

The Synthesis and Thermal Properties of Oligo-3-hydroxybenzaldehyde Synthesized by Oxidative Polycondensation

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ABSTRACT: Polymerization of 3-hydroxybenzaldehyde was investigated by oxidative polycondensation (OP) method. No polycondensation reaction was observed both in acidic (in CH_3COOH) and organic (in THF) media. Polycondensation was carried out with hydrogenperoxide (H_2O_2) in an aqueous alkaline medium at 90°C . The product was characterized by ^1H NMR, ^{13}C NMR, FTIR, UV-vis, and elemental analysis. The number average molecular weight, mass average molecular weight, and polydispersity index values of O-3HBA were found to be 3600, 8000 g mol^{-1} , and 2.22, respectively. The product (O-3HBA) with reactive al-

dehyde and hydroxyl group was soluble in most polar organic solvents and was composed of phenylene units. Thermal properties of the oligomer were investigated by thermogravimetric analyses under an air atmosphere. The weight loss of O-3HBA was found to be 5 and 50% at 231 and $>1000^\circ\text{C}$, respectively. The carbonaceous residue of the O-3HBA was 54% at 1000°C . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 892–897, 2006

Key words: oxidative polycondensation; polyaromatics; polyphenols; oligomers

INTRODUCTION

Phenolic polymers are commercially important materials. A series of phenolic polymers and phenol formaldehyde resins are widely used in a number of electronic and industrial applications.^{1,2} Recently, serious concern has been raised about the continued use of phenol–formaldehyde resins due to toxic effects of formaldehyde.³ Enzymatic syntheses of polyphenols have extensively been studied. Because of no use of toxic formaldehyde, this method has gained much attention.⁴ Another alternative method for the preparation of phenolic resins not involving formaldehyde is the oxidative polycondensation (OP) of phenols. OP method is simply the reaction of compounds including aromatic —OH groups and active functional groups (—NH₂, —CHO, —COOH) in their structure with the oxidants like NaOCl, H_2O_2 , and air oxygen. Polycondensation is often carried out in an aqueous alkaline, acidic, and organic medium. During the polymerization, the powder is precipitated. The OP reaction products are generally black or dark brown in

color. Recently this method has received much attention because of the following advantages.

- (i) Easily found, cheap and simple structured oxidants;
- (ii) ease of product separation from the reaction mixture;
- (iii) enhanced thermal stability of polymers;
- (iv) increased solubility of polymers.

OP method has been used in syntheses of oligophenols and Schiff base oligomers.^{5–7} Oligomers synthesized by OP method have useful properties such as, paramagnetism, thermal stability, antimicrobial activity, and as antistatic agent.^{8–11} Recently, the OP reaction of salicylaldehyde and 4-hydroxybenzaldehyde was investigated by our research group.^{12,13} In OP reaction the keeping of —OH and —CHO groups in the structure of O-3HBA is an important advantage because these groups can make the synthesis of different compounds, such as epoxy resins, Schiff base oligomers, copolymers etc, possible. For these reasons, in the present article, the synthesis, characterization, and thermal properties of O-3HBA are described.

EXPERIMENTAL

Materials

3-HBA, 1,4-dioxane, ethanol, benzene, acetone, acetic acid, tetrahydrofuran THF, H_2O_2 (30% solution in water), dimethylformamide, DMF, dimethylsulfoxide, DMSO, chloroform, and toluene are from Merck

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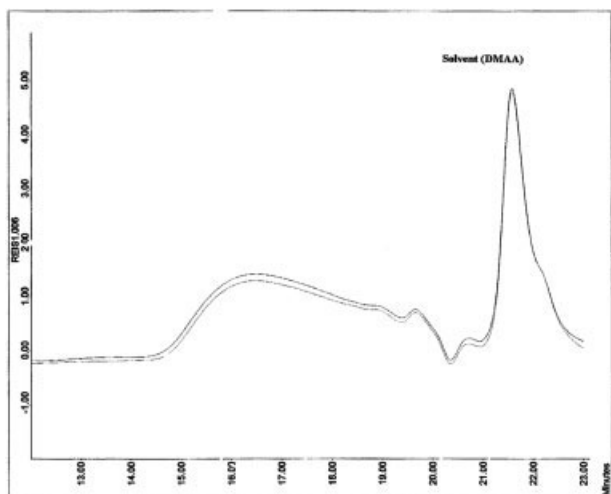


Figure 1. GPC curve of O-3HBA.

