

Synthesis and Antioxidant Activities in Polyolefin of Dendritic Antioxidants with Hindered Phenolic Groups and Tertiary Amine

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ABSTRACT: Two novel primary antioxidants with dendritic structure and hindered phenolic groups were synthesized using 3-(3,5-diter-butyl-4-hydroxyphenyl) propionic acid as raw material and dendritic poly(amido-amine) (PAMAM) as linker in chloroform. The antioxidant activities of the dendritic antioxidants were evaluated in polyolefin by melt flow index (MFI), yellowness index (Y.I.), and oxidation induction time (OIT). The dendritic antioxidants had excellent processing property and oxidation resistance behavior in polyolefin. At the same weighed amount of antioxidant, the MFI and Y.I. values of multiple-extruded polyethylene (PE) stabilized with the dendritic antioxidants were smaller than those of the commercial antioxidants, as well as the OIT values of polyethylene (PE) stabilized with the dendritic antioxidants were larger. Applying to polypropylene, the antioxi-

dant ability of the second-generation dendritic antioxidant (G2.0 dendritic antioxidant) with larger molecular weight was superior to the commercial antioxidants and that of the first-generation dendritic antioxidant (G1.0 dendritic antioxidant) was equal to the commercial antioxidants. The dendritic antioxidants can prevent polyolefin from breaking of macromolecular chain in processing and had stabilizing effect in polyolefin in service life by donating H-atoms and electron to free radicals. The dendritic antioxidants combined with Irgafos 168 had improvement of antioxidant activities of the dendritic antioxidants in polyolefin. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4127–4135, 2012

Key words: dendrimer; hindered phenolic antioxidant; PAMAM; dendritic antioxidant; antioxidant activity

INTRODUCTION

The past decades have seen a rapid expansion in the use of polymers. Traditional materials such as wood and metals have been displaced in favor of lighter and stronger synthetic materials.¹ Unfortunately, the synthetic polymers are subjected to heat and shearing forces during processing, and they are exposed to oxygen, light, heat, and water during their service life.² All of these factors cause oxidative degradation of the polymer, resulting in changes of chemical, physical, mechanical, and aesthetical properties. To avoid polymer oxidative degradation, antioxidants are added to polymers in small amounts. Antioxidants can be divided into two broad classes, primary

and secondary, depending on their mode of operation. Primary antioxidants break the degradation chain by donating H-atoms to free radicals, which polymers degradation formed, thus preventing those radicals from propagating the chain reaction.^{3,4} The most ones are hindered phenols and aromatic amines. Hindered phenolic antioxidants with steric hindrance are white and have good thermal stability, so they have good pollution-free and nondiscoloring properties. Hindered phenolic antioxidants that are widely used in industry are very effective primary antioxidants. They displace aromatic amine antioxidants that are toxic and can cause discoloration.⁵ One of the earliest and simplest hindered phenols is 2,6-diter-butyl-4-methyphenol (BHT). Unfortunately, the antioxidant has higher volatility, and it readily forms highly colored by-products under thermo-oxidative conditions. Currently, the majority of phenolic antioxidants that have fully sterically hindered phenol were synthesized using β -(3,5-diter-butyl-4-hydroxyphenyl) propionic acid as raw material and organic micromolecular compound as linker. For example, Irganox 1010 and Irganox 1098 produced by Giba-Geigy (Switzerland) were synthesized using

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TABLE I
Amounts of Reagents and Heating Time for Synthesizing the Dendritic Antioxidants

Synthesis no	PAMAM		3,5-Propionyl chloride	TEA	Chloroform (mL)	Reacting time (h)
	Generation	Amount				
1	G1.0	1.80 g (0.005 mol)	7.41 g (0.025 mol)	5.64 g (0.020 mol)	50	8
2	G2.0	3.13 g (0.003 mol)	8.89 g (0.03 mol)	5.92 g (0.021 mol)	70	12

pentaerythritol and ethylenediamine as linker, respectively. However, these phenolic antioxidants with lower molecular weight have poor compatibility and long-term stability in polymer, which limit their application.¹ In recent years, the unique properties of dendrimers, such as high degree of branching, multi-valency, globular architecture, and well-defined molecular weight, have attracted close attention to the fields of science^{6,7} and shown bright application prospects in drug delivery, liquid crystal material, host-guest chemistry, and catalyst.^{8–11} Hindered phenolic antioxidant using dendrimer as linker is not reported so far. In this study, two novel hindered phenolic antioxidants with dendritic structure were synthesized using different generation dendritic poly(amidoamine) (PAMAM) as linker and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic acid (3,5-propionic acid) as material. The large molecules of the dendritic antioxidants make them less prone to loss by volatilization and migration. Unlike linear polymers, they would also have a large number of antioxidant groups attached to the same molecule. Both of these factors indicate that dendritic antioxidants may prove to be better than conventional low-molecular weight analogues. This article reports the synthesis and evaluation of two dendritic antioxidants.

