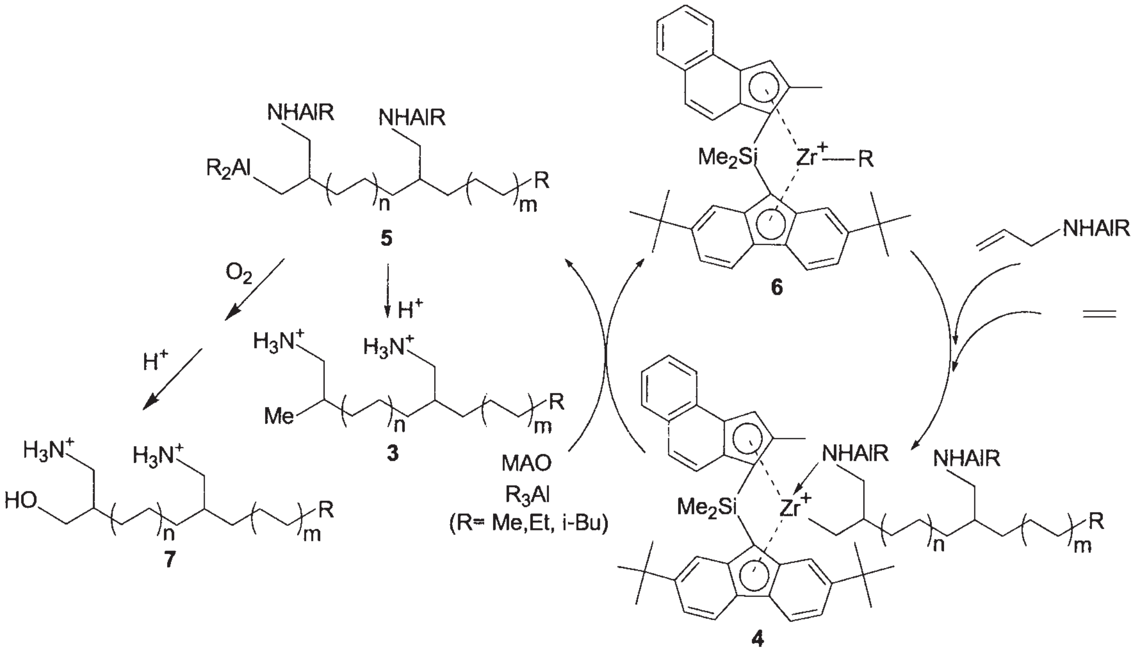
Concerning amino groups, tertiary amine-functionalized olefins are easy to copolymerize with group IV catalysts, provided that sufficient steric hindrance is present around the nitrogen atom.[25] However, direct polymerizations of primary or secondary amines have not been successfully carried out, with one exception. This is in a secondary amine having a long chain spacer, namely the copolymerization of *N*-phenyl-10-undecenamine with 1-hexene using $TiCl_3/Et_2AlCl$ catalyst system.[26] We have also succeeded in the first copolymerization of ethylene with a masked primary amine which is allylamine having two reactive hydrogens and one CH_2 chain spacer.[27,28]

Subjection of the toluene solution of IFZ catalyst **2** and MAO to the solution of allylamine masked by triethylaluminum (TEA) or triisobutylaluminum (TIBA) and ethylene, led to the predominant production of **3**. The results are shown in Table 3. By use of TEA, allylamine was incorporated into a chain end, although the concomitant incorporation to the inner site also occurred. Furthermore, analysis of end groups by

Table 3. Ethylene/Allylamine Polymerization Using IFZ Catalyst **2**/MAO Catalyst System

Entry	**2** /mmol	MAO /mmol	$R_3Al^{a)}$	Ethylene	Temp. /°C	Time /min	Yield /g	Activ.$^{b)}$	$M_n$$^{c)}$	MD$^{c)}$		Number of NH_2 group$^{e)}$	
				L/h							mol%$^{d)}$	end	in
1	0.025	1.57	TEA	2	50	60	4.98	0.20	6500	2.41	0.57	0.86	0.33
2	0.025	1.57	TIBA	2	50	75	1.26	0.043	25000	2.49	0.22	0.94	1.17
3	0.250	7.90	TEA	>5	100	180	43.5	0.053	3700	2.39	0.30	0.19	n.d.

Conditions: 0.1 MPa pressure, toluene; 500 mL, R_3Al; 48 mmol, allylamine; 40 mmol. a) Allylamine was treated with R_3Al before adding toluene solution of MAO and **1**. b) kg-polymer•mmol-Zr^{-1}•h^{-1}•atm^{-1}. c) M_w/M_n by GPC analysis. d) Comonomer content in polymer determined by ^1H NMR analysis. e) This value is based on one polymer chain determined by ^{13}C NMR analysis.