Chemical in chromatographic grade, and they were used as received. Hydrochloric acid (HCl, 37% solution in water) and KOH were supplied by Carlo Erba (Italy).

Characterization

The infrared and UV-vis spectra were measured by Jasco 300 FTIR and Shimadzu UV-160, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FTIR spectra were recorded using KBr discs ($4000\text{--}400\text{ cm}^{-1}$). UV-vis spectrum (200–800 nm) of HBA and O-3HBA were determined by using DMF. 3-HBA and O-3HBA were characterized using ^1H NMR and ^{13}C NMR spectra (Bruker AC FT-NMR 400 MHz spectrometer) recorded at 25°C using deuterated DMSO as solvent. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were determined by GPC of HP 1100 from Agilent Technologies. For GPC investigations, eluent: dimethylacetamide (0.4 mL min^{-1}), 2 Zorbax PSM 60 + 300 columns ($25\text{ cm} \times 6.2\text{ mm ID}$), and poly(2-vinylpyridine) standards were used. The sample concentration was 2 mg/mL . A refractometric detector (at 25°C) was used to analyze the product. Differential thermal analyses (DTA) and thermogravimetry (TG) were performed with a Shimadzu DTA-50 and TGA-50 thermal analyzer. The TG measurements were made between 0 and 1000°C (in air, rate 5°C min^{-1}).

Preparation of O-3HBA

O-3HBA was synthesized through the OP of 3-HBA with aqueous solution of H_2O_2 (0.050 mol, 30%). The 3-HBA (3.05 g, 0.0250 mol) was dissolved in an aqueous solution of KOH (10%, 0.0250 mol) and placed into

a 50 mL three-necked round-bottomed flask. It was fitted with a condenser, a thermometer and a stirrer, in addition to a funnel containing H_2O_2 . After heating to 70°C , H_2O_2 was added drop-wise over about 30 min. The reaction mixture was stirred at 90°C for 10 h. The mixture was neutralized with 2.18 mL HCl (0.0250 mol, 37%) at room temperature. Then, unreacted 3-HBA was washed with hot water and methanol, filtered and dried in an oven at 105°C (0.94 g, yield 30.8%).

^1H NMR (DMSO, 400 MHz): $\delta = 9.3\text{--}9.8$ (—OH, 1H, s); 9.9 (—CHO—, 1H, s); 6.3–8.1 (Arom, H; s). ^{13}C NMR (DMSO, 400 MHz): $\delta = 115, 123, 132, 138, 143$ (arom. C); 192 (aldehyde C) FTIR (KBr, cm^{-1}): 3416(s), 1693 (s), 1599(s), 1451 (w), 1366 (w), 1245 (s), 882 (w), 835 (w), 792 (w)

Elemental analyses: C: 70.00 (69.21 found), H: 3.33 (3.41 found).

RESULTS AND DISCUSSION

The OP reaction of 3-HBA was investigated in different media. No polycondensation reaction was observed in both acidic (in CH_3COOH) and organic (in THF) medium. The OP reaction was also tried by using NaOCl. But, no polycondensation reaction was determined in this condition. For these reasons, H_2O_2 was used as an oxidizing agent. The OP product of 3-HBA with H_2O_2 in aqueous alkaline medium was black solid powders. As a controlled experiment, the OP reaction of 3-HBA in the absence of H_2O_2 did not occur. The solubility of O-3HBA was studied at room temperature at a concentration of 0.1% (W/V). The solubility of O-3HBA is quite different from those of the polyphenols and polyphenylenes. These polymers often show low solubility toward organic solvents, which restricts their applications as polymeric materials. However, O-3HBA was soluble in the aqueous solution of alkaline, THF, DMSO, DMF, acetone, and ethylalcohol. It was insoluble in water, 1,4-diox-