EXPERIMENTAL

Materials and instruments

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-propionic acid purchased from Lingyi Sanfeng Chemical (China) and pyridines, *n*-hexane, chloroform, sodium hydroxide, thionyl chloride, ethanol, sodium hydrogen carbonate, and hydrochloric acid (HCl) obtained from Tianjin Kemiou Chemical reagent development center (China) were all of analytical reagent grade. Antioxidants 1010 and 3114 purchased from Ciba Specialty Chemicals (Shanghai, China) were chemical reagent grade. PAMAM dendrimers with ammonia core were synthesized in our laboratory, and the purities in them were above 99%.¹² Unstabilized polypropylene (PP) and linear low-density polyethylene (PE) were supplied by Daqing Chemical Engineering Research Center (China) and were stored in the dark. ¹H-NMR was recorded on a Varian NOVA 400-MHz NMR spectrometer using the solvent

(CDCl₃) signal as an internal standard. Infrared spectrum was performed on a Nicolet FT-IR750 using KBr pellets. Elemental analysis was carried out using German Heraeus element analyzer. Liquid chromatography–mass spectrometry was performed using Agilent 1100. Thermal analysis was performed on a DuPont 2100 with heating from 50°C to 500°C at 10°C/min in a nitrogen atmosphere.

Synthesis

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionyl chloride

3,5-Propionic acid (5.56 g; 0.020 mol) was dissolved in 30 mL of chloroform at 25°C. Thionyl chloride (6.56 g; 0.05 mol) was added dropwise to 3,5-propionic acid solution with stirring at 0°C for a period of 20 min under nitrogen atmosphere. Then, the reaction mixture was heated slowly to 50°C and reacted for 5 h. The solvent and the unreacted thionyl chloride were removed by rotary evaporation to give a white–yellow needle-like crystal. Yield: 65%, *M_p*: 72.0°C. Anal. Found: C, 68.81; H, 8.42; Cl, 12.99. Calcd.: C, 68.80; H, 8.44; Cl, 12.98. ¹H-NMR(CDCl₃, δ ppm): 5.10 (s, 1H, Ar–OH), 1.42–1.49 (m, 18H, –C(CH₃)₃), 6.91–7.18 (m, 2H, Ar–H), 2.49–2.51 (m, 2H, Ar–CH₂–), 2.69 (s, 2H, Ar–C–CH₂–COCl).

Dendritic antioxidants

An amount of PAMAM (see Table I) was added in chloroform and heated slowly to 40°C until the PAMAM was dissolved. A solution of triethylamine (TEA) in 10-mL chloroform was prepared and added to the PAMAM solution at 15°C with stirring under nitrogen atmosphere. The 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionyl chloride was added dropwise at 15°C for a period of 30 min. Then the reaction mixture was heated slowly to 45°C (Table I-reacting time). The solvent and unreacted triethylamine were removed by rotary evaporation, and the solid residue was dissolved in 20-mL ethanol. Deionized water (50 mL) was added slowly, and the solid was precipitated. The mixture was left overnight at room temperature and filtered to give yellow solid, which was washed three times with a 1 : 1 solution of ethanol and NaOH (1 mol/L). Between each wash, it was with water to remove residues of the

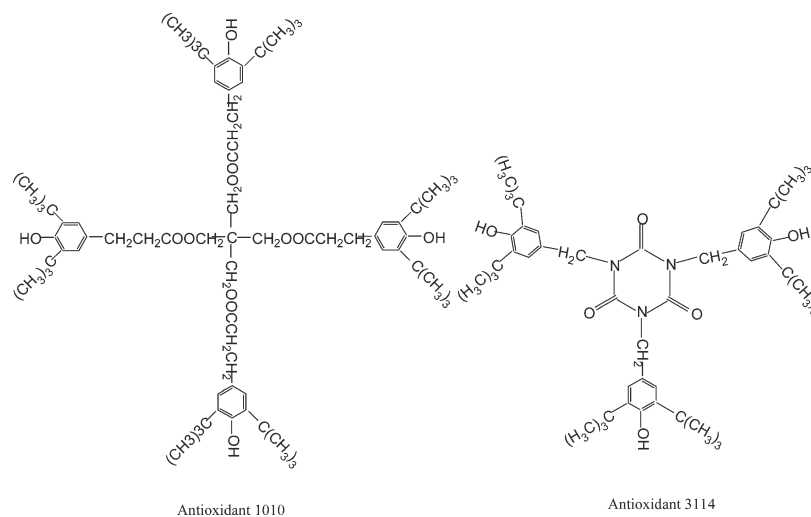


Figure 1 The commercial antioxidants 1010 and 3114.

washing solution. The product was then dried to a white solid under vacuum for 8 h at 50°C. The synthesized antioxidant prepared with the first-generation dendritic PAMAM (G1.0 PAMAM) was named as the first-generation dendritic antioxidant (G1.0 dendritic antioxidant) and with the second-generation dendritic PAMAM (G2.0 PAMAM) as the second-generation dendritic antioxidant (G2.0 dendritic antioxidant).

