Novel Stabilization System for Polypropylene via the Ziegler–Natta Catalyzed Polymerization in the Presence of Aluminum Aryloxide

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ABSTRACT: The aluminum aryloxide was prepared via the reaction of phenolic antioxidant, 3-(3,5-di-t-butyl-4-hydroxyphenyl)-N-octadecylpropionamide, with triethyl aluminum. Propylene polymerization using supported Ziegler–Natta catalyst systems was carried out in the presence of the antioxidant or its aluminum aryloxide. Although the antioxidant gave rise to decrease in catalyst yield and change in hydrogen response, the aluminum aryloxide had no influence on the catalytic polymerization behavior, and thus the obtained polymer characteristics such as molecular weight, polydispersity, and meso pentad as a stereoregularity were comparable to that polymerized without the antioxidant and the aluminum aryloxide. Polypropylene obtained in the presence of the aluminum aryloxide was well stabilized for oxidation and its stability was over 1000 h at 100°C (estimated to be over 30 years at room temperature). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1350–1358, 2006

Key words: aluminum aryloxide; antioxidant; polypropylene; stability; Ziegler–Natta catalyst

INTRODUCTION

A half-century has elapsed since the discoveries of organometallic catalysis for olefin polymerization by Ziegler and of stereospecific polymerization of propylene by Natta.[1] This led to the development of a new branch of the chemical industry, and to the large volume production of polyethylene, polypropylene, as well as other polyolefins. Ever since the initial production of isotactic polypropylene in late 1957, the commercial development was rapid and extensive due to the polymers' versatility and inherent properties coupled with the development of catalyst, production process, and compounding and processing (fabrication) technologies. In the course of the commercial progress in market, the performance requirements for polypropylene have become quite diversified. Catalyst development in Ziegler–Natta catalysts and metallocene catalysts allowed highly stereospecific polymerization and superior comonomer reactivity, leading to high quality and a wide variety of polymers.[2,3,4] The achievements in catalyst technology also triggered the revolution in manufacturing process technology, i.e., the gas phase process, which resulted in reducing production costs and energy consumption.[5] The drastic production energy savings can be achieved by the gas phase polymerization process in combination with highly active Ziegler–Natta catalyst. Thus, the major energy savings are of polymerization stage. On the other hand, twin-screw extruders, instead of single-screw extruders, led to both excellent dispersion and/or compounding of stabilizers and additives into polypropylene and saving the operating energy.[6,7] However, no essential change in the melt-blend methodology "pelletizing" of additives has been made throughout the polypropylene industrial history. Pelletizing consumes one-third of total energy of polypropylene production.[8,9] Annual production of polypropylene in 2001 was reported to be over 36.8 million tons a year worldwide, resulting in consuming huge energy in the pelletizing.[10] Energy saving process of stabilizer addition instead of pelletizing is believed to contribute the reduction of carbon dioxide generation as well as an appropriate growth of polypropylene industry.

Several attempts for the development of stabilizer addition technologies have been made for simplifying the production process or saving energy consumption.[11–16] These stabilizer addition technologies can be divided into two categories as follows: an addition in the olefin polymerization stage and an addition after the olefin polymerization stage. In the former technologies, a certain type of stabilizers including hindered phenols, organic phosphates, and hindered amines

has been demonstrated to addition into olefin polymerization system, resulting in stabilizing the obtained polymer. However, a direct stabilizer addition such as pentaerythrityltetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] into Ziegler–Natta polymerization system was reported to cause a drastic decrease in Ziegler–Natta catalyst activity. It was reported that a certain complex of stabilizers such as 2,6-di-*tert*-butyl-4-alkylphenol and/or 3-(3,5-di-*tert*-butyl-4-hydoxyphenyl) propionic alkyls with alkyl aluminum was effective for the stabilization of olefinic elastomers having lower crystallinity under 10% without poisoning the catalysts.[12] But the application of the technologies is limited in particular polymerization system. As one of the later categories, it was demonstrated that the obtained polypropylene powders are stabilized by coating of stabilizers with a certain type of binder such as waxes.[15] This technology has been commercialized, but the spreading of the technology as a standard stabilization process was not so significant. Cost merits and/or social requirements concerning environment are necessary to motivate the molders to adopt the products via new technologies. Thus, providing definite merits is very important from the viewpoint to spread the postpelletizing technologies.

To achieve the objectives of the Kyoto protocol based on the cost-effective reductions and removals of greenhouse gases, NEDO, New Energy and Industrial Technology Development Organization, which is one of the administrative organs of Ministry of Economy, Trade and Industry of Japan has been promoting 24 programs for the technology development on carbon dioxide reduction. As one of the programs, the project on the energy reduction of polyolefin production has started in 2002 and is focused on reduction of polypropylene powder pelletizing energy in plants, that is, the development of polypropylene production process without pelletizing unit operation.[8,9] To realize the practical effects on reducing carbon dioxide generation, we have been promoting the basic research on the stabilization technology of polypropylene powders, without pelletizing.