Scheme 2. Proposed reaction pathway in this catalyst system.

^{13}C NMR revealed signals of α,ω-end groups due to aminomethyl and Et (Me) groups only, while signals which were attributable to the carbon of vinyl or vinylidene (114.4, 39.1 ppm) were not detected. This result implies that the chain termination predominantly occurred at the incorporated masked allylamine unit by alkylaluminums (TEA, MAO).

The use of TIBA relatively increased the incorporation of allylamine into the inner site. Analysis of this copolymer by ^{13}C NMR showed that one chain end group was aminomethyl (94%) and the other end group was alkyl (methyl: 62% and isobutyl: 44%) due to the predominant chain termination by alkylaluminum. This result of chain termination indicates that both alkylaluminums (MAO, TIBA) act almost comparably as chain transfer reagents in the chain transfer reaction. The relative increase of inner aminomethyl group in a polymer chain and the increased molecular weight ($M_n = 25000$) of this copolymer may be caused by the lower chain transfer rate compared to Entry 1. In contrast to the result of copolymerizing masked allyl alcohol with ethylene,[24] the numbers of incorporated allyl amine were different: 10 for allyl alcohol, 1 for allylamine, respectively, when TIBA was used as masking alkylaluminums. A sequence analysis of the copolymer revealed that amine incorporated into a polyethylene backbone was isolated. It is intriguing that the numbers of incorporated polar monomers are significantly lower than those in cases in allyl alcohol under similar reaction condition. The degree of electronic interactions between Zr cation and oxygen or nitrogen atoms of inserted polar monomers may determine whether the reaction pathway goes to the chain transfer reaction or to successive ethylene insertion, when the steric hindrance of alkyl aluminum is the same (Scheme 2). Direct observation of the intermediate **4** by using NMR technique was unsuccessful. These unique regioselectivities would be caused by the combination of IFZ catalyst **1** and alkylaluminums having different steric hindrances.

Polymerization under the condition of IFZ catalyst **1**/MAO = 0.25 mmol/7.90 mmol at higher ethylene supply and temperature (>5 L/h. and 100 °C) for longer polymerization time (3 h) was conducted (Entry 3) to obtain a large amount of polymer. The obtained polymers, however, were the mixtures of allylamine-functionalized polyethylene (10%) and homo-polyethylene (90%) having lower molecular weight ($M_n = 3700$), probably due to more frequent chain transfer to alkylaluminums at the activated bond between Zr and ethylene units, unlike the polymerization behavior in Entry 1 or 2. Thus, this active polymer mixture before quenching was subjected to the aerobic oxidation followed by an acid hydrolysis, and we have obtained the mixtures consisting of aminohydroxyl-capped polyethylene **7** (7%), amino-capped polyethylene **3** (3%), and hydroxyl-capped polyethylene (60%) besides homo-polyethylene (30%). The assignment of **7** ($-CH_2OH$: 64.2 ppm, $-CH_2NH_3^+$: 43.5 ppm, $-CH-$: 38.7 ppm), **3** ($-CH_2NH_3^+$: 45.5 ppm), and hydroxyl-capped polyethylene ($-CH_2OH$: 62.7 ppm) was determined by ^{13}C NMR analysis. The chemical yield of **7** obtained by aerobic oxidation from **5** was estimated reasonably from the literature[29] at 70% using ^{13}C NMR technique. This is a one-pot synthesis of regioselective A,B-functionalized polyolefin **7**. Moreover this polyolefin **7** is a new polymer structure in which polyethylene polymer chain was specifically end capped by different functional groups (amino and hydroxy group).

Conclusion

We have succeeded in developing advanced supported metallocene catalysts for commercialization. These catalysts have unique advantages over conventional Ziegler–Natta catalysts. This new type of catalysts brought us tailor-made polymers those have not been produced by conventional catalysts. One feature of metallocene catalyst is its single active site and another is that the comonomer can be incorpolated uniformly into the polymer chain. So this catalyst enables scientists to produce a wide range of polyolefins, from elastomers to rigid polymer.

We have also succeeded in producing long chain branched ethylene copolymers with narrow molecular weight distribution but excellent melt properties by the use of catalyst technologies to control the branches in a polymer chain. This catalyst has capability for producing various kinds of PE with excellent properties. This technology will cover the production not only of pure LLDPE but also of LDPE-like LLDPEs.

Moreover we have found the first example of a metallocene-catalyzed allyl alcohol or allylamine incorporation having only one CH_2 chain spacer into the nonpolar polymer backbone using new metallocene and methylaluminoxane. This catalyst system provided new synthetic methodologies of predominant chain end and/or site-selective introduction of polar groups into the polyolefins.

We conclude that metallocene catalysts will open up the new regions for the polyolefin industry in the near future.

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