

# Synthesis and Characterization of Hindered-Phenol-Containing Amine Moieties as Antioxidants for Polypropylene Copolymers

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**ABSTRACT:** (4-Ethylphenyl)-3,5-ditertiarybutyl-4-hydroxybenzylamine, 1-phenyl-4-(3,5-ditertiarybutyl-4-hydroxybenzyl)piperazine, and 1-(3,5-ditertiarybutyl-4-hydroxybenzyl)piperidine were synthesized and characterized, and their performance in polypropylene copolymer (PPCP) was tested by multiple extrusions in a Brabender plasticorder. The thermooxidative stability of PPCP was assessed by the measurement of oxidative induction time at  $200 \pm 1^\circ\text{C}$ , and the thermal stability was assessed by observation of the change in the melt flow rate. A comparative study of the synthesized antioxidants

with the commercially available antioxidant 2,6-ditertiarybutyl-4-methylphenol was made. The presence of phenolic and amino groups influenced the performance of the antioxidants. The performance of the antioxidants influenced the thermal stability of the PPCP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1097–1103, 2004

**Key words:** antioxidants; extrusion; melt; poly(propylene) (PP)

## INTRODUCTION

All commercial organic polymers are susceptible to oxidative degradation due to the formation of free radicals during processing and end use. So they require protection with antioxidants to retain their physical properties and to ensure an adequate service life. Hindered phenols and aromatic secondary amines are the major classes of antioxidants presently used as radical-trapping agents in plastics, elastomers, fuels, lubricants, and foods. Steric hindrance is provided by bulky substituents ortho to the hydroxy group in the ring, and they also influence the specificity of the phenols by blocking phenoxy radicals from abstracting the hydrogen atom from the organic substrate. Secondary amines serve as a source of hydrogen atoms and show the same competitive reactions found with hindered phenols. Tertiary amines are frequently used as metal deactivators, which chelate metal ion and increase the potential difference between oxidized and reduced states of metal ions. This decreases the ability of the metal ion to produce radicals from hydroperoxide by oxidation and reduction.<sup>1</sup> Most of the aromatic amine antioxidants are colored or produce color during oxidation, limiting their use to applications where discoloration can be tolerated.<sup>2</sup>

Wasson and Smith<sup>3</sup> reported that a *tert*-butyl group at the ortho position, and an alkyl group at the para position positions resulted in the most effective antioxidant activity in the alkyl phenolic type of antioxidants, of which, 2,6-ditertiarybutyl-4-methylphenol (BHT) is well known.

Antioxidants are used to provide protection to a polymer during processing. They must be capable of migrating freely throughout the polymer bulk to reach the large number of initiation sites that are generated at elevated temperatures.<sup>4</sup> For this reason, low-molecular-weight antioxidants such as BHT are preferred. However, BHT suffers a major drawback because of its high volatility, which can be minimized by the replacement of its methyl group at the para position of the hydroxy group with a long aliphatic group. Polypropylene copolymer (PPCP), because of its high heat-deflection temperature, can be subjected to higher processing temperatures and more severe service conditions. The stabilization of PPCP is achieved through the use of high-molecular-weight antioxidants. BHT was initially used as an antioxidant for PPCP, but because of its high volatility, it was replaced by Irganox 1076 (hindered phenol). Some of the phosphite stabilizers are sensitive to hydrolysis, which can lead to the formation of phosphorus acid. This can cause the corrosion of processing equipment.<sup>5</sup> Thus, efforts are being made to improve the additive package for PPCP.

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In our earlier studies,<sup>6–9</sup> we modified the structure of BHT by introducing a bulky group at a para position to the OH group. Novel antioxidants, based on hindered phenol in combination with acid hydrazides and thiosemicarbazones, were synthesized. Their performances were tested in isotactic polypropylene homopolymer and were comparable with commercially available antioxidants. In the continuation of our efforts to find new antioxidants, in this article, we report the synthesis and characterization of antioxidants based on hindered phenol in combination with amines. We tested the efficiency of these antioxidants in PPCP with a view to study the effect of synergism of two stabilizing moieties in the molecule by following the change in melt flow rate (MFR) and the oxidative induction time (OIT), respectively.