The yield of G1.0 dendritic antioxidant was 75%. Anal. Found: C, 69.43; H, 9.12; N, 7.96. Calcd.: C, 69.54; H, 9.22; N, 8.60. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 5.05 (s, 3H, Ar-OH), 1.40–1.45 (m, 54H, $-\text{C}(\text{CH}_3)_3$), 6.90–6.99 (m, 6H, Ar-H), 2.43–2.48 (m, 6H, Ar- CH_2 -), 2.66 (s, 6H, Ar-C- CH_2 -), 7.03 (t, 6H, $-\text{CONH}$ -), 1.22–1.30 (t, 12H, $-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ -), 3.66 (t, 6H, $-\text{N}-\text{C}-\text{CH}_2-\text{C}=\text{O}$), 2.70–2.88 (t, 6H, $\text{N}-\text{CH}_2-\text{C}-\text{C}=\text{O}$). EI-MS(m/z): 1140.2[$\text{M} + 1$] $^+$, 1121.3[$\text{M} - 18$] $^+$, 1103.3[$\text{M} - 36$] $^+$, 1085.4[$\text{M} - 54$] $^+$, 1066.3[$\text{M} - 73$] $^+$, 920.3[$\text{M} - 219$] $^+$.

The yield of G2.0 dendritic antioxidant was 63%. Anal. Found: C, 66.89; H, 10.08; N, 11.11. Calcd.: C, 67.77; H, 9.10; N, 10.22. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 5.25 (s, 6H, Ar-OH), 1.35–1.40 (m, 108H, $-\text{C}(\text{CH}_3)_3$), 6.86–6.95 (m, 12H, Ar-H), 2.44–2.50 (m, 12H, Ar- CH_2 -), 2.69 (s, 12H, Ar-C- CH_2 -), 7.06 (t, 15H, $-\text{CONH}$ -), 1.20–1.29 (t, 24H, $\text{O}=\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{C}=\text{O}$), 3.58 (t, 18H, $-\text{N}-\text{C}-\text{CH}_2-\text{C}=\text{O}$), 2.72 (t, 18H, $-\text{N}-\text{CH}_2-\text{C}-\text{C}=\text{O}$), 2.78 (t, 6H, O

$=\text{C}-\text{N}-\text{CH}_2-\text{C}-\text{N}$ -), 2.88 (t, 6H, $\text{O}=\text{C}-\text{N}-\text{C}-\text{CH}_2-\text{N}$ -). EI-MS(m/z): 2605.4[$\text{M} + 1$] $^+$, 2550.5[$\text{M} - 54$] $^+$, 2475[$\text{M} - 129$] $^+$, 2496.5[$\text{M} - 108$] $^+$, 1821[$\text{M} - 783$] $^+$.

Sample preparation

To evaluate the efficiency of the dendritic antioxidants, they were compared with the commercial antioxidants 1010 and 3114. The chemical structures of the two commercial antioxidants were shown in Figure 1. The molecular weight of the four antioxidants by the method of cryoscopy and other characteristics was summarized in Table II. The polyolefin powder and appropriate quantity of antioxidant (see Table III) were mixed using mixer at high speed, and then the polyolefin and the mixtures were extruded multiply in an SJ-65 twin screw extruder (China) having cylinder diameter of 30 mm and length of 100 mm at 100 rpm.

Melt flow index of multiple-extruded polyolefin measurements

Melt flow index (MFI) was measured using an Italian Creast melt flow indexer 6542 at an extrusion temperature of 230°C with 2.16-kg load using a small die ($\phi 0.095$ mm) according to ASTM-1238.

TABLE II
Physical Properties of Antioxidants Investigated

Characterization	1010	3114	1.0G	2.0G
Phenolic conc. (mol/kg)	3.40	4.02	2.63	2.30
Antioxidant group conc. (mol/kg)	3.40	4.02	3.51	3.84
Molecular weight	1176	747	1139	2604
Color	White crystal	White crystal	White powder	White powder
Melting temperature (°C)	110.0–125.0	212.0–216.0	204.5–206.5	226.0–229.5

TABLE III
Amounts of the Antioxidants in Polyolefin

Sample no	Commercial antioxidant		Dendritic antioxidant		Secondary antioxidant 168	Polyolefin (g)
	1010 (g)	3114 (g)	1.0G (g)	2.0G (g)		
1	0	0	0	0	0	500
2	0.5	0	0	0	0	500
3	0	0.5	0	0	0	500
4	0	0	0.5	0	0	500
5	0	0	0	0.5	0	500
6	0	0	0.5	0	0.5	500
7	0	0	0	0.5	0.5	500

Y.I. of multiple-extruded polyolefin measurements

Polymer discoloration can be monitored by change in yellowness index (Y.I.). The pure polyolefin pellets and those stabilized with antioxidants were directly measured with a HunterLab colorimeter according to ASTM D-1925.

