

Effect of Phenolic, Phosphite, Lactone, and Their Mixtures of Antioxidants on Ziegler–Natta Catalyst Performance During Propylene Polymerization

A. Ranji,^{1,2} H. Arabi,¹ Y. Jahani¹

¹Department of Polymerization Engineering, Iran Polymer and Petrochemical Institute, Tehran, Iran

²C.O.R&D Group, Research and Technology Company, National Petrochemical Company, Tehran, Iran

This study investigated the use of antioxidants and mixtures of these antioxidants during slurry propylene polymerization using the Ziegler–Natta catalyst. Antioxidant masking using triethylaluminum is the key to reducing the destructive effect of antioxidants containing OH phenolic groups on Ziegler–Natta catalyst performance. According to the synergistic properties, antioxidant mixtures with different ratios were evaluated for their masking conditions and amounts of antioxidant added. Polymer characteristics such as catalyst activity, isotacticity, oxidative induction time, and particle-size distribution of the products in the presence of different amounts of antioxidants were evaluated. The results showed that phosphite and lactone antioxidants have more effect on catalyst performance during polymerization than phenolic antioxidants. J. VINYL ADDIT. TECHNOL., 21:299–304, 2015. © 2014 Society of Plastics Engineers

INTRODUCTION

Polypropylene (PP) has been widely used for diverse applications. Recently, the annual consumption growth is reported to be 3.7% worldwide. The amount that will be consumed in 2013 is estimated to be about 69 million tons [1]. In spite of its desirable physical and mechanical properties, PP has low thermal resistance and is easily destroyed during polymer processing and over its service life. Consequently, the use of antioxidants in propylene production is inevitable that will result in the production of a wide variety of antioxidants [2].

Antioxidants are divided into primary and secondary types. In primary antioxidants, the propagation step terminates in a terminal reaction with P[•] and PO₂[•] radicals that prevent polymer degradation. Of the primary antioxidants, hindered phenols are widely used for PP stabilization. Secondary antioxidants decompose hydroperoxides into nonradical, nonreactive, and thermally stable products. Of

the secondary antioxidants, organic phosphites, and phosphonates are widely used. Alcohol and phosphate are produced in these reactions, preventing polymer degradation [3].

Improvements in the field of antioxidants have produced a wide variety of mixed or neat antioxidants. A combination of primary and secondary antioxidants in PP is most frequently used to obtain synergistic stabilization effects.

Conventionally, antioxidants are mixed with PP by extrusion under high temperatures and shear rates, thereby producing pellets [4, 5]. Pelletizing consumes a significant amount of PP production energy, about one-third of the total energy [6, 7]. To save energy, it would be advantageous to develop a technique that eliminates the extrusion step by adding additives and antioxidants during propylene polymerization [4, 6, 8–13]. However, the addition of antioxidants during polymerization creates disadvantages such as catalyst activity depression and an undesirable influence on morphology and its properties.

Phenolic antioxidants, the most widely used antioxidants, contain OH groups that have a destructive effect on Ziegler–Natta catalyst performance. The reaction between phenolic OH groups of antioxidants and Ziegler–Natta catalysts causes the deactivation of catalyst activity during propylene polymerization. Masking of the antioxidant with triethylaluminum (TEAL) has been found to be effective in reducing Ziegler–Natta catalyst deactivation [6]. It is well-known that TEAL reacts with OH phenolic groups, generating aluminum aryloxide compounds. These compounds easily regenerate with the addition of water and alcohol after polymerization.