Advanced highly active supported-type Ziegler–Natta catalysts enable us to polymerize propylene with extremely high activity and high stereospecificity. The supported type catalyst is more sensitive for the several contaminants compared with $TiCl_3$ based Ziegler–Natta catalyst, because of its high activity. The active sites of the catalysts are deactivated by several impurities of ppm to ppb levels in polymerization system. Since most additives, including antioxidants, contain polar functional groups such as phenolic OH groups, these compounds deactivate the catalyst. Indeed, typical phenolic antioxidant was reported to decrease the catalyst activity as mentioned above. It is considered that the masking or protection of phenolic OH group of antioxidants is the key for stabilization of polypropylene via an addition of antioxidants into polymerization system.

It is known that phenols react with aluminum alkyls, resulting in generating aryloxide compounds of aluminum.[17] It was demonstrated by Hearly et al. that the sterically hindered phenol 2,6-di-*tert*-butyl-4-methylphenol (BHT) in combination with trimethyl aluminum generated aluminum aryloxide, $AlCH_3(BHT)_2$.[18] Cp_2ZrCl_2 (dicyclopentadienyl zirconiumdichloride) in combination with trimethylaluminum was reported to allow to polymerize ethylene in spite of the existence of $AlCH_3(BHT)_2$ in the polymerization system.[19,20] Williams et al. reported that $AlCH_3(BHT)_2$ appeared to be an example of a "noninteracting" scrubbing agent for the metallocene/borate catalytic system $Cp_2Zr(CH_3)_2$/$[Ph_3C][B(C_6F_5)_3]$, and led to pronounced improvements in catalytic activity.[21] Thus, the conversion of conventional phenolic antioxidants to noninteracting aryloxide compound may be regarded as possible. In addition, it is very important that regeneration of OH group is either possible or not, since the phenolic OH group is the key for the performance as an antioxidant. Aluminum aryloxide and aluminum alkoxide compounds are known to be decomposed by the addition of oxygen, water, alcohol and so on.[22] To confirm the regeneration of phenolic OH group, ethanol was used in the course of our study. It was reported that AO-20, tris(3,5-di-*t*-butyl-4-benzyl)isocyanurate, and AO-50, octadecyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate, as market available phenolic antioxidants were confirmed to be masked by tirethylaluminum (TEAL) resulted in inert compounds for Ziegler–Natta catalyst. Phenolic OH was confirmed to be regenerated during hydrolysis of aluminum aryloxide, but the other part of phenolic antioxidants were decomposed.[19]

In this study, the propylene polymerization was conducted by using supported type Ziegler–Natta catalysts in combination with hindered phenols having no decomposable functional groups as phenolic antioxidants and/or their aluminum aryloxides derived from the reaction of antioxidants with aluminum alkyls. The influence of the aluminum aryloxides on catalyst performance, polymerization behavior, polymer characteristics, and the stabilization level of resulted polypropylene powders were evaluated from the standpoint of applicability of postpelletizing method. In addition, new phenolic antioxidant, which was suitable for addition into polymerization stage as an aryloxide, was developed.

EXPERIMENTAL

Preparation of 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-*n*-octadecylpropionamide

Synthesis of 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-*N*-octadecylpropionamide was conducted by 0.5-dm³ glass

vessel. All operations were carried out under the nitrogen atmosphere. Methyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (60.1 g (0.205 mmol); Asahi Denka, Japan) and octadecylamine (66.3 g (0.246 mmol); FARMIN 80, Kao, Japan) were charged into the glass vessel, and the mixture was heated up to 60°C. 4.6 cm^3 of sodium methoxide solution (28 wt % methanol solution, Wako Chemicals, Japan) was instilled into the above mixture, and the mixture was heated at 150°C for 6 h, and then cooled to 80°C, followed by adding toluene (Wako Chemicals) of 0.2 dm^3 In addition, the mixture was held at 50°C, and then aqueous phosphoric acid (1.9 cm^3 (85 wt %); Kokusan Chemical Works, Japan) was added for neutralization of the system. Precipitated solid was filtrated, and the obtained solid was dried in vacuo. Obtained powder, i.e., 3-(3,5-di-t-butyl-4-hydroxyphenyl)-N-octadecylpropionamide (AO-1), was recrystallized from methanol and was filtrated, followed by drying in vacuo. The yield was 79.5 g (73 wt % to theoretical) to methyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate as a starting material, and the purity was over 99 wt %, based on the gas chromatography (GC-14A, Shimadzu, Japan) with a column of OV-17 (ø = 2.6 mm, l = 50 cm). The identification was conducted by using ^{1}H-NMR (Hitachi R-1900 FT-NMR, Japan).

Preparation and characterization of aluminum aryloxide

0.1 g of 1,3,5-Trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (phenolic antioxidant, ADK STAB AO-330, Asahi Denka) was added into heptane (20 cm^3; Wako Chemicals treated with molecular sieves and degassed by nitrogen), followed by an addition of 0.4 cm^3 of triethylaluminum (TEAL, 1 mol/dm^3 heptane solution, Tosoh FineChem, Japan) under nitrogen atmosphere. After TEAL addition, AO-330 was completely dissolved into heptane, as an aluminum aryloxide. This solution was added for the polymerization system. The generation of aluminum aryloxide of AO-330 with TEAL was analyzed using ^{1}H-NMR (Hitachi R-1900 FT-NMR) at room temperature. Sample solution was prepared as follows: 10 mg of AO-330 was dissolved into CDCl$_3$ (chloroform-d, stabilized with silver foil having 0.03 vol/vol % TMS, Acros Organics, Fair Lawn, NJ), then 0.2 cm^3 of TEAL solution was added, and thus the solution was analyzed. The resulted aluminum aryloxide was quenched using ethanol, followed by filtration, and thus obtained solution was analyzed by means of ^{1}H-NMR, with the condition as mentioned earlier. Aluminum aryloxide of 3-(3,5-di-t-butyl-4-hydroxyphenyl)-N-octadecyl propionamide (phenolic antioxidant, AO-1) was prepared according to the procedure mentioned earlier, except the amount of TEAL (0.6 cm^3) addition.