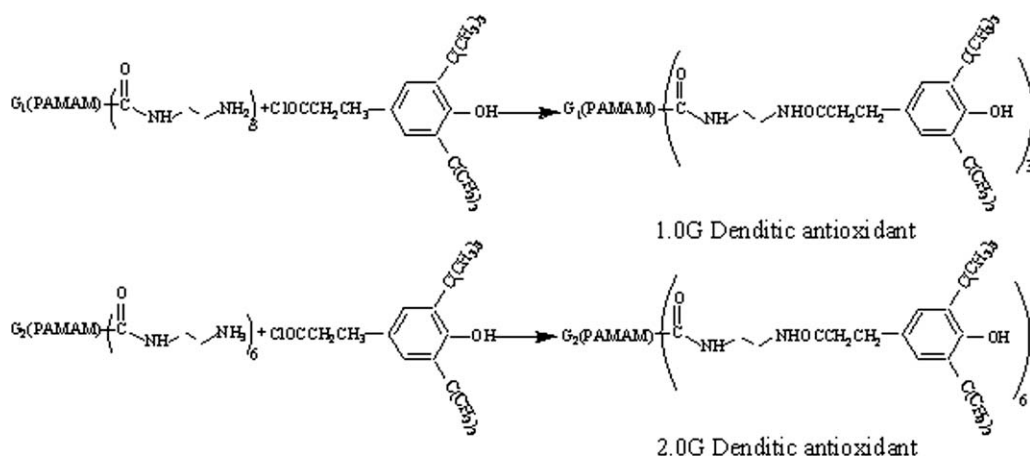
Oxidation induction time measurements

The method used for oxidation induction time (OIT) tests was based on ASTM D 3895-07 "Oxidation-Induction Time of Polymolefins by Differential Scanning Calorimetry." The OIT was determined with American Epout DSC 910 with gas switch equipment between nitrogen and oxygen in this article. The OIT measurements were performed by heating the sample to 200°C at a rate of 20°C/min and maintaining the sample at 200°C. Oxygen was supplied as purge gas at a flow rate of 50 mL/min throughout the whole experiment. The consumption of antioxidants during the nonisothermal period was negligible. The OIT was obtained as the intersection between the isothermal baseline and the tangent to the curve at the point which deviated exothermally by 1 mW from the isothermal baseline.

RESULTS AND DISCUSSION

Synthesis and characterization

The dendritic antioxidants G1.0 and G2.0 were prepared using dendritic polymers PAMAM G1.0 and G2.0 as linker, respectively. Reaction equations were described in Scheme 1. To synthesize dendritic antioxidants with high degree of substitution, the active groups (3,5-propionyl chloride) were used in excess, which means there was unreacted 3,5-propionyl chloride left in the reacted mixture. The unreacted 3,5-propionyl chloride was removed by washing the solid product with a 1 : 1-solution of EtOH : NaOH (1 mol/L). The dendritic antioxidants were characterized by elemental analysis, IR spectroscopy, ¹H-NMR, EI-MS, and TG. The IR spectra of dendritic antioxidants indicated that the dendritic antioxidants were fully substituted as the broad amidine peak at 3200 cm⁻¹ had disappeared and the strong phenolic hydroxyl peak at 3628 cm⁻¹ and 1164 cm⁻¹ had appeared (Fig. 2). For the two dendritic antioxidants, the acylamino groups vibrating peak appeared around 1535 cm⁻¹ and 1630 cm⁻¹ and the tertiary butyl peak appeared at 1240 cm⁻¹ and 1390 cm⁻¹. The elemental analysis, ¹H-NMR (Fig. 3), and EI-MS were summarized in the synthesis section. They



Scheme 1 Conceptual scheme for the synthesis of dendritic antioxidants.

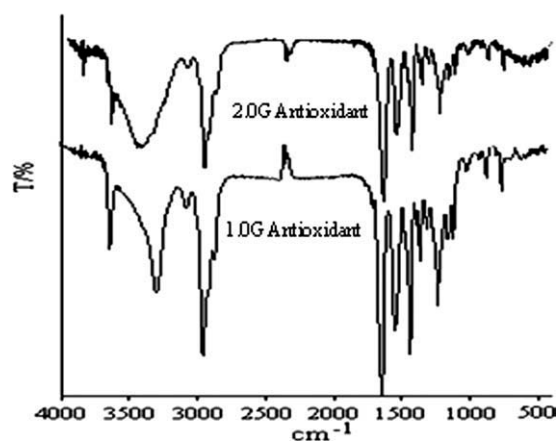


Figure 2 Infrared spectra of dendritic antioxidants.

agreed well with the FTIR data to confirm the structure of the dendritic antioxidants. The thermal characteristics of the dendritic antioxidants measured in nitrogen atmosphere were illustrated in Figure 4. Dendritic antioxidants synthesized were nonvolatile and stable thermally under 200°C. The weight loss of dendritic antioxidant G1.0 reached above 90% at 430°C and those of dendritic antioxidant G2.0 reached above 90% at 470°C.

MFI of multiple-extruded polyolefin stabilized with antioxidants

In case of polyolefin, chain scission and thermo-oxidative degradation of the macromolecules result in a decrease in the molecular weight of polyolefin with the increase of MFI.¹³ So the thermo-oxidative and thermomechanical antioxidant activities of antioxidants in melt processing of polyolefin are characterized using MFI of multiple-extruded polyolefin sta-

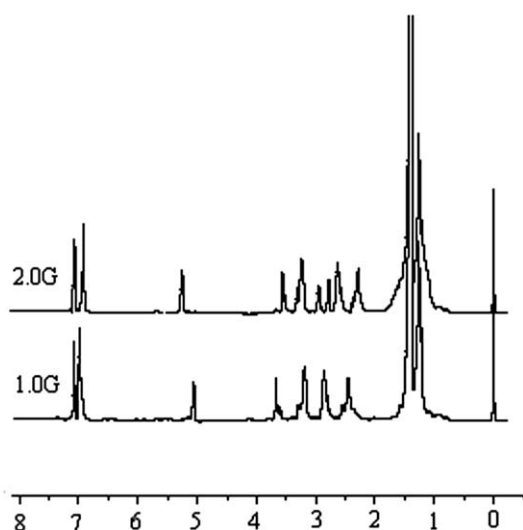


Figure 3 ¹H-NMR spectra of dendritic antioxidants (solvent: CDCl₃).