Previous studies using antioxidants during propylene polymerization have focused on several antioxidants individually [6, 8]. The objective of the present study was to decrease the harmful effect of antioxidant formulation caused by the destructive influence of phenolic antioxidants on Ziegler–Natta catalyst performance. Antioxidants based on organic lactone and phosphite were found to be effective for this purpose because of their synergistic antioxidant properties. The effect of the amount and

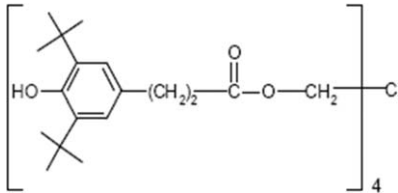
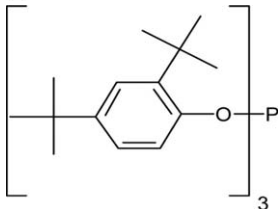
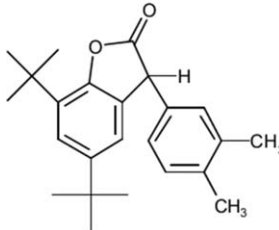
Correspondence to: H. Arabi; e-mail: H.Arab@ippi.ac.ir

DOI 10.1002/vnl.21394

Published online in Wiley Online Library (wileyonlinelibrary.com).

© 2014 Society of Plastics Engineers

TABLE 1. Chemical structure and formula of used antioxidants.

Name	Chemical structure	Abbreviate name
Tetrakis(3-(3, 3-di- <i>tert</i> -butyl)-4-hydroxyphenyl) propionyloxy methyl methane (Irganox 1010)		AO ₁
Tris(2,4-di- <i>tert</i> -butylphenyl)phosphate (Irgafos 168)		AO ₂
A mixture of 90% of 5,7-di- <i>tert</i> -butyl-3-(3,4-dimethylphenyl)3 <i>H</i> -benzofura-2-one and 10% of 5,7-di- <i>tert</i> -butyl-3-(2,3-dimethylphenyl)3 <i>H</i> -benzofura-2-one (Irganox HP-136)		AO ₃
A mixture of Irganox 1010 and Irgafos 168(1:1)	AO ₁ +AO ₂ (1:1)	AO ₄
A mixture of Irganox 1010 and Irgafos 168(1:2)	AO ₁ +AO ₂ (1:2)	AO ₅
A mixture of Irganox 1010 and Irgafos 168, Irganox 136(42,5,42,5,15)%	AO ₁ +AO ₂ +AO ₃ (42,5,42,5,15)%	AO ₆

properties of modified antioxidant, antioxidant blending, masking function, and its role during polymerization via the Ziegler–Natta catalyst was investigated.

Polymerization runs were carried out in the absence of H₂ in the slurry phase. Heptane was used as a solvent and all polymerization runs were performed at a temperature of 70°C and pressure of 7 bar with a total reaction time of 140 min. M-AO compound was added to the reactor prior to catalyst injection. After polymerization, heptane was evaporated and the final products were analyzed.

EXPERIMENTAL

Materials

Ziegler–Natta catalyst (MgCl₂/TiCl₄/DIBF) was provided by Maroon Petrochemical Co. (Iran). Extra pure polymerization-grade propylene was obtained from Tabriz Petrochemical Co. (Iran). Heptane as a solvent was provided by Bandar Imam Petrochemical Co. (Iran). It was dried over CaH₂ and kept over 4 Å/13X type molecular sieves and sodium wires to hold its water content below 2 ppm.

TEAL of 93% purity and donor was obtained from Sigma Aldrich. The AO products (BASF Schweiz AG) used were:

- AO₁: tetrakis(3-(3, 3-di-*tert*-butyl)-4-hydroxyphenyl) propionyloxy methyl methane (Irganox 1010) as a phenolic antioxidant

- AO₂: tris(2,4-di-*tert*-butylphenyl) phosphite (Irgafos 168)
- AO₃: a mixture of 90% 5,7-di-*tert*-butyl-3-(3,4-dimethylphenyl)3*H*-benzofura-2-one and 10% 5,7-di-*tert*-butyl-3-(2,3-dimethylphenyl)3*H*-benzofura-2-one (Irganox HP-136)
- AO₄: a mixture of 50% Irganox 1010 and 50% Irgafos 168 (Irganox B225)
- AO₅: a mixture of 33% Irganox 1010 and 67% Irgafos 168 (Irganox B215)
- AO₆: a mixture of 42.5% Irganox 1010 and 42.5% Irgafos 168 and 15% HP-136 (Irganox HP2225)

Masking of Antioxidant

To mask the phenolic moiety in the antioxidant and generate aluminum aryloxyde, Irganox 1010 was dissolved in 10 mL dried heptane followed by the addition of a sufficient amount of TEAL (2 mol in dried heptane).