Polymerization

The Ziegler–Natta catalyst used in this study was prepared by reaction of Mg(OC$_2$H$_5$)$_2$ (Wako Chemicals) with TiCl$_4$ (Wako Chemicals) in xylene (Wako Chemicals), in the presence of di-i-butylphthalate (Wako Chemicals) as an internal electron donor, at a temperature of 130°C, according to a previous paper.[23] The catalyst contained titanium of 2.6 wt %. All operations were carried out under nitrogen atmosphere. The catalyst was used in combination with TEAL as a cocatalyst and dicyclepentyldimethoxsilane (DCPDMS: Yuki Gosei Kogyo, Japan) as an external electron donor with a molar ratio of Al/Si/Ti = 200/20/1. Typical polymerization procedure was as follows: polymerization was conducted by 1-dm^3 glass autoclave reactor (Taiatsu Glass, Japan) equipped with a turbine blade mechanical agitator, according to the following procedure. Catalyst was prepared as heptane slurry of 1.9 mg cm^{-3}, and DCPDMS was prepared as heptane solution of 0.1 mol cm^{-3}. The reactor was replaced by nitrogen, then 0.4 dm^3 of heptane, 5 cm^3 of TEAL, 5 cm^3 of DCPDMS solution, and 8 cm^3 of phenolic antioxidant solution or its aryloxide solution (40 mg as phenolic antioxidant) were added into the reactor at room temperature. The reactor was flushed by propylene (Takachiho, Japan, research grade) to degas of nitrogen, and then prepolymerization was carried out at a temperature range from 30 to 50°C and a pressure of 0.1 MPaG (gauge pressure), with an agitation speed of 300 s^{-1} for 10 min. After prepolymerization, propylene in the autoclave was purged. Hydrogen (150 cm^3; Uno Sanso, Japan) of standard temperature and pressure as a chain transfer agent was introduced into the system, and then propylene was pressured. Propylene polymerization was carried out at a pressure of 0.5 MPaG (gauge pressure) and a temperature of 70°C, with an agitating speed of 600 s^{-1} for 1 h. Polymerization was quenched by an addition of 50 cm^3 of ethanol (Wako Chemicals). Polypropylene was collected via evaporation of the whole slurry followed by drying at 60°C in vacuo for 24 h. The target content of phenolic antioxidant was 1000 wt ppm to the obtained polymer. Practical content was confirmed as follows: phenolic antioxidant was extracted by the Soxhlet extraction with chloroform (12 h) followed by acetone (6 h). The collected solvents were analyzed by liquid chromatography (LC-6A, Shimadzu Corp; Shodex GPC KF-802 column, Showa Denko K.K., Japan). Recovered amount of phenolic antioxidant by the extraction was about over 93 wt %.

Characterization of polypropylene

Molecular weight and polydispersity of polypropylene were determined by means of gel permeation chromatography (GPC, Waters 2000, Milford, MA),

having polystyrene gel column (Styragel HT6E of two column and Styragel HT2 of one column in series, Waters, USA) with a o-dichlorobenzene (ODCB, Wako Chemicals) as a solvent at a temperature of 145°C. To prevent the oxidation of polypropylene during GPC measurement, 2,6-di-t-butyl-p-cresol (BHT, Wako Chemicals) as an antioxidant was added to ODCB (~0.01 wt %). Melting and crystallization temperatures of polypropylene were measured as exothermic or endothermic peaks by using differential scanning calorimetry (Perkin–Elmer Diamond DSC, USA) with the following temperature program, respectively: samples were preheated at 10°C min^{-1} to 230°C, held for 10 min, cooled at 10°C min^{-1} to −30°C, and heated again at 10°C min^{-1} to 230°C to obtain melting temperature, T_m. Isotacticity of polypropylene as meso pentad sequence [mmmm] was determined by using ^{13}C-NMR (JEOL EX-400 FT-NMR, Japan) at 130°C with 8000 scans. Sample solution was prepared using mixture of ODCB and C_6D_6 of 4 : 1 in volume, and the concentration of polypropylene was 10 wt/vol %.

Accelerated degradation

To evaluate the stability of polypropylene powder, an accelerated degradation method at 100°C under atmosphere was employed in an oven (ST-120, Espec, Japan). Powder was settled in the aluminum foil tray (~4.5 cm (w) × 4.5 cm (l) × 1 cm (h)) for the oven test. The degree of degradation was estimated from the changes in molecular weight obtained by the GPC method. Relationship in degradation between room temperature and 100°C was estimated by using Arrhenius' plots based on degraded polypropylene at several temperatures: 1-h stability at 100°C in an oven was estimated to be comparable to 262-h stability at room temperature.[24,25] Yellowness index of polymer was evaluated using Multi Spectro Color Meter (MSC-IS-2DH, Suga Test Instruments, Japan).