The synthesis of 2,6-ditertiarybutyl-4-chloromethylphenol was achieved by the introduction of a chloromethyl group at the para position to the hydroxy group in 2,6-ditertiarybutyl phenol with a method reported by Geigy.<sup>10</sup> 1-Phenyl-4-(3,5-ditertiarybutyl-4-hydroxybenzyl)piperazine (AO2) was synthesized according to the method by Nair et al.<sup>11</sup> The antioxidants (4-ethylphenyl)-3,5-ditertiarybutyl-4-hydroxybenzylamine (AO1) and 1-(3,5-ditertiarybutyl-4-hydroxybenzyl)piperidine (AO3) were synthesized by the condensing of a chloromethyl derivative with 4-ethylaniline and piperidine, respectively. AO3 could also be synthesized by the application of the Mannich reaction on 2,6-ditertiarybutylphenol with piperidine. These synthesized antioxidants were mixed with PPCP and were subjected to melt mixing and multiple extrusions. After multiple extrusion, the melt flow behavior of the extruded samples was studied,<sup>12</sup> and the OIT values of the first extruded samples were measured.<sup>13</sup> The OIT is the time before the onset of thermal oxidation in the melt, and it indicates the thermooxidative stability of a polymeric formulation. The measurement of OIT is one of the most practical and commonly used methods for obtaining information on polymer stability, antioxidant effectiveness, and degree of degradation incurred during polymer processing.<sup>14</sup>

All of the newly synthesized antioxidants were characterized by elemental analysis, IR, and <sup>1</sup>H-NMR spectral techniques.

## EXPERIMENTAL

### Materials

2,6-Ditertiarybutylphenol was supplied by Lancaster (England). Triethylamine, *para*-formaldehyde, acetic acid, *p*-ethylaniline, 1-phenylpiperazine, and piperidine were obtained from BDH (England). All of the solvents used were reagent grade and were purified by distillation. Unstabilized PPCP with 6–8% ethylene in powder form (M/s Indian Petrochemical Corp.,

Ltd., Baroda, India) was used for the study. The MFR of PPCP, measured at a 230°C/2.16 kg load as per ASTM D 1238, was 4.3 g/10 min.

### Instruments

Elemental analyses were performed with a PerkinElmer 2400 (Norwalk, CT) C, H, N, and S analyzer. IR spectra were recorded on a Shimadzu IR 408 (Japan) spectrophotometer with KBr pellets. NMR spectra were recorded on a Brukers 200-mHz (Wissensbourg, France) spectrophotometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Signal positions ( $\delta$  value) were measured relative to the TMS signal ( $\delta$  0). Analytical thin-layer chromatography (TLC) was performed on precoated E. Merck silica gel 60 F<sub>254</sub> aluminium plates. The OIT tests were conducted on a DSC 2910 (M/s TA Instruments). MFR values are expressed in grams 10 per min. The melt flow behavior of the samples was studied with a melt flow indexer (Devenport, England). Multiple extrusions were carried out with a Brabender plasticorder PLV-151 (Duisburg, Germany) with a temperature profile of 180–210–230–205°C at a screw speed of 50 rpm.

### Synthesis

#### AO1

To a solution of 4-ethylaniline (0.3 mol) in dry benzene (50 mL), 2,6-ditertiarybutyl-4-chloromethylphenol (0.1 mol) was added in portions, followed by triethylamine (0.15 mol). The reaction mixture was refluxed for 6 h. The benzene layer was washed with HCl (35%) followed by distilled water and was removed by distillation. The product obtained was recrystallized from benzene [melting point (mp) = 197°C; yield = 70%]. TLC showed a single spot at  $R_f$  = 0.46 in 10% benzene: petroleum ether.

ANAL. Calcd for C<sub>23</sub>H<sub>33</sub>NO (339.52): C, 81.29%; H, 9.72%; N, 4.12%. Found: C, 81.03%; H, 9.78%; N, 3.79.

IR (KBr, cm<sup>-1</sup>,  $\gamma_{\max}$ ) 3610 (OH), 3300 (NH). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.20 (3H, t, CH<sub>3</sub>); 1.37 [18H, s, 2xC(CH<sub>3</sub>)<sub>3</sub>]; 2.52 (2H, q, CH<sub>2</sub>—CH<sub>3</sub>), 4.41 (2H, s, CH<sub>2</sub>—Ph), 5.10 (1H, s, OH), 6.7 (2H, d, ArH), 7.05 (2H, s, ArH), 7.15 (2H, d, ArH) ppm (Fig. 1).