Polymerization Procedure

Polymerization reactions were carried out in a 1-L stainless steel (Büchi) reactor. Oil utility was used in the reactor jacket for cooling/heating and controlling temperature. The reaction mixture was stirred continuously using a controlled speed stirrer (Büchi Magnetic Drives) equipped with an anchor blade impeller.

Before starting the reaction, the reactor was heated to 110°C and then purged with argon to remove oxygen and humidity. The reactor was cooled to 25°C under argon purging. Afterward, the reactor was charged with 500 mL

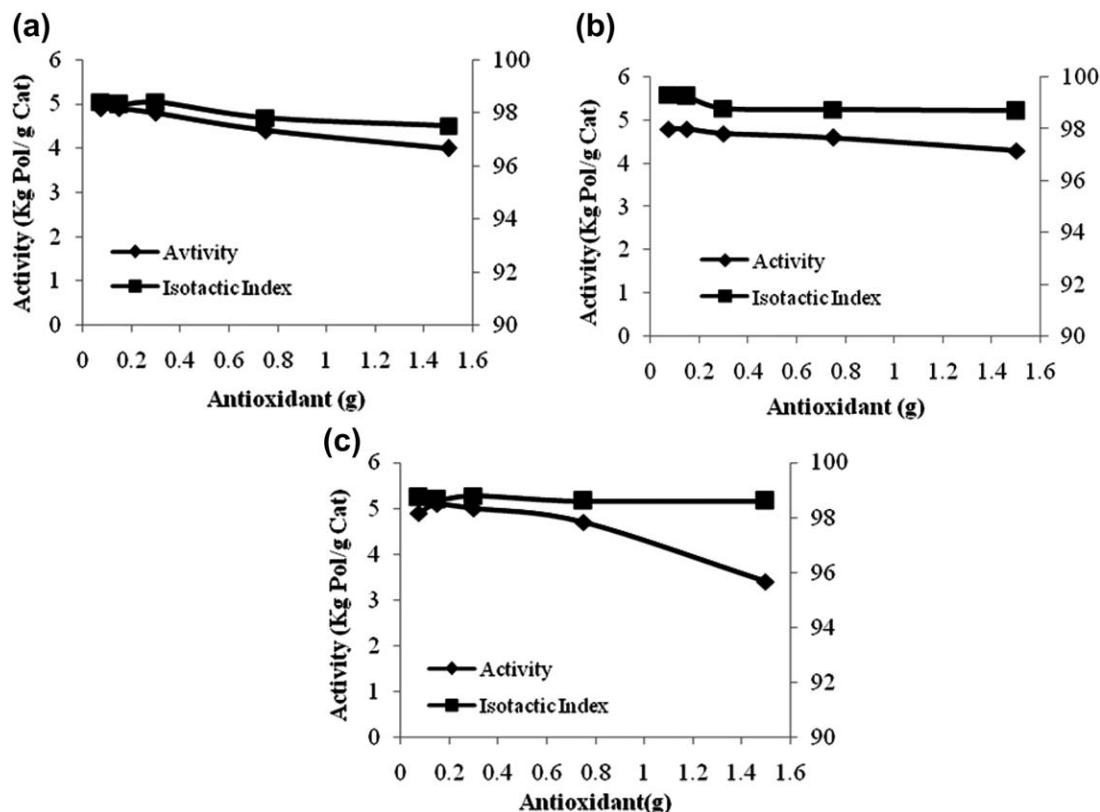


FIG. 1. The effect of different amounts of antioxidants addition on Ziegler–Natta catalyst activity and isotactic index. (a) M-AO₁. (b) AO₂. (c) AO₃.