RESULTS AND DISCUSSION

Phenolic antioxidants having isocyanurate or ester groups of AO-20 and AO-50 were found to be unstable compounds for the regeneration from aryloxide via hydrolysis by ethanol. Here, AO-330 was chosen, because AO-330 has no active functional groups, excluding phenolic OH group. As seen in Figure 1(a), the phenolic OH related signal 4.93 ppm was observed for AO-330 by ^{1}H-NMR. After the addition of TEAL, the above-mentioned OH-related signal disappeared [Fig. 1(a)]. This suggests that TEAL reacted with phenolic OH group of AO-330, resulting in generating aluminum aryloxide, which is similar to the above-mentioned BHT with trimethylaluminum. Aluminum aryloxide of AO-330 solution was hydrolyzed using ethanol; and then, the obtained solution was analyzed
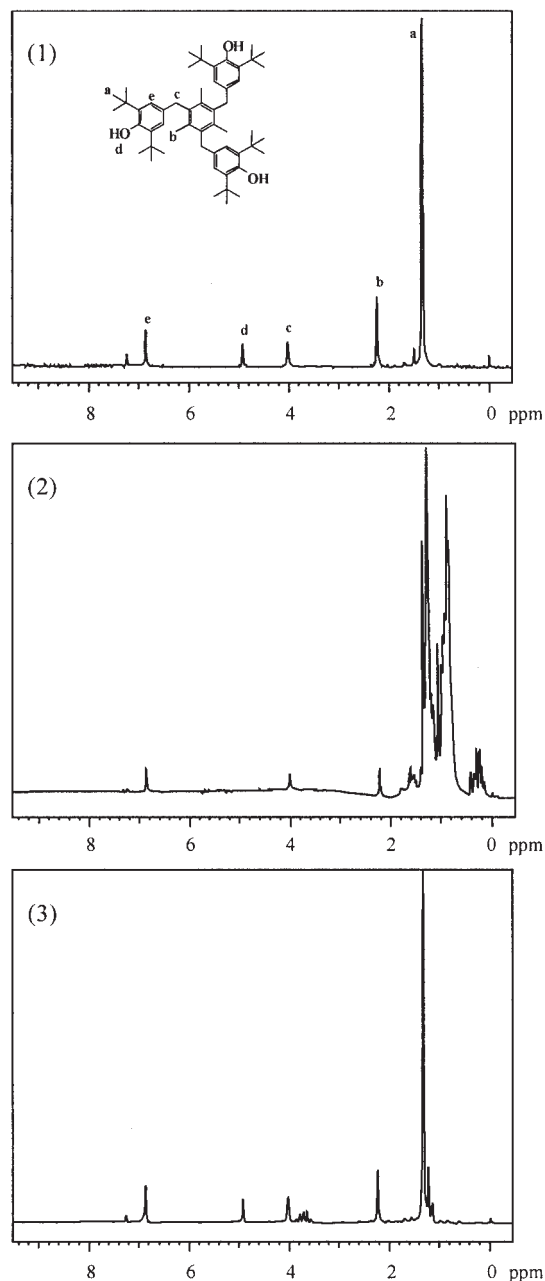

Figure 1 ^{1}H-NMR charts of AO-330 and aryloxide of AO-330. (a) AO-330; (b) aryloxide of AO-330 (mixture of AO-330 and TEAL); and (c) regenerated AO-330 from aryloxide by hydrolysis with ethanol. Signals around 1 ppm excluding signal "a" in chart (b) was ascribed to the TEAL.

using ^{1}H-NMR. The signal associated with the phenolic OH group of AO-330 (4.93 ppm) was observed again and no decomposition of AO-330 was observed [Fig. 1(c)]. This result indicates that the OH group of phenolic antioxidant can transform into noninteracting compounds for catalyst system by the addition of TEAL and the phenolic antioxidant, that is phenolic OH group, can be regenerated easily by the addition of ethanol. In addition, AO-330 was suggested to be stable during masking and regeneration process. Since

TABLE I
Ziegler-Natta Catalyzed Polymerization Results Using Phenolic Antioxidants A-330
and its Aluminum Aryloxide, and Resulted Polymer Characteristics

	Yield (g-PP/g-cat.)	$\bar{M}_w \times 10^{-5a}$	$\bar{M}_w/\bar{M}_n{}^{\text{b}}$	[mmmm] (%)[b]	T_m (°C)[c]
Non	9400	4.0	5.1	97.1	163.7
AO-330	8000	4.2	4.8	96.6	163.4
Aryloxide of AO-330	9200	4.1	5.1	96.5	163.2

[a] Measured by OPC.
[b] Measured by ^{13}C-NMR.
[c] Measured by DSC.

the aryloxide is easily hydrolyzed as mentioned earlier, the regeneration in practical production process can be achieved by moist nitrogen, which is used for catalyst deactivation at finishing process.