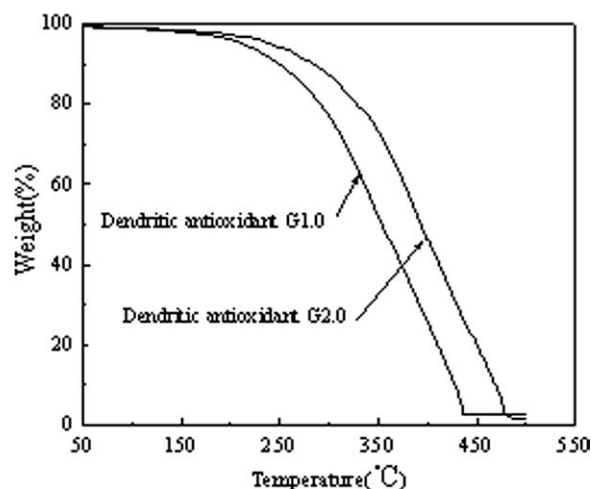


Figure 4 The TG curves of dendritic antioxidants.

bilized with antioxidants. Polyolefin are subjected to heat and shearing forces during processing, which caused degradation and decrease of molecular weight of polyolefin. The polyolefin had a better fluidity in the melt processing of polyolefin, and the MFI values increased. Antioxidants were added to polyolefin in small amounts to avoid polyolefin degradation, and the MFI value of polyolefin stabilized with antioxidants was smaller than those of pure polyolefin.¹⁴

Figures 5 and 6 displayed the MFI values of PP and PE stabilized with different antioxidants after the corresponding extrusion pass, respectively. For the hindered phenol antioxidants, the more of phenol groups means the better stabilization in polyolefin. At the weighed amount of antioxidants, antioxidant 3114 had the most hindered phenol groups, and G2.0 dendritic antioxidant had the least ones (Table II).

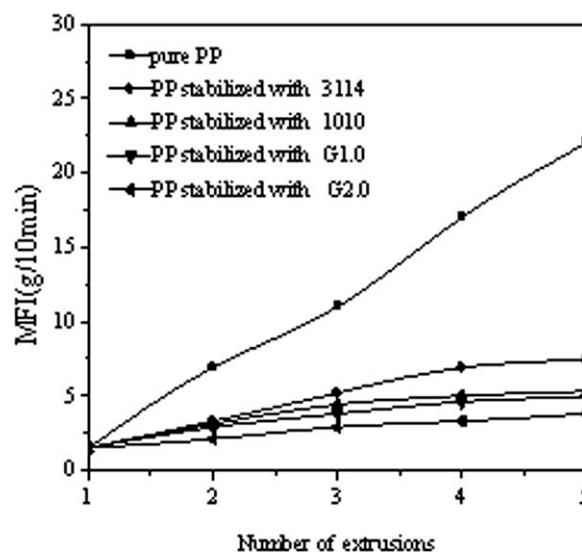


Figure 5 MFI of multiple-extruded PP stabilized with different antioxidants. Antioxidant concentration: 1 mg/g.

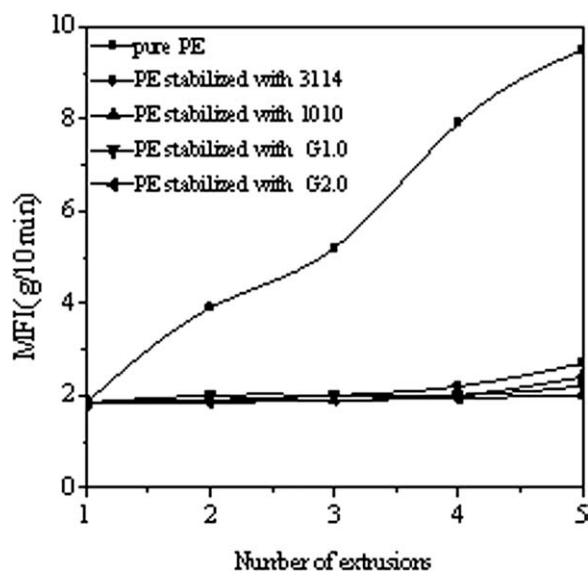


Figure 6 MFI of multiple-extruded PE stabilized with different antioxidants. Antioxidant concentration: 1 mg/g.

However, the antioxidant activity of antioxidant 1010 and 3114 were equal to that of G1.0 dendritic antioxidant but much worse than that of G2.0 dendritic antioxidant at the same weighed amount of antioxidant (Figs. 5 and 6). The dendritic antioxidants were intramolecular complex antioxidants with hindered phenol groups and tertiary amine, and they can prevent polyolefin from thermal oxidative degradation by donating H-atoms and electrons to free radicals. The dendritic antioxidants had intramolecular synergic effect in processing of polyolefin.