n-heptane under argon atmosphere. The proportional amount of masked antioxidant was injected; the catalyst was then added to the TEAL/donor mixtures diluted in heptane. After 20 min, the precontacted mixture of the catalyst and cocatalyst was transferred to the reactor. Immediately after the last injection was done, the propylene valve was opened. Reactor heating and continuous propylene feeding were started simultaneously to reach the desired operating conditions. In this case, nonisothermal prepolymerization was used. The reaction temperature increased from 25 to 70°C within 20 min. The polymerization reaction was deactivated using 40 mL ethanol (Merck) and the product was dried overnight in an oven at 40°C.

For all polymerization runs, the Al/Ti and Al/Si ratios were kept constant at 400 and 20, respectively, and, typically, 40 mg of catalyst was used.

Characterization of PP

The isotacticity index of PP was obtained by soxhlet extraction in *n*-heptane for 12 h and was determined by the ratio of insoluble fraction mass to total mass.

Oxidative stability of products was measured by oxidative induction time (OIT, Mettler Toledo) at 190°C.

RESULTS AND DISCUSSION

Chemical structures of the used antioxidants are shown in Table 1. Previous studies by the authors have estimated

the molar ratio of TEAL/AO₁ to be 16 to generate aluminum aryloxide (M-AO₁); therefore, this molar ratio was used for masking in all tests.

AO₂ and AO₃ (no OH group was observed) were added directly into the polymerization reactor without further chemical modification, but AO₁ was masked with TEAL and then was introduced into reactor. Figure 1 shows the effect of the amount of antioxidant on catalyst activity and the isotactic index. The results indicate that the addition of up to 5000 ppm AO₂ and AO₃ did not affect Ziegler–Natta catalyst activity significantly. Catalyst activity was maintained with the addition of masked AO₁; however, using antioxidants without groups that affect catalyst activity, such as AO₂ and AO₃, is more suitable during polymerization.

It should be noted that the use of AO₂ and AO₃ individually resulted in an antioxidant with poor properties; therefore, these antioxidants should be used along with phenolic antioxidants like AO₁ [14]. An antioxidant blending technique was used to reduce the proportion of AO₁ antioxidant.

AO₄, AO₅, and AO₆ were tested using two approaches. In the first approach, precise amounts of masked AO₁, AO₂, and AO₃ antioxidants were added separately into the reactor to achieve masked AO₄, masked AO₅, and masked AO₆ formulations. Figure 2 demonstrates the effect of different amounts of antioxidants on Ziegler–Natta catalyst activity and isotactic index.

In the second approach, by calculating the amount of AO₁ in the AO₄, AO₅, and AO₆ antioxidant formulations,