Table I summarizes the results of heptane slurry polymerization of propylene by using the supported Ziegler–Natta catalyst system in the presence of AO-330 and its aluminum aryloxide, and the characteristics of the obtained polypropylene. Here, the 40 mg of AO-330 for both as a direct addition and as an aryloxide was added into the polymerization system, respectively. This amount was targeted to be 1000 wt ppm to the obtained polymer if the catalyst yield was same with that without an additive. In general, phenolic antioxidants of 300–1000 wt ppm are loaded at pelletizing. The loading level in this study was settled to be upper loading level of usual additive package to clarify the influence of additives on catalytic behavior. The results of standard polymerization without additives was demonstrated to be a catalyst yield of 9400 g-PP g-cat^{-1} (based on the amount of the supported Ziegler–Natta catalyst), [mmmm] of 97.1%, weight-averaged molecular weight, $\bar{M}_w$ of 4.0 × 10^5, and polydispersity $\bar{M}_w/\bar{M}_n$ of 5.1. This was typical polymerization behavior of the supported type catalyst under the conditions. A decrease in catalyst yield was observed for the polymerization with AO-330 and was of 85% of the standard catalyst yield. In the case of A-330 aryloxide addition, the yield was 9200 g-PP g-cat^{-1}. The decrease in catalyst yield was succeeded to be reduced and the yield was almost comparable to that of standard polymerization without additives. This suggests that the masking of phenolic OH group as an aryloxide was very effective to reduce the deactivation of the active sites of Ziegler–Natta catalyst. The amount of AO-330 added into the polymerization system was 52 μmol (40 mg). Sufficient amount of TEAL, 5 mmol, existed in the polymerization system in the standpoint of the amount of AO-330. Nevertheless, AO-330 deactivated some of the catalyst active sites, and the yield was ~85% of the standard polymerization. This indicates that competitive reaction of AO-330 with TEAL and Ti species as catalyst active sites was undergone. Thus, the convertion of AO-330

to aryloxide that preceded the addition into polymerization system was of great consequence for the maintaining of catalyst activity.

No changes in molecular weight ($\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) was observed between polymers obtained by standard and aryloxide addition polymerizations. This indicates that there was no change in the hydrogen response between them. On the other hand, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ of polymers with A-330 addition was found to be almost comparable to that of the standard, or slightly higher than that of standard. In general, the decrease in catalyst yield that is ascribed to a decrease in active sites leads to lower molecular weight, because the relative hydrogen concentration as a chain transfer agent in the system increases for the concentration of active sites. Although the catalyst yield was decreased to be 85% of the standard in the case of the AO-330 addition, the $\bar{M}_w$ was comparable to or slightly higher than that of standard as mentioned earlier. This leads to the possibility that A-330 affected not only the active sites but the hydrogen dissociation sites on the catalyst, because no change in $\bar{M}_w$ was observed for the aluminum aryloxide addition, resulting in decreasing the efficiency of hydrogen as a chain transfer agent. The meso pentad fraction [mmmm] was observed to be lowered by the addition of both AO-330 and its aluminum aryloxide. In both cases, the [mmmm] was almost the same among them. Thus, it is considered that AO-330 as a direct addition deactivated the active sites irreversibly and that only the aluminum aryloxide affected the stereospecificity of the catalyst. However, the influence of the aryloxide on the stereospecificity was not so strong because the $\bar{M}_w$ was maintained.

Figure 2 shows the ^{1}H-NMR chart of the recovered AO-330 from polypropylene powder, which was polymerized in the presence of aryloxide of A-330 listed in Table I. Comparison with NMR chart in Figure 1(a), the chart in Figure 2 was comfirmed to be of AO-330: AO-330 was regenerated by the hydrolysis, without any decomposition of AO-330. This suggests that the phenolic OH was succeeded to be regenerated from aryloxide by ethanol quench without any decomposition. Figure 3 shows the accelerated degradation re-
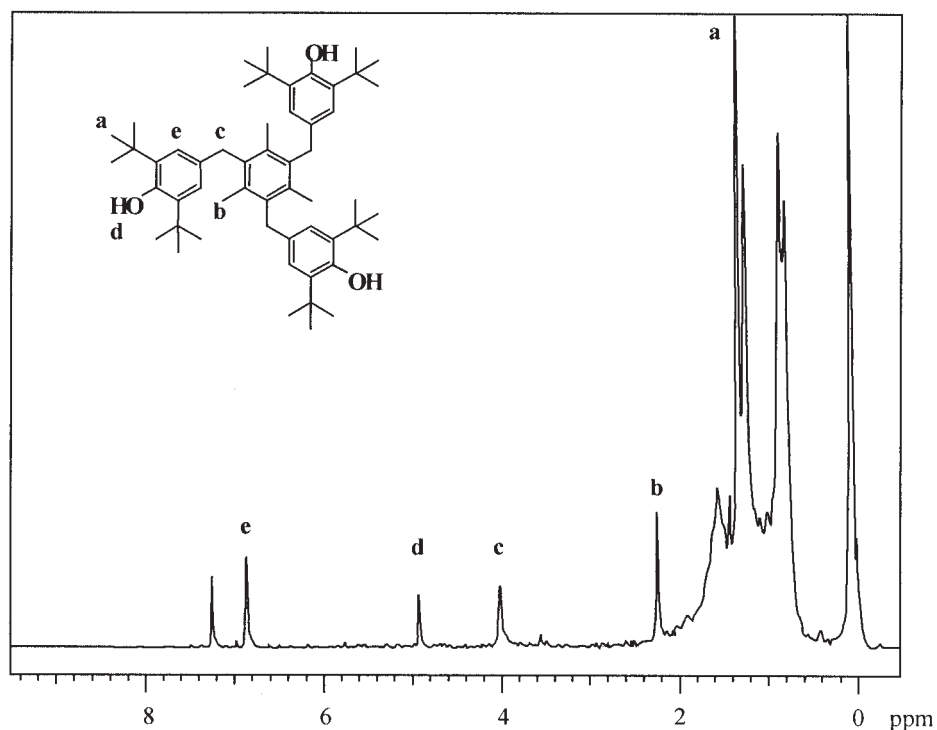
Figure 2 ^{1}H-NMR chart of AO-330 recovered from polypropylene powders obtained in the presence of aryloxide of AO-330. Signals around 1 ppm, excluding signal "a," was ascribed to the atactic polypropylene extracted from polypropylene powders with AO-330.