#### AO2

AO2 was synthesized according to a reported procedure.<sup>11</sup>

#### AO3

*Method 1.* To a solution of 2,6-ditertiarybutyl-4-chloromethylphenol (0.1 mol) in dry benzene (50 mL),

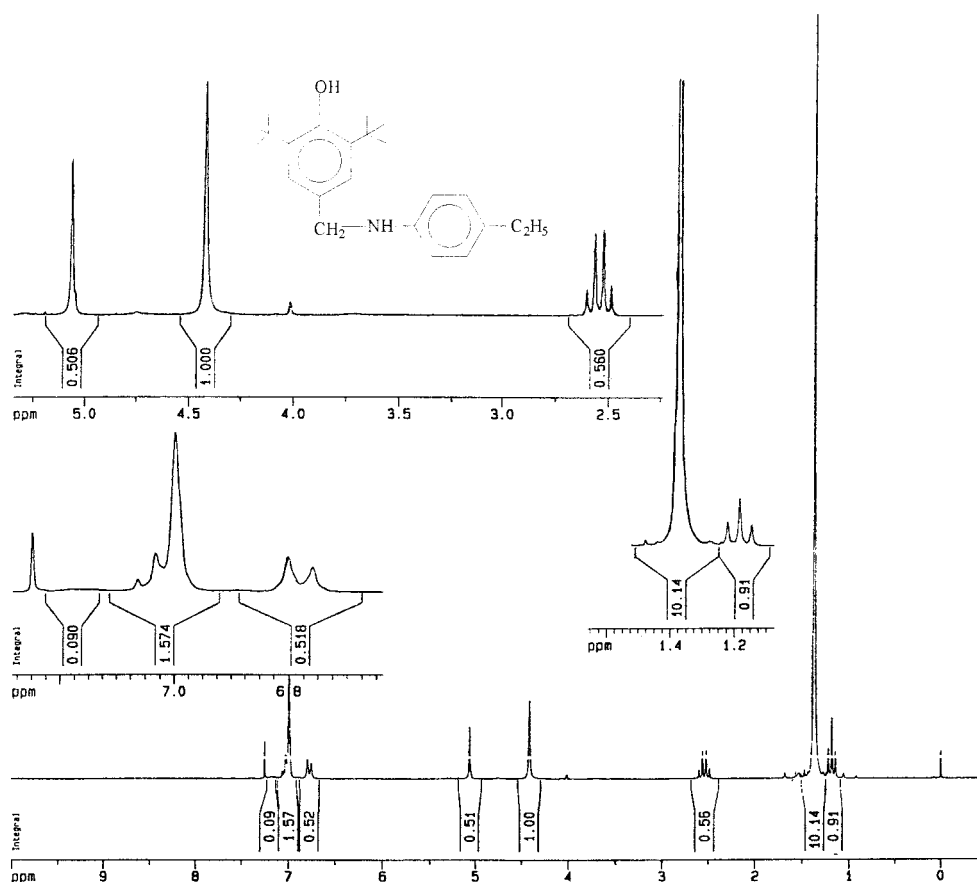


Figure 1  $^1\text{H-NMR}$  spectrum of antioxidant AO1.

piperidine (0.1 mol) was added followed by triethylamine (0.15 mol). The reaction mixture was refluxed for 6 h. The benzene layer was washed with HCl (35%) followed by distilled water. The AO3 product obtained after removal of benzene was recrystallized from petroleum ether (yield = 82%).

**Method 2.** Piperidine (0.1 mol) was added to a solution of 2,6-ditertiarybutylphenol (0.1 mol) in ethanol (50 mL) and 30% formalin (0.35 mol). The reaction mixture was refluxed for 5 h. The AO3 obtained by the pouring of the reaction mixture into cold water was recrystallised from petroleum ether (yield = 90%).

AO3 showed a single spot at  $R_f = 0.52$  in 2% ethyl acetate:petroleum ether (mp = 80°C).