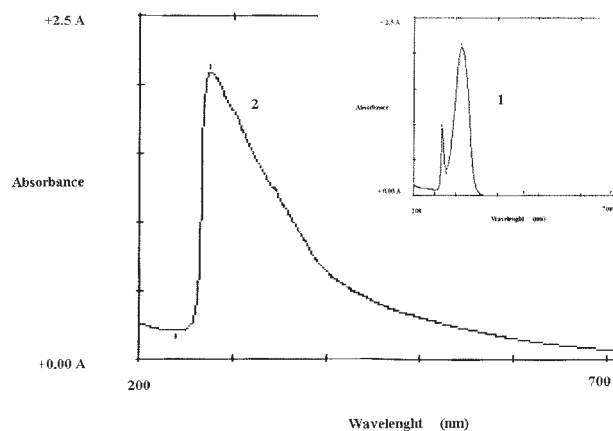


Figure 2. UV-vis spectrum of 3-HBA (1) and O-3HBA (2).

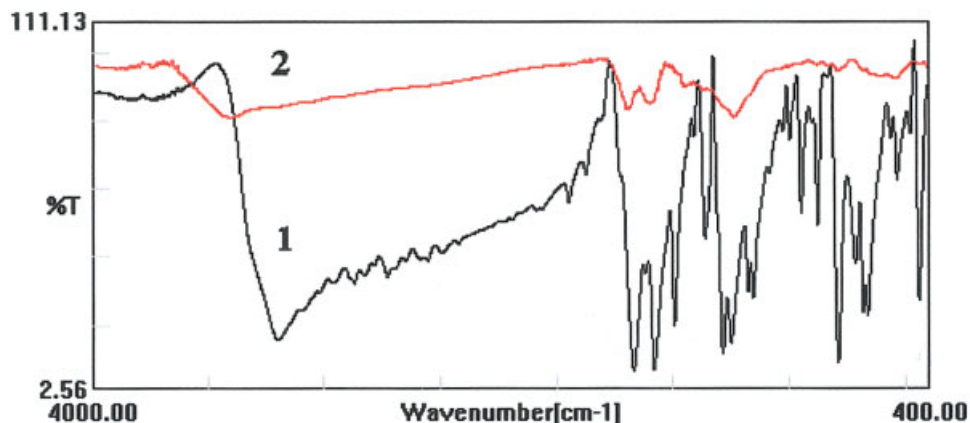


Figure 3. FTIR spectrum of 3-HBA (1) and O-3HBA (2). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ane, CHCl_3 , CCl_4 , and aromatic (benzene and toluene) solvents.

The number average molecular weight, mass average molecular weight and PDI values of O-3HBA were found to be 3600, 8000 g mol^{-1} , and 2.22, respectively, (Fig. 1). These data are the average values received after two measurements.

The UV-vis spectra of 3-HBA and O-3HBA (Fig. 2) were carried out in DMF. In the UV-vis spectrum of 3-HBA two peaks, 268 and 314 nm, were observed. In the UV-vis spectrum of O-3HBA only one broad peak (276 nm) was observed. These values of 3-HBA and O-3HBA spectra may be attributed to $\pi \rightarrow \pi^*$ transitions of the aromatic $-\text{C}=\text{C}-$ bonds. As being different from 3-HBA, O-3HBA's absorption region, 400–700 nm, can be caused by its long oligomer structure system. The FTIR spectra of 3-HBA (Fig. 3). The stretching vibration band of phenol OH group and aldehyde group were observed at 3208 and 1671 cm^{-1} , respectively. Also, the sharp absorption band at 786 cm^{-1} of 3-HBA was because of three neighboring C—H groups the aromatic ring. Four important absorptions were observed in the spectra of O-3HBA (Fig. 3). The first is peak at 3416 cm^{-1} is assigned to the