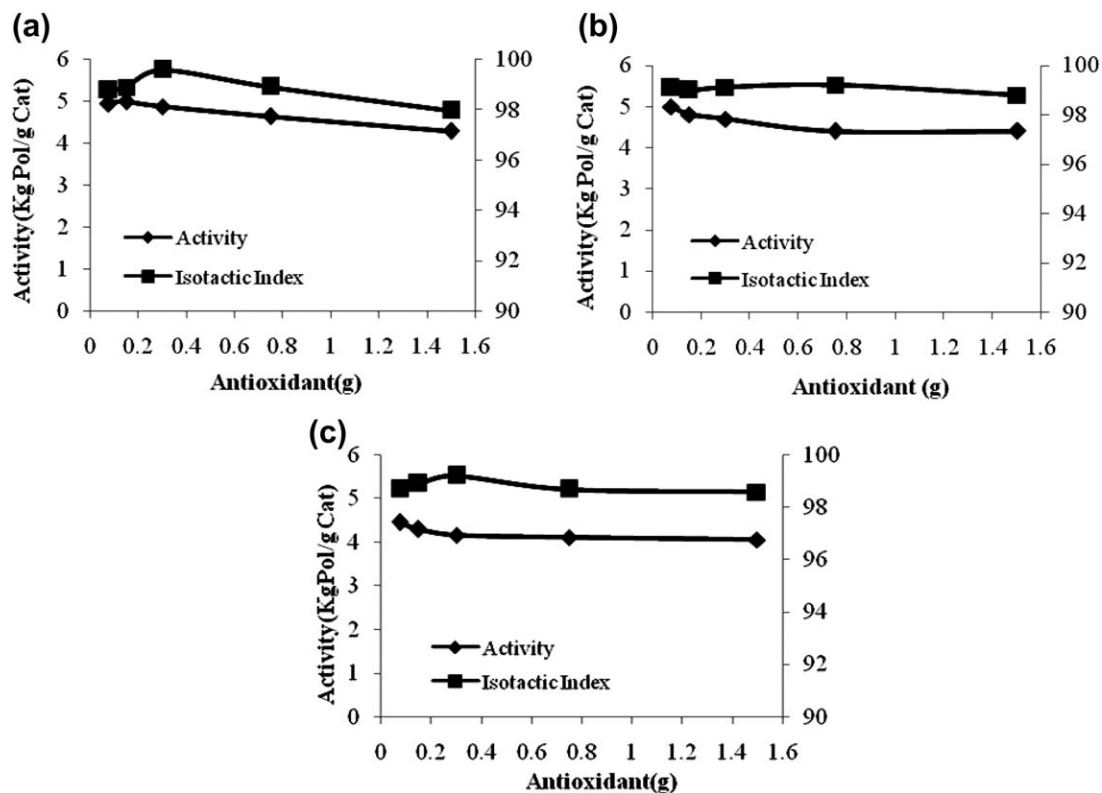


FIG. 2. The effect of different amounts of antioxidant on catalyst activity and isotactic index. (a) S-AO₄. (b) S-AO₅. (c) S-AO₆.

the right amount of TEAL (equivalent to 16 times the molar ratio) was introduced to the AO₄, AO₅, and AO₆ antioxidants. The masked AO₄, AO₅, and AO₆ were added into the polymerization reactor. Figure 3 shows the effect of antioxidant concentration on Ziegler–Natta catalyst activity and the isotactic index.

A comparison of Figs. 2 and 3 shows that adding the modified antioxidant separately into the reactor produces somewhat better results than simultaneous modification before introducing the mixture into the reactor. For instance, the addition of 750 mg of M-AO₄ antioxidant individually led to 4.65 kg pol/g catalyst activity, while modifying the antioxidant mixture and its simultaneous addition to the polymerization media led to 4.25 kg pol/g catalyst activity.

As synergism (mixing antioxidants) was used to improve thermal stability, the addition of AO₄, AO₅, and especially AO₆ was preferred to adding AO₁ alone. This is an advantage of using this antioxidant during polymerization. As stated above, when added up to 5000 ppm, AO₂ and AO₃ do not have a negative impact on catalyst activity. For equal amounts of antioxidant, the amount of masking in AO₄, AO₅, AO₆ antioxidants is lower when compared with that of AO₁. Therefore, the use of these antioxidants is preferable to AO₁ during propylene polymerization.

Polymer particle size is important to the PP industry; therefore, the influence of antioxidants such as AO₄, AO₅, and AO₆ (750 mg) on polymer particle size was examined. Figure 4 shows that the polymer particle size

of separated masked forms of AO₄, AO₅, and AO₆ during polymerization did not change significantly.