ANAL: Calcd for  $\text{C}_{20}\text{H}_{33}\text{NO}$  (303.49): C, 79.16%; H, 10.80%; N, 4.60%. Found: C, 78.70%; H, 10.94%; N, 4.28%.

IR (KBr,  $\text{cm}^{-1}$ ,  $\gamma_{\text{max}}$ ) 3615 (OH).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ). 1.40 [18H, s,  $2 \times \text{C}(\text{CH}_3)_3$ ], 3.2–3.4 (10H, m,  $\text{CH}_2$ ), 4.0 (2H, s,  $\text{CH}_2\text{-Ph}$ ), 5.30 (1H, s, OH), 7.20 (2H, s, Ph) ppm (Fig. 2).

#### Testing of PPCP with the synthesized and commercial antioxidant

The melt-mixing of PPCP was carried out with different concentrations of a commercially available antioxi-

idant and with the synthesized antioxidants to identify a suitable concentration of antioxidant required for PPCP stabilization. The stability of the polymer melt was assessed through the measurement of MFR values at three different loads as a function of time and temperature. The performance of antioxidants in polymer processing was tested in the polymer melt and was assessed by multiple extrusions. The multiple extrusions of PPCP were carried out with the identified concentration of the commercially available antioxidant and the synthesized antioxidants.

#### Process for melt-mixing

To 100 g of unstabilized PPCP, 0.05 wt % calcium stearate, 0.06 wt % glycerine monostearate (GMS), and 0.03 wt % synthetic hydrotalcite (SHT) were added. BHT and the synthesized antioxidants were added individually in a concentration range of 0.07–0.09 wt %. The mixture was extruded at a temperature profile of 180–210–230–205°C with a screw speed of 50 rpm. The extrudate was converted to granules and dried at  $80 \pm 2^\circ\text{C}$  for 1.5 h. MFR values were recorded at 230°C with 1.00-, 2.16-, and 3.16-kg loads to identify a suitable concentration antioxidant with which to impart stability to PPCP.

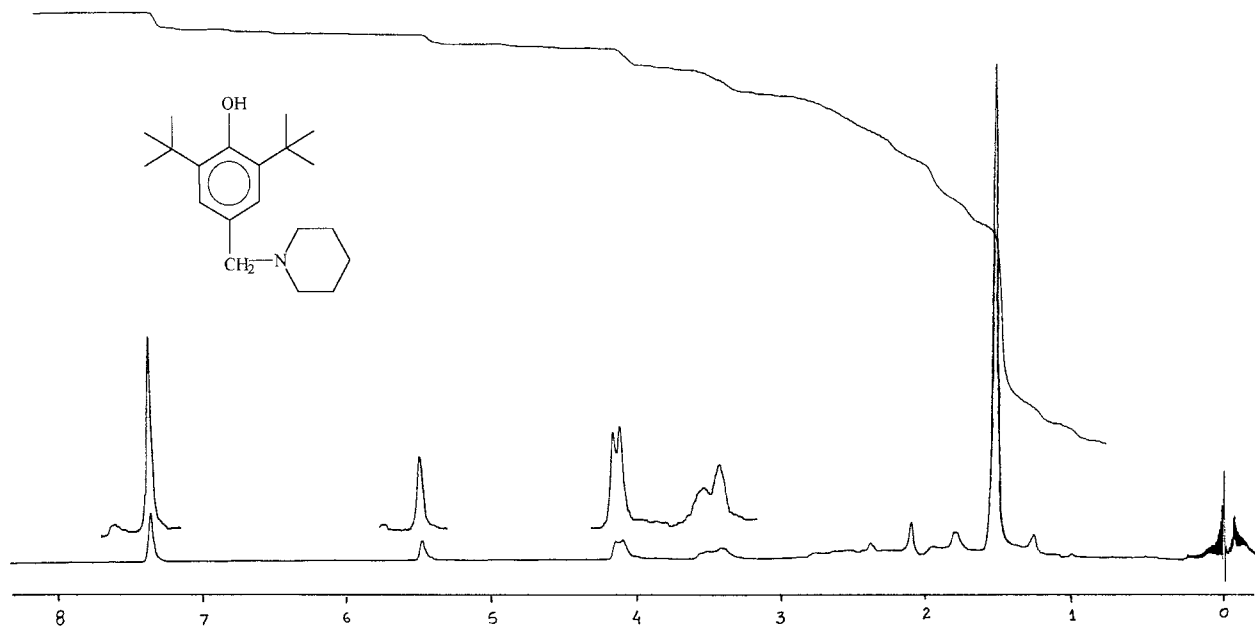


Figure 2  $^1\text{H-NMR}$  spectrum of antioxidant AO3.