stretching vibration bands of OH groups and hydrogen bond formation in the oligomer. The second absorption of interest is a peak at 1693 cm^{-1} , attributed to the aldehyde ($-\text{CHO}$) group. Third important absorption peak at 1599 cm^{-1} is assigned to $-\text{C}=\text{C}-$ bands of the aromatic nucleus. The last absorption band at 1245 cm^{-1} is assigned to the bending vibration phenol OH groups. A comparison of the oligomer spectrum with that of the 3-HBA indicates that the 3-HBA absorption peak at 786 cm^{-1} disappeared after polycondensation. Also, FTIR spectra of O-3HBA showed absorption band at 882 cm^{-1} , this band being most intense and characteristic of isolated C—H group of the aromatic ring.¹⁴ Since no peaks around 1100–1250 cm^{-1} for C—O—C linkages were found in the FTIR spectra of oligomer it seems obvious that O-3HBA synthesized by OP method is composed of phenylene units. The ^1H NMR spectrum of 3-HBA show very sharp peaks. After polycondensation, however, the peaks become very broad. This broadening of the proton NMR resonance peaks is attributed to polymerization. The ^1H NMR spectrum of O-3HBA (Fig. 4) shows a broad singlet peak around 6.3–8.1 ppm and broad peak around 9.3–9.8 ppm that may be assigned to the aromatic proton and hydroxyl proton of phenol group, respectively. The sharp singlet at 9.9 ppm can be attributed to aldehyde proton. The other sharp peaks observed in the proton NMR spectrum of O-3HBA can be attributed to the end groups proton. No carboxyl group proton was observed in the ^1H NMR spectrum of O-3HBA.

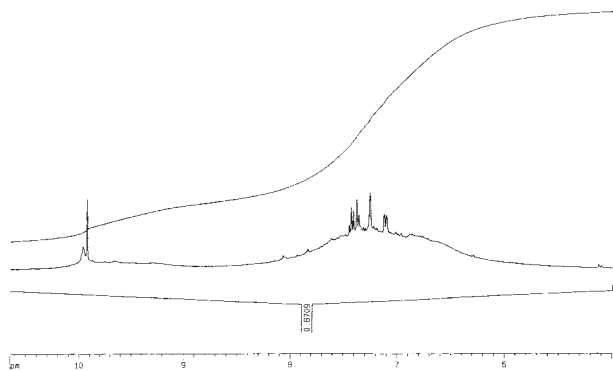


Figure 4. ^1H -NMR spectrum of O-3HBA.

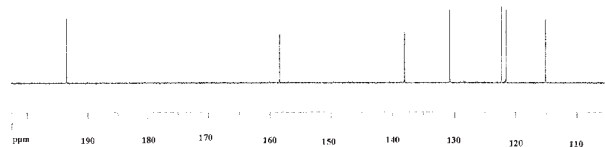


Figure 5. ^{13}C -NMR spectrum of 3-HBA.

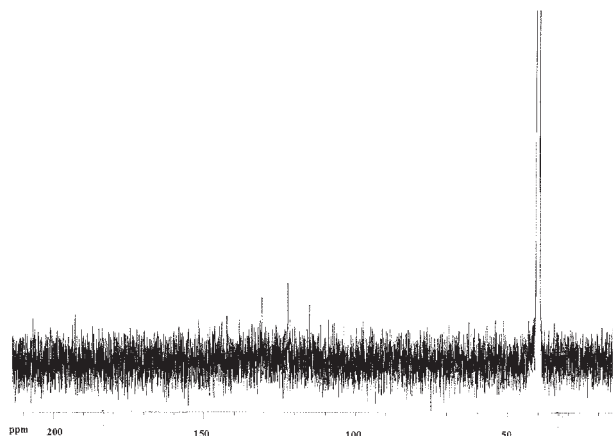


Figure 6. ^{13}C -NMR spectrum of O-3HBA.

To understand the structures of O-3HBA, the ^{13}C NMR spectrum of 3-HBA (Fig. 5) and O-3HBA was also received (Fig. 6). The ^{13}C NMR spectrum of 3-HBA show peaks at 115, 122, 123, 131, 138, 158, and 194 ppm, respectively, indicating the seven carbon atoms of 3-HBA. Nevertheless, the ^{13}C NMR spectrum of O-3HBA was not clear but mainly composed of signals at 115, 123, 132, 138, 143, and 192 ppm. From these results, it can be clearly suggested that the peaks from 115 to 143 ppm of O-3HBA can be assigned to aromatic carbons and the peak at 192 ppm attributed to aldehyde group carbon.