sults of PP powders of the standard and the aluminum aryloxide of AO-330 addition listed in Table I. The loading level of AO-330 in the polymer (powders)
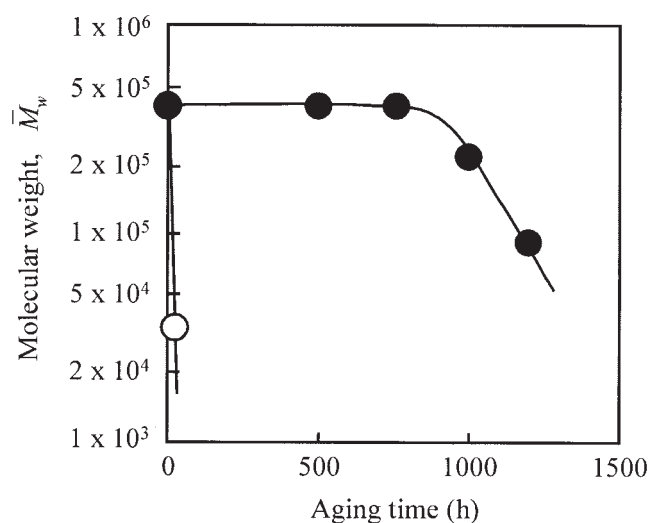

Figure 3 Changes in weight-averaged molecular weight $\bar{M}_w$ of polypropylene by the accelerated degradation as a function of aging time. Degradation condition was an oven temperature of 100°C under atmosphere. (○): polymerized without additives (control), (●): polymerized with aluminum aryloxide of AO-330. The content of AO-330 in polypropylene was estimated to be 1030 wt ppm.

obtained in the presence of aluminum aryloxide of AO-330 was estimated to be 1030 wt ppm. Polymer obtained by standard polymerization degraded drastically: $\bar{M}_w$ decreased to be less than 5×10^4 within 24 h. On the other hand, excellent stabilization was achieved by AO-330 aryloxide addition, and the $\bar{M}_w$ was maintained over 750 h at 100°C, but degraded at 1000 h. Here, 750 h at 100°C is estimated to be over 20 years at room temperature.[24,25] Thus, the addition of aluminum aryloxide into polymerization system is a superior method to give highly stabilized polymers.

As mentioned above, the addition of aryloxide of AO-330 enabled us to provide superior stability (maintained $\bar{M}_w$), but yellowness index (YI) of powder was found to increase because of AO-330 oxidation. The YI = 5.3 for 0 h changed drastically to be the YI = 15.2 for 4 days at 100°C: Oxidized AO-330 exhibited color in the visible light region up to 350 nm. Taking this disadvantage of AO-330 into consideration, another type of phenolic antioxidant 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-*N*-octadecylpropion amide (AO-1), which has a simple structure compared with AO-330, was designed and used to prevent the above-mentioned drawbacks. AO-1 has long aliphatic chain, and thus its solubility into polymerization media such as heptane and its chain is expected to improve the affinity to polypropylene. In addition, AO-1 has no conjugated structure, excluding phenolic group. Large
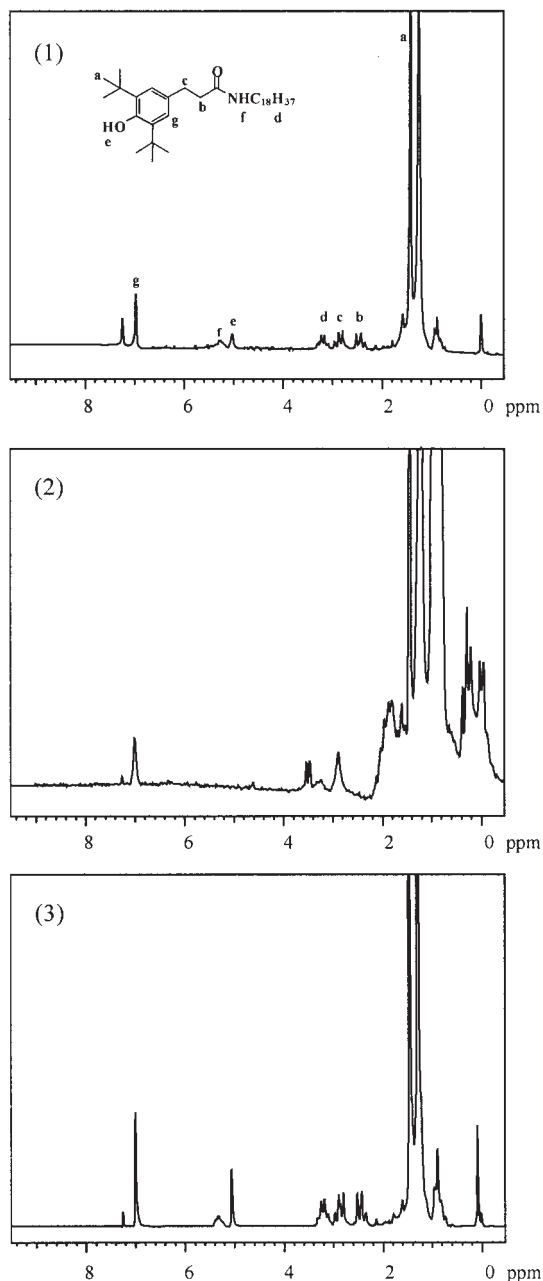
Figure 4 ^{1}H-NMR charts of AO-1 and aryloxide of AO-1. (a)AO-1; (b) aryloxide of AO-1 (mixture of AO-1 and TEAL; and (c) regenerated AO-1 from aryloxide by hydrolysis with ethanol. Signals around 1 ppm, excluding signal "a," in chart (b) was ascribed to the TEAL.