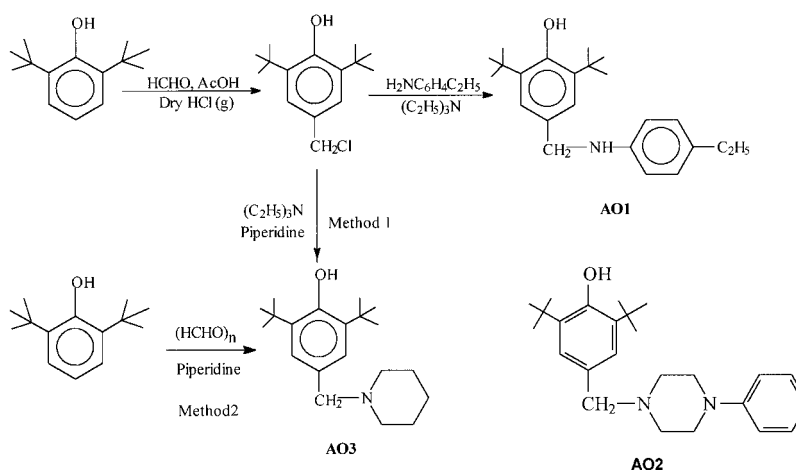
### Process for multiple extrusions

Suitable concentrations of the commercial antioxidant BHT and the synthesized antioxidants (AO1, AO2, and AO3) were mixed individually with 0.05 wt % calcium stearate 0.06 wt % GMS, wt % SHT 0.03 and 1000 g of PPCP powder and were extruded in the Brabender plasticorder with a temperature profile of 180–210–230–205°C at a screw speed of 50 rpm. The extrudate was granulated, dried at  $80 \pm 2^\circ\text{C}$  for 2 h, and subjected to a second extrusion. Thus, extrusions were carried out six times with each antioxidant. The degradation study of PPCP was carried out by the comparison of the melt flow behavior of the extruded sample with that of the reference sample extruded

with SHT, GMS, and calcium stearate without antioxidant under similar conditions.

### Process for oxidative induction time (OIT) measurement

The OIT tests were conducted with a TA DSC 2910 instrument. The instrument was temperature-calibrated at  $1^\circ\text{C}/\text{min}$  with tin and indium standards. Each sample was placed in an oxidized copper pan, as recommended in ASTM D 3895-95. An empty oxidized copper pan was used as a reference. Each sample and each reference pan were heated to  $200^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  with a 50 mL/min nitrogen flow rate. After



Scheme 1 Synthetic route for AO1 and AO3.

**TABLE I**  
MFR Values of PPCP Extruded with Commercial and Synthesized Antioxidants at Different Concentrations

Antioxidant	Concentration (ppm)	Melt flow rate at 230°C with a load of		
		1.00 kg	2.16 kg	3.16 kg
BHT	0.07	1.34	2.84	5.73
	0.08	1.42	3.02	6.09
	0.09	1.50	3.22	6.36
AO1	0.07	1.09	2.82	5.41
	0.08	1.08	2.78	5.20
	0.09	1.12	2.81	5.26
AO2	0.07	1.33	3.05	5.81
	0.08	1.38	3.30	6.42
	0.09	1.21	2.90	5.71
AO3	0.07	1.22	3.05	5.67
	0.08	1.66	3.44	6.20
	0.09	1.33	3.24	5.90

MFR values were measured in grams per 10 min.

equilibrium was attained, the environment was changed from nitrogen to oxygen at the same flow rate, and the instrument was kept in an isothermal mode until the sample degraded. The OIT was taken as the time corresponding to the point at which the extrapolated exotherm intersected the extended base line.

## RESULTS AND DISCUSSION

As reported earlier,<sup>2</sup> the color-producing nature of the aromatic amine antioxidants restricts their use in various applications, even though they possess high antioxidant activity. By combining an aromatic amine and nonhindered heterocyclic amine moieties with hindered phenol, we prepared antioxidants that did not impart any color after they were incorporated into PPCP.