OIT-DSC test was conducted for stabilized PP containing 450 mg masked antioxidant, which was introduced separately into the reactor. Table 2 summarized OIT results. The result revealed that using the mixture of antioxidant results in better thermal stability.

Mixed antioxidants (AO₄, AO₅, and AO₆) require less masking than AO₁ antioxidant, thus, utilization of antioxidant mixtures is a promising method for in-reactor stabilization of PP. The results revealed that using up to 750 mg of antioxidant (AO₄, AO₅, and AO₆) did not change particle-size distribution markedly.

Overall, the particle-size distribution, catalyst activity, and OIT results of products showed that the use of AO₄, AO₅, and AO₆ antioxidants was better than the other options.

CONCLUSIONS

This study evaluated the effect of antioxidant type on Ziegler–Natta catalyst performance. The addition of phosphite and lactone antioxidants (AO₂ and AO₃) during propylene polymerization did not affect Ziegler–Natta catalyst performance notably. Introducing AO₁ antioxidant, because of its OH phenolic groups, decreased Ziegler–Natta catalyst activity. This indicates that TEAL should be used for masking.

Reducing the proportion of AO₁ in the final antioxidant formula during polymerization was a main goal in

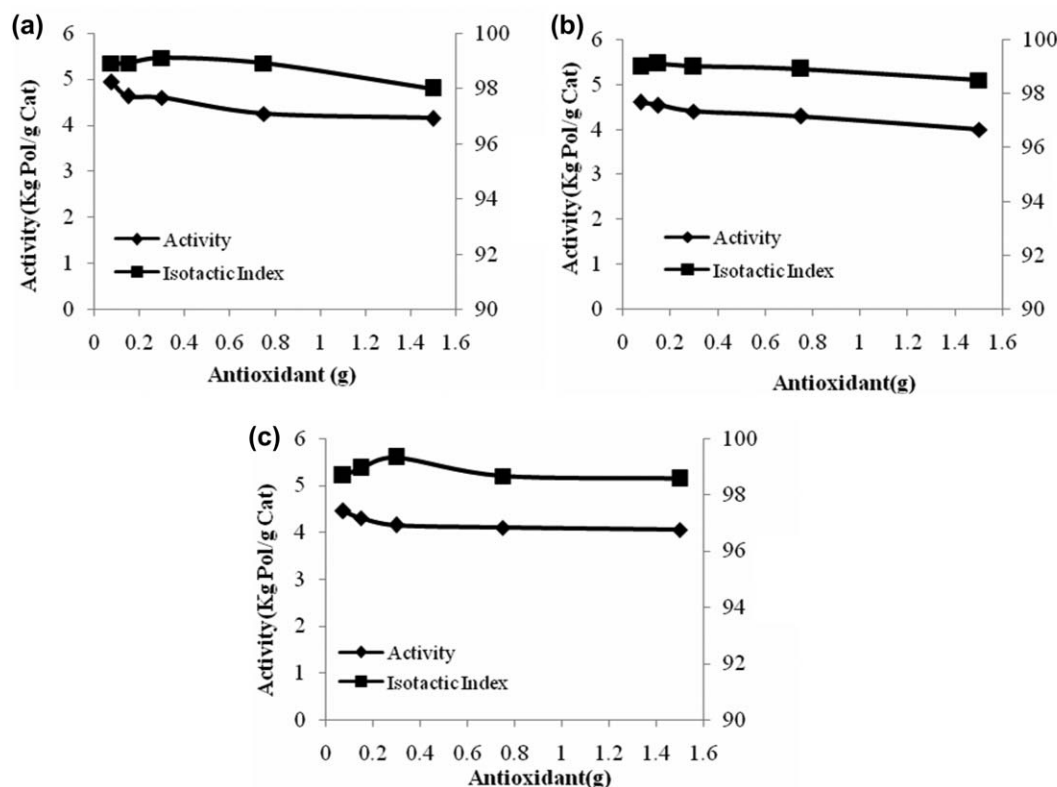


FIG. 3. The effect of different amount of antioxidant addition on Ziegler-Natta performance and isotactic index. (a) M-AO₄. (b) M-AO₅. (c) M-AO₆.