As aldehyde group is sensitive to oxidation reaction, during the OP reaction this group can turn to carboxyl group. To check out the presence of aldehyde group the control experiment was carried out using aniline. With the reaction between aldehyde group of O-3HBA and amino group of aniline, the Schiff base oligomer was synthesized¹² The FTIR (Fig. 7) and ^1H NMR spectrum of the Schiff base was received.

In the FTIR spectrum of the Schiff base, because of condensation reaction between O-3HBA and aniline (while the $-\text{CHO}$ group absorption of O-3HBA, 1693 cm^{-1} , disappeared) the $-\text{CH}=\text{N}-$ absorption band occurred at 1600 cm^{-1} . The strong stretching frequency observed at 2919 and 2852 cm^{-1} for Schiff base can be assigned to either the presence of a $\text{O}-\text{H} \dots \text{N}$ intramolecular hydrogen bond or aromatic and aliphatic $\text{C}-\text{H}$ bond. In addition, the FTIR spectrum of Schiff base showed absorption bands in the region of 692 cm^{-1} , corresponding to out of plane deformation vibrations of the aromatic $\text{C}-\text{H}$ bonds. This band was a result of five neighboring unsaturated $\text{C}-\text{H}$ groups of the aromatic ring in the structure of Schiff base. In the ^1H NMR spectrum of the Schiff base, the $-\text{CH}=\text{N}-$ group proton was observed at 8.5 ppm as a singlet. These indications confirm that the $-\text{CHO}$ group of

O-3HBA is protected during the OP reaction and therefore O-3HBA has aldehyde group. It should be noted that the results of Schiff base reactions of O-3HBA will be given in detail in another report.

The ^1H NMR, ^{13}C NMR, FTIR, and elemental analyses results suggest that the polymerization of 3-HBA by OP may take place at C_2 , C_4 , and C_6 positions and structure of O-3HBA can be given as in Scheme 1.

Thermal properties of 3-HBA and O-3HBA were determined by TG and DTA analyses in the air medium. The curve of these analyses are given in Figures 8 and 9. 3-HBA was completely decomposed at 210°C . Five and fifty percent weight loss temperature of the O-3HBA were 231 and $>1000^\circ\text{C}$, respectively, (Fig. 9). O-3HBA has the higher 5 and 50% weight loss temperature than that of oligosalicylaldehyde¹² and oligo-4-hydroxybenzaldehyde.¹³ Among the oligohydroxybenzaldehydes, O-3HBA had the highest carbonaceous residue at 1000°C , 54%. The residuum is supposed to be a graphite-like polymer. For this reason, this property of O-3HBA may be useful for graphite materials technologies. Like other oligophenols, O-3HBA has relatively high thermooxidation parameters. So for these reasons, the syntheses of new oligophenols are very important in the preparation of the new thermally stable materials.

CONCLUSIONS

Oligo-3-hydroxybenzaldehyde was synthesized by OP method with hydrogen peroxide in aqueous alkaline medium. O-3HBA with reactive aldehyde and hydroxy group was readily soluble in most polar organic solvents such as THF, DMSO, DMF, acetone, and ethylalcohol and hence will find useful applications, such as syntheses of Schiff base oligomers, resins, and copolymer. The weight loss of O-3HBA was found to be 5 and 50% at 231 and $>1000^\circ\text{C}$, respectively. The carbonaceous residue of the O-3HBA was 54% at 1000°C . As the carbonaceous residuum is supposed to be a graphite-like polymer, this properties of O-3HBA may be useful for graphite materials technologies.

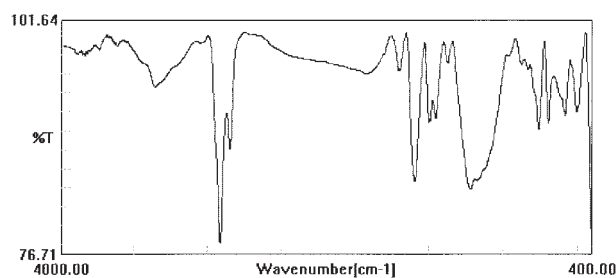


Figure 7. FTIR spectrum of the Schiff base.