intramolecular conjugation is considered to cause the discoloration in the same way as AO-330. To prevent the decomposition during regeneration by hydrolysis, phenolic group was connected with aliphatic chain via amide group, based on the results on AO-50.[24,25] Polar groups of AO-1, such as phenolic OH and amide, can be easily masked by TEAL. By ^{1}H-NMR as seen in Figure 4, the signals of phenolic OH group, 5.04 ppm, and amide group, 5.30 ppm, were disappeared by the addition of TEAL [comparison of Figs. 4(a) with 4(b)],

and the regeneration of these groups by the ethanol addition was also confirmed without any decomposition of AO-1 [Fig. 4 (c)].

Ziegler–Natta catalytic polymerization results in the presence of AO-1 and its aluminum aryloxide were summarized in Table II, in which the polymerization was carried out in the same procedure for AO-330 evaluation. Here, the additives as AO-1 of 40 mg (75 μmol) were added into the polymerization system. Catalyst yield in the presence of aluminum aryloxide of AO-1 was comparable to the control run, while the decrease in the yield was caused by the direct addition of AO-1: 75% of the standard. The decrease with AO-1 was larger than that with AO-330. AO-1 has two functional groups, phenolic OH and amide group. Thus the concentration of them in the polymerization system was ~150 μmol. On the other hand, AO-330 has three phenolic OH groups. Thus the concentration was ~156 μmol. From the viewpoint of the catalyst poisons, both AO-330 and AO-1 was considered to be in similar situation. Nevertheless, AO-1 was found to be more strong poisons for the catalyst. Since the AO-330 is a symmetric compound, the phenolic OH groups are seated away from each other. When one of the phenolic OH group makes an attack onto the active site, other OH groups cannot make an attack onto the active sites because of the sterical reason. This is believed to be the difference in the deactivation magnitude among them. No differences in polymer characteristics such as $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, [mmmm], and T_m were observed among polymers listed in Table II. It should be noted that [mmmm] was found to be maintained in spite of the presence of aluminum aryloxide of AO-1. This is one of the great advantages of AO-1 when compared with AO-330. In the case of direct addition of AO-1 with a decrease in the yield, the $\bar{M}_w$ was comparable to that of standard. This is suggested to be associated with the similar reasons for the case of the direct addition of AO-330 as mentioned earlier.

Figure 5 shows the ^{1}H-NMR chart of the recovered AO-1 from powder polymerized in the presence of AO-1 aryloxide. From Figure 4(a) and 5, it can be stated that AO-1 was regenerated without any decomposition during polymerization and hydrolysis by ethanol. Figure 6 shows the accelerated degradation results for the polymers of standard and AO-1 aryloxide addition. The amount of AO-1 in the polymer (powder) obtained in the presence of AO-1 aryloxide was estimated to be 1020 wt ppm. Excellent antioxidation performance was observed for the polymer obtained in the presence of AO-1 aryloxide. The polymer obtained with AO-1 aryloxide maintained the molecular weight even over 1000 h at 100°C (estimated to be over 30 years at room temperature). In addition, the aryloxide of AO-1 was found to reduce the increase in YI compared with that by AO-330: YI = 2.6 for 0 h changed to be YI = 6.5 for 4 days. As mentioned

TABLE II
Ziegler-Natta Catalyzed Polymerization Results Using Phenolic Antioxidants AO-1 and its Aluminum Aryloxide, and Resulted Polymer Characteristics

	Yield (g-PP/g-cat.)	$\bar{M}_w \times 10^{-5a}$	$\bar{M}_w/\bar{M}_n{}^b$	[mmmm] (%)[a]	T_m (°C)[c]
Non	9400	4.0	5.1	97.1	163.7
AO-1	7100	3.9	4.8	97.0	163.6
Aryloxide of AO-1	9100	4.0	5.1	97.2	163.4

[a] Measured by ^{13}C-NMR.
[b] Measured by GPC.
[c] Measured by DSC.

earlier, the YI of the polymer with AO-330 was 15.2 for 4 days. AO-1 was found to reduce the increase in YI and thus was more suitable phenolic antioxidant as an additive for Ziegler–Natta polymerization system when compared with AO-330.