The synthetic route for AO1 and AO3 is shown in Scheme 1. The influence of different concentrations of antioxidants on the MFR values of PPCP, measured under different loads, is illustrated in Table I. The concentration at which minimum MFRs at different loads occurred was identified, and multiple extrusions were carried out with that identified concentration of antioxidant. Different synthesized antioxidants exhibited optimum performance at different concentrations. It is reported in the literature that antioxidants show optimum activity at particular concentration levels. Increasing the concentration further is not economical and may introduce adverse effects.<sup>15</sup> The following concentrations were selected for each of the antioxidants for multiple extrusion based on the minimum MFR values observed for 1000 g of PPCP: 0.07 wt % BHT, 0.08 wt % AO1, 0.09 wt % AO2, and 0.07 wt % AO3.

**TABLE II**  
MFR Values of PPCP After Multiple Extrusions Carried Out at a Melt Temperature Profile of 180–210–230–205 and a Screw Speed of 50 rpm

Antioxidant	MFR (g/10min) at a 230°C/2.16 kg load after extrusion cycles						$\Delta$ MFR
	1	2	3	4	5	6	
— <sup>a</sup>	4.60	5.20	6.03	8.90	11.53	16.58	11.98
BHT	2.80	3.10	3.38	4.16	4.71	6.09	3.29
AO1	2.91	3.24	3.53	4.00	4.79	5.60	2.69
AO2	2.83	3.13	3.35	4.00	4.46	5.50	2.57
AO3	3.06	3.39	3.80	4.27	4.96	5.94	2.88

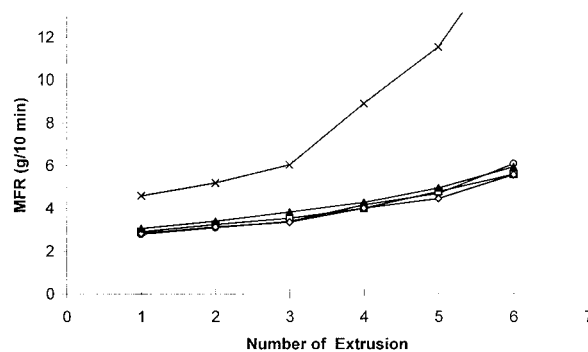
<sup>a</sup> MFR values of PPCP extruded without antioxidant.

Table II and Figure 3 show the variation in MFR values after each extrusion. As shown in Table II and Figure 3, MFR values of the extruded sample increased with the number of extrusions for PPCP stabilized with BHT and with the synthesized antioxidants.

For PPCP without any antioxidants, when subjected to multiple extrusions, the MFR values increased from the first to the sixth extrusions, that is, from 4.60 to 16.58. The difference in melt flow rate values between the sixth and first extrusion ( $\Delta$ MFR) was 11.98, indicating rapid degradation of PPCP in the absence of antioxidant.

Table I shows that minimum MFR values for BHT at all three tested loads were observed with a 0.07 wt % concentration. Hence, that particular concentration was selected for multiple extrusions. When extrusion was carried out with BHT, the MFR values did not increase rapidly. As shown in Table II, the MFR values after the first and sixth extrusions were 2.80 and 6.09, respectively. The  $\Delta$ MFR value was 3.29, which implied positive activity of BHT toward PPCP.

With the increase in the number of extrusions, the polymer was degraded, and its molecular weight and,



**Figure 3** MFR values plotted against the number of extrusions: (○) BHT, (□) AO1, (◇) AO2, and (▲) AO3. The MFR value for (×) unstabilized PPCP after the sixth extrusion was 16.58.