Y.I. of polyolefin stabilized with antioxidants

Polyolefin discoloration during processing and exposing to oxygen, light, heat, and water in their service life is a serious commercial problem. Some products of sacrificial or depleting consumption of antioxidants arising during polymer lifetime as a consequence of reactions of antioxidants with alkylperoxy radicals and atmospheric pollutants is one of principal contributors to discoloration of polyolefin which can be monitored by change in yellowness index (Y.I.).¹⁵ Antioxidants forming strongly discoloring products cannot be tolerated in most white or light-colored polymeric materials. Under the conditions, the discoloration due to the oxidation of antioxidants has drawn more and more attention. The discoloration that depends on the structure and concentration of the phenol transformation products can be attributed to the formation of conjugated diene compounds, arising as a consequence of sacrificial trapping of alkylperoxy radicals by phenolics. Peroxycyclohexadienones are formed transiently in low

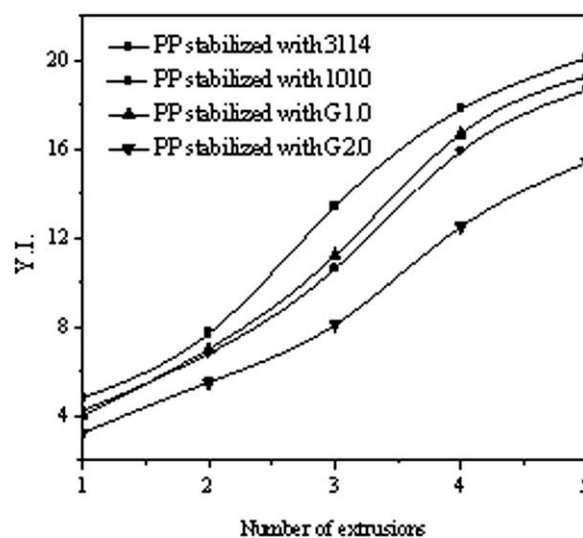


Figure 7 Y.I. of multiple-extruded PP stabilized with different antioxidants. Antioxidant concentration: 1 mg/g.

concentrations and themselves do not discolor the polymer matrix.¹⁶

In this article, the Y.I. values of multiple-extruded polyolefin stabilized with different hindered phenolic antioxidants with multiphenolic groups were measured to study the effect of these antioxidants on the discoloration of polyolefin (Figs. 7 and 8). The Y.I. values of PP and PE stabilized with 2.0G dendritic antioxidant were smaller than those stabilized with other antioxidants after corresponding pass. With multifunctional phenols, the efficiency of stabilization is closely related to the concentration of phenol groups. The greater activity allows the use of lower antioxidant concentration without sacrificing performance. At the same weighed amount of antioxidant, G2.0 dendritic antioxidant had least phenol

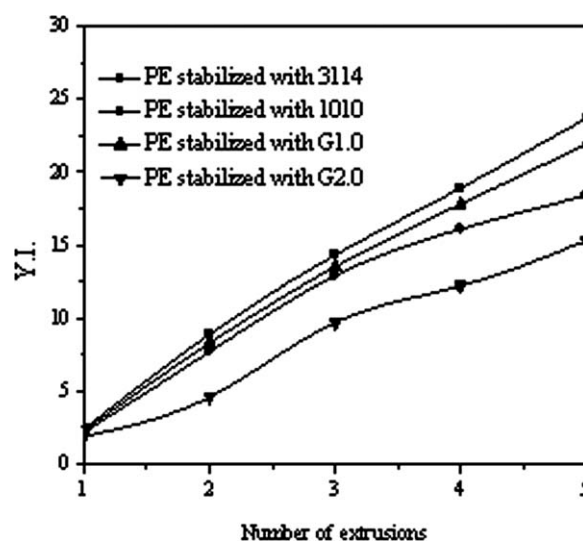


Figure 8 Y.I. of multiple-extruded PE stabilized with different antioxidants. Antioxidant concentration: 1 mg/g.

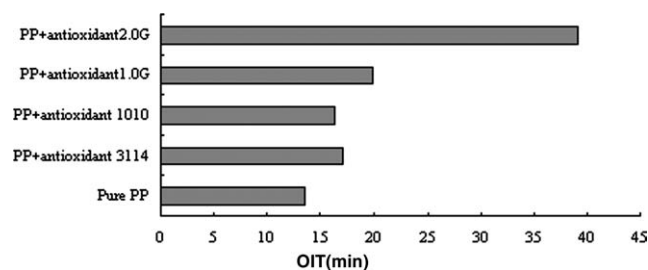


Figure 9 Results of OIT measurement with antioxidants in PP. Phenol group concentration: 2.3 mmol/kg.

concentration (Table II), and the Y.I. values of the two polyolefin stabilized with G2.0 dendritic antioxidant were smallest due to the reactions such as aryl-aryl peroxide and stibenequinone formation, which caused discoloration (Figs. 7 and 8). The Y.I. values of the two polyolefin stabilized with antioxidant 1010 was smaller than those stabilized with G2.0 dendritic antioxidant and antioxidant 3114, respectively, although the phenol concentration of antioxidant 1010 was larger at the same weighed amount of antioxidant. The reactions that caused discoloration also reduced because of steric considerations. In addition, the dendritic antioxidants reduced the thermo-oxidative degradation of polymer that caused discoloration because of intramolecular synergic antioxidation effect.