CONCLUSIONS

Phenolic antioxidant, 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-*N*-octadecylpropion amide (AO-1), was designed as an additive for the use in the Ziegler–Natta catalytic polymerization system to improve the drawbacks of market available phenolic antioxidants. The aluminum aryloxide of AO-1 led to no significant decrease in catalyst yield, hydrogen response, and stereospecificity, and

then the resulted polymer characteristics were found to be comparable to the standard polymerized one in molecular weight, polydispersity, and stereoregularity. Excellent stability of obtained polymer in oxidation was demonstrated by the addition of the aluminum aryloxide into polymerization system: the polymer exhibited superior stability over 1000 h at 100°C, which was estimated to be comparable to the stability over 30 years at room temperature. The structure of AO-1 is considered to be one of the most suitable phenolic antioxidants for the use as an aluminum aryloxide in the Ziegler–Natta polymerization catalyst system. Conclusively, the demonstrated novel stabilization system using aluminum aryloxides of AO-1 is a superior method to stabilize polypropylenes without any drawbacks in polymeriza-
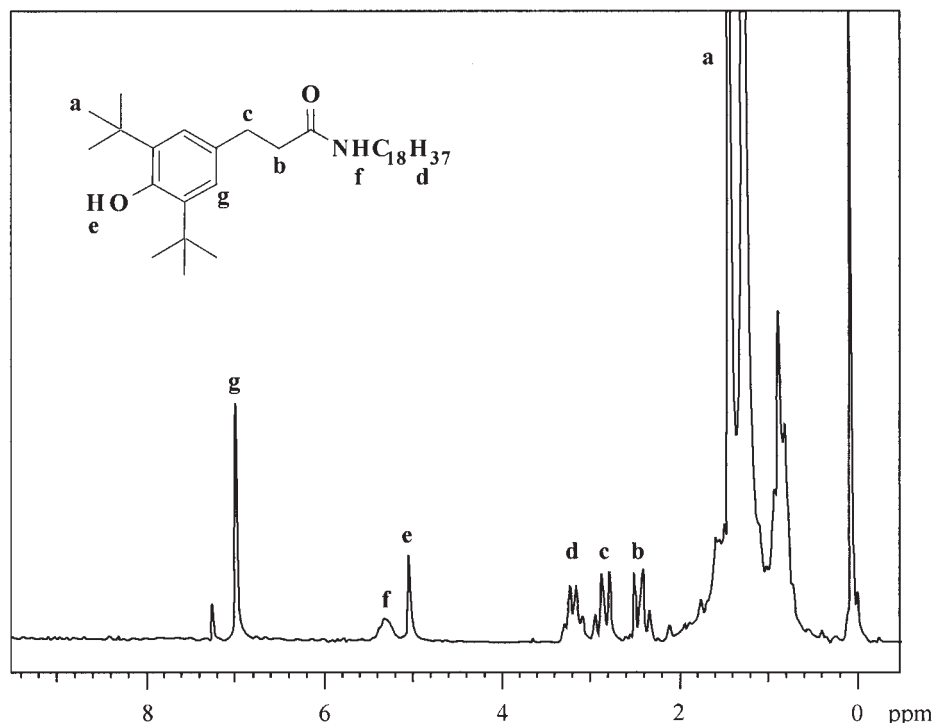

Figure 5 ^{1}H-NMR chart of AO-1 recovered from polypropylene powders obtained in the presence of aryloxide of AO-1. Signals around 1 ppm, excluding signal "a," was ascribed to the atactic polypropylene extracted from polypropylene powders with AO-1.
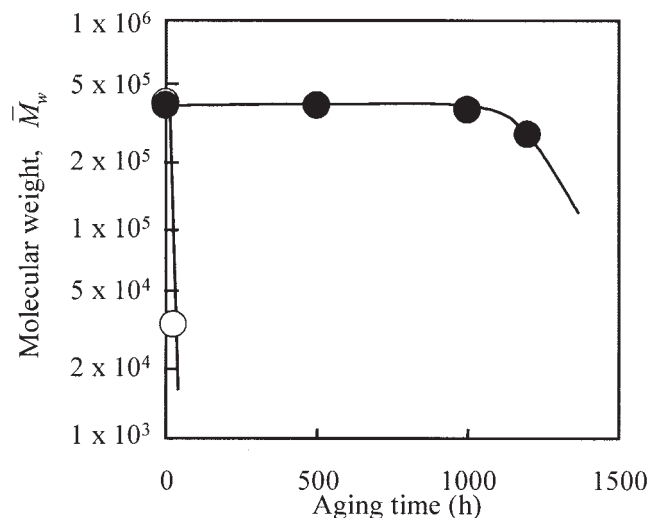
Figure 6 Changes in weight-averaged molecular weight $\bar{M}_w$ of polypropylene by the accelerated degradation as a function of aging time. Degradation condition was an oven temperature of 100°C under atmosphere. (○): polymerized without additives (control), (●): polymerized with aluminum aryloxide of AO-1. The content of AO-1 in polypropylene was estimated to be 1020 wt ppm.

tion system and polymer characteristics, and without large energy consumption as pelletizing. This finding is one of the great consequent results for the establishment of lower energy polypropylene stabilization process without conventional pelletizing process.

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