this investigation. Based on the synergistic properties of antioxidants and the decrease in the amount of AO₁ antioxidant, it is better to use a mixture of antioxidants for in-reactor stabilization of PP. The results indicated that masked AO₁ with a mixture of AO₂ and AO₃ during PP polymerization did not affect catalyst activity, isotacticity, OIT, and particle-size distribution of the products. It can be noted that adding antioxidants individually was more effective than adding simultaneously in reactor polymerization.

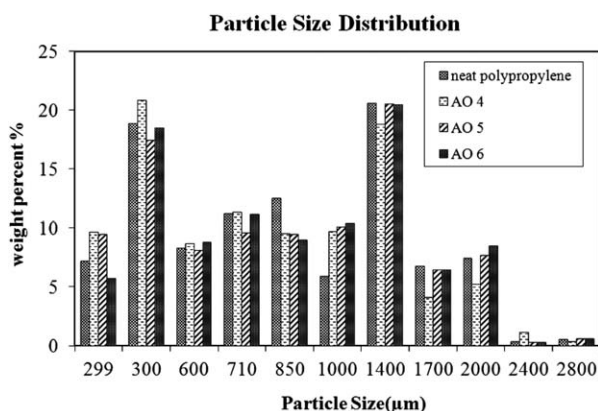


FIG. 4. Polymer particle-size distribution for stabilized and unstabilized PP.

TABLE 2. OIT result of products in 190°C.

AO (450 mg)	AO ₁	AO ₂	AO ₃	AO ₄	AO ₅	AO ₆
OIT (min)	14	1.8	8.5	16.79	14.8	20.35

REFERENCES

1. A. Alshaiban, *Propylene Polymerization using 4th Generation Ziegler-Natta Catalysts: Polymerization Kinetics and Polymer Microstructural Investigation*, Ph.D thesis, University of Waterloo, Waterloo, ON (2011).
2. R. Gensler, C. Plummer, H. Kausch, E. Kramer, J. Pauquet, and H. Zweifel, *Polym. Degrad. Stab.*, **37**, 195 (2000).
3. H. Zweifel, *Plastic Additives Handbook*, Gavl Hanser Verlag, Munich (2011).
4. R. Oliveira, M. Forrester, and M. Marques, *Macromol. Symp.*, **299**, 215 (2011).
5. W. Voigt and R. Todesco, *Polym. Degrad. Stab.*, **77**, 397 (2002).
6. N. Kawamoto, T. Horikoshi, K. Nomura, H. Yokota, Y. Negishi, E. Tobita, and M. Terano, *J. Appl. Polym. Sci.*, **99**, 1350 (2006).
7. H. Yokota, K. Nomura, T. Horikoshi, Y. Negishi, N. Kawamoto, E. Tobita, and M. Terano, *Novel energy and cost saving polypropylene stabilization via addition of antioxidant into polymerization system, studied in surface science and catalysis*, 1st ed., Elsevier, Amsterdam, **13** (2006).

8. B. Rotzinger and M. Brunner, *Polym. Degrad. Stab.*, **93**, 316 (2008).
9. A.M. Chatterjee and R.C. Job, U.S. Patent 4,818,799 (1989).
10. A.M. Chatterjee, U. S. Patent 4,853,426 (1989).
11. A.M. Chatterjee, U.S. Patent 4,879,141 (1989).
12. A.M. Chatterjee, U.S. Patent 5,064,878 (1991).
13. E. Tobita, N. Kawamoto, and T. Horikoshi, U.S. Patent 7,662,893 (2010).
14. A. Mar'in, L. Greci, and P. Dubs, *Polym. Degrad. Stab.*, **76** 489 (2002).