OIT of polyolefin stabilized with antioxidants

Antioxidants can inhibit polyolefin from thermal oxidative degradation in service life. The OIT is the time that it takes before the sample starts to oxidize. The more resistant the sample is to oxidation, the longer the OIT is.¹⁷ The OIT values were determined from the DSC thermograms. The computer was used to calculate the second derivative of the enthalpy versus time curve. The first peak of this second derivative was taken as the onset of oxidation (the OIT value).¹⁸ According to the generally accepted mechanism underlying the oxidation of polyolefin first described by Bolland and Gee,¹⁹ the oxidation degradation process of polyolefin is dominated by free

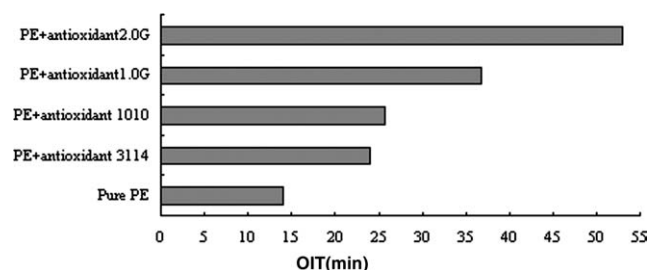


Figure 10 Results of OIT measurement with antioxidants in PE. Phenol group concentration: 2.3 mmol/kg.

radical chain reactions. Light energy, heat, or shear would lead to polyolefin chain breakage and the concomitant formation of chain free radicals that will usually react first with oxygen to form peroxides or peroxy radicals. The new radicals formed by the decomposition of these peroxides would initiate new oxidation cycles and accelerate polyolefin oxidation degradation.^{20,21} Antioxidants can prevent these radicals from propagating the chain reaction by donating H-atoms to the free radicals, thus breaking the degrading chain.

There is a very close relationship between the antioxidant activity and the concentration of phenol group for phenol antioxidants. The results of the OIT measurements in polyolefin revealed that the dendritic antioxidants were more effective at stabilization of the polyolefin than the commercial antioxidant 1010 and 3114. The OIT value of the polyolefin stabilized with antioxidant 2.0G was longest (Figs. 9 and 10) at the same concentration of phenol groups. This is perhaps that the dendritic antioxidants with hindered phenolic groups and tertiary amine were intramolecular complex antioxidants, and they can prevent polyolefin from thermal oxidative degradation by both of donating H-atoms to free radicals and terminating free radicals by electron transfer. The dendritic antioxidant G1.0 and G2.0 have 0.8 and 1.5 mmol/kg tertiary amine, respectively, when the concentration of phenol group for the four antioxidants in polyolefin was 2.3 mmol/kg.

However, the most relevant way of determining the most cost-efficient stabilizer in industrial

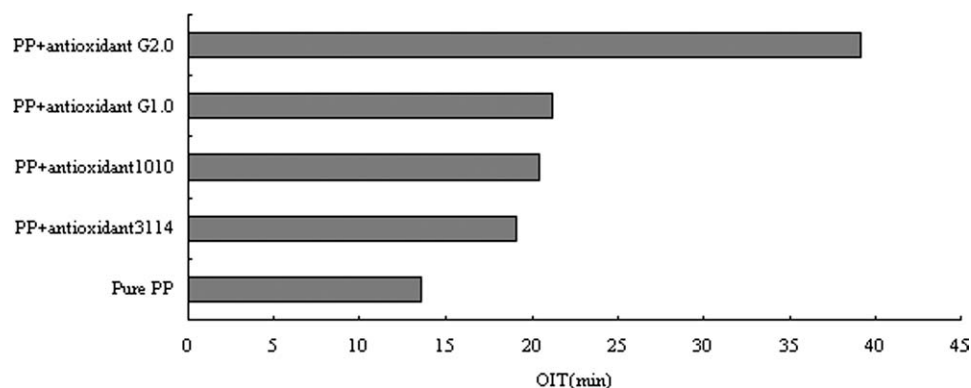


Figure 11 Results of OIT measurement with antioxidants in PP. Antioxidant concentration: 1 mg/g.

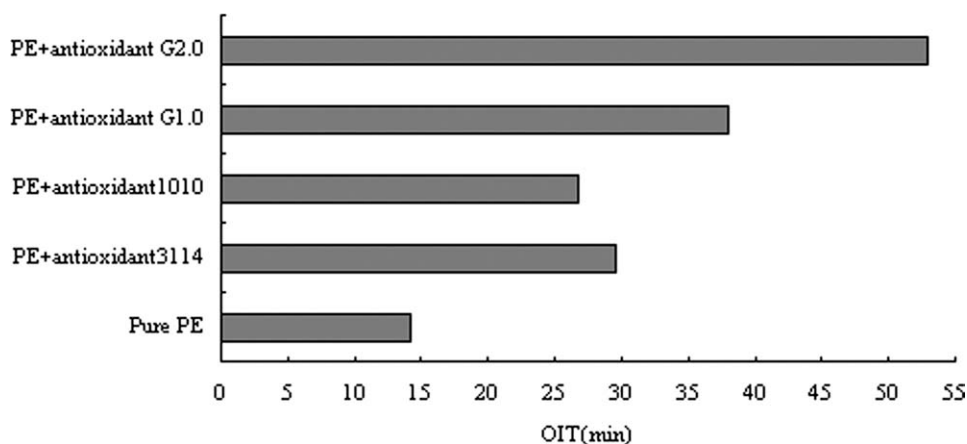


Figure 12 Results of OIT measurement with antioxidants in PE. Antioxidant concentration: 1 mg/g.