**TABLE III**  
**OIT Values After the First Extrusion for PPCP Stabilized with Various Antioxidants**

Antioxidant	OIT (min)
BHT	0.54
AO1	2.03
AO2	2.91
AO3	1.28

hence, its melt viscosity decreased, which was manifested as an increase in the MFR values.<sup>16</sup>

As shown in Table I, the polymer exhibited stability in its melt flow when the antioxidant AO1 was present at 0.08 wt %, and hence, this concentration was identified as optimum for multiple extrusions. This concentration was higher compared to that selected for BHT (0.07 wt %). As shown in Table II, AO1 at higher concentrations could stabilize PPCP to a greater extent than BHT. The MFR values, in the case of AO1 after the first and sixth extrusions, were 2.91 and 5.60, respectively, and the  $\Delta$ MFR value for AO1 was 2.69, which implied that the degradation of PPCP in the presence of AO1 was lower. This indicated that AO1 offered enhanced antioxidant activity for the stabilization of PPCP.

As shown in Table I, the minimum MFR value for AO2 was 0.09 wt %. In the presence of AO2, the MFR values increased gradually from 2.83 to 5.50 from the first to the sixth extrusions with a  $\Delta$ MFR value of 2.57, which was lower than that of AO1. These values indicated that stabilization efficiency of AO2 was higher than those of BHT and AO1 toward PPCP.

The minimum value for AO3 was 0.07 wt % at all three loads, as shown in Table I. With the synthesized antioxidant AO3, the MFR values increased from 3.06 to 5.94 between the first to the sixth extrusions, and the  $\Delta$ MFR value was 2.88. These values indicated that AO3 offered less antioxidant activity than AO1 and AO2 and more activity than BHT for PPCP.

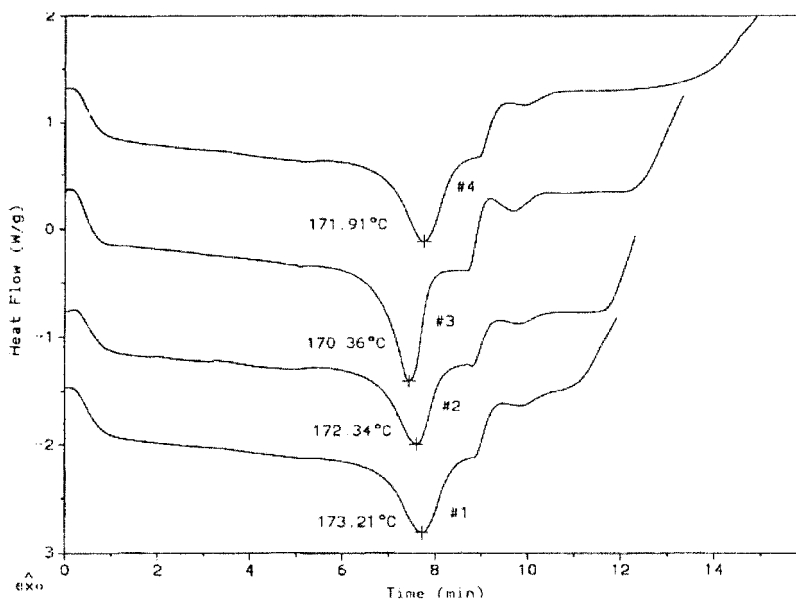
The OIT data from Table III and Figure 4 suggest that the hindered-phenolic-group-containing antioxidant, BHT, prevented the oxidation of PPCP for 0.54 min, whereas antioxidants with a combination of hindered phenol and various amine moieties prevented the oxidation of PPCP for longer times: the OIT value for was 2.03, min for AO1, 2.91 min for AO2, and 1.23 min for AO3. AO2 showed a higher antioxidant activity than the other antioxidants.

These observations supported the effect of synergism. For AO1, AO2, and AO3, hindered phenol was present in combination with an amine, and their stabilization efficiency toward PPCP was better than that of BHT.

The degree of stabilization and, hence, antioxidant activity toward PPCP for the antioxidants under study was as follows: AO2 > AO1 > AO3 > BHT.

The molecular weights of AO2, AO1, AO3, and BHT were 380.5, 339.52, 303, and 220, respectively. Literature data reveal that a high-molecular-weight antioxidant ensures a lower volatility.<sup>5</sup> From this, we conclude that, by increasing the molecular weight of the antioxidant, we increased the activity toward PPCP due to a decrease in volatility.

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**Figure 4** OIT thermogram for PPCP stabilized with various antioxidants: (1) BHT = 0.54 min, (2) AO3 = 1.28 min, (3) AO1 = 2.03 min, and (4) AO2 = 2.91 min as per ASTM D 3895-95.

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