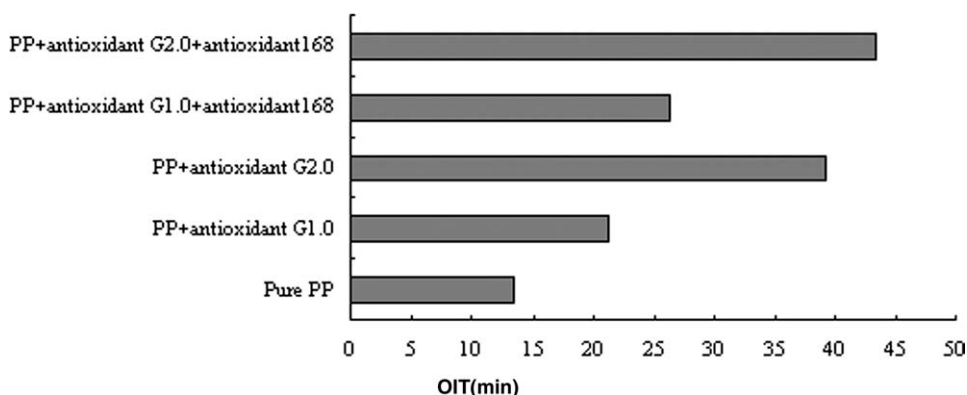


Figure 13 Results of OIT measurement with antioxidants in PP. Primary and secondary antioxidants concentration respectively: 1 mg/g.

application is perhaps that antioxidants were added to the same weighed amount. So the OIT in polyolefin for the four antioxidants at the same mass were studied. The results of the OIT measurements in polyolefin at the same weighed amount of antioxidant revealed that the OIT of the polyolefin stabilized with antioxidant was longer than that of the pure

polyolefin, and the synthesized antioxidant was more effective at stabilizing the polyolefin than the commercial antioxidant 1010 and 3114 (Figs. 11 and 12). Overall, as a novel antioxidant, the dendritic antioxidants were found to overperform the standard commercial antioxidant 1010 and 3114. This would make the dendritic antioxidants be effective

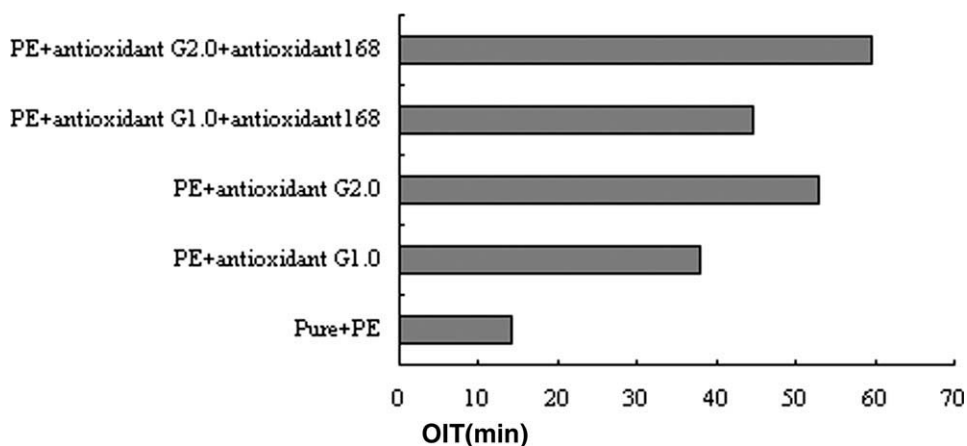


Figure 14 Results of OIT measurement with antioxidants in PE. Primary and secondary antioxidants concentration respectively: 1 mg/g.

as long-term stabilizers for polyolefin instead of traditional commercial antioxidants.

During the service lifetime of polyolefin, the primary antioxidants could only scavenge the chain free radicals because of polyolefin degradation. The new radicals formed by the decomposition of these peroxides would initiate new oxidation cycles and accelerate polyolefin oxidation degradation. Secondary antioxidants act as peroxide decomposers and inhibit polyolefin oxidation degradation. Primary and secondary antioxidants are used in combination to take advantage of the observed synergy. The dendritic antioxidants combined with Irgafos 168 had improvement of antioxidant activities of the dendritic antioxidants in polyolefin (Figs. 13 and 14).

CONCLUSIONS

The dendritic antioxidants G1.0 and G2.0 were prepared using dendritic polymers PAMAM as linker and used to prevent polyolefin from thermal oxidation degradation. The antioxidative groups were attached to the two different dendritic PAMAM. The synthesis was successful with high degree of substitution. As a novel kind of phenolic antioxidants, the dendritic antioxidants have lower volatility and migration compared with traditional phenolic antioxidant because of its high molecular weight and can prevent polyolefin from thermal oxidative degradation effectively by both of donating H-atoms to free radicals and terminating free radicals by electron transfer. Moreover, the dendritic antioxidants combined with Irgafos 168 have improvement of antioxidant activities of the dendritic antioxidants in polyolefin thermo-oxidative degradation processing. The mechanism and other properties of novel primary antioxidant would be studied in our further works, and the dendritic antioxidants with more

antioxidative groups would be further synthesized and applied to polyolefin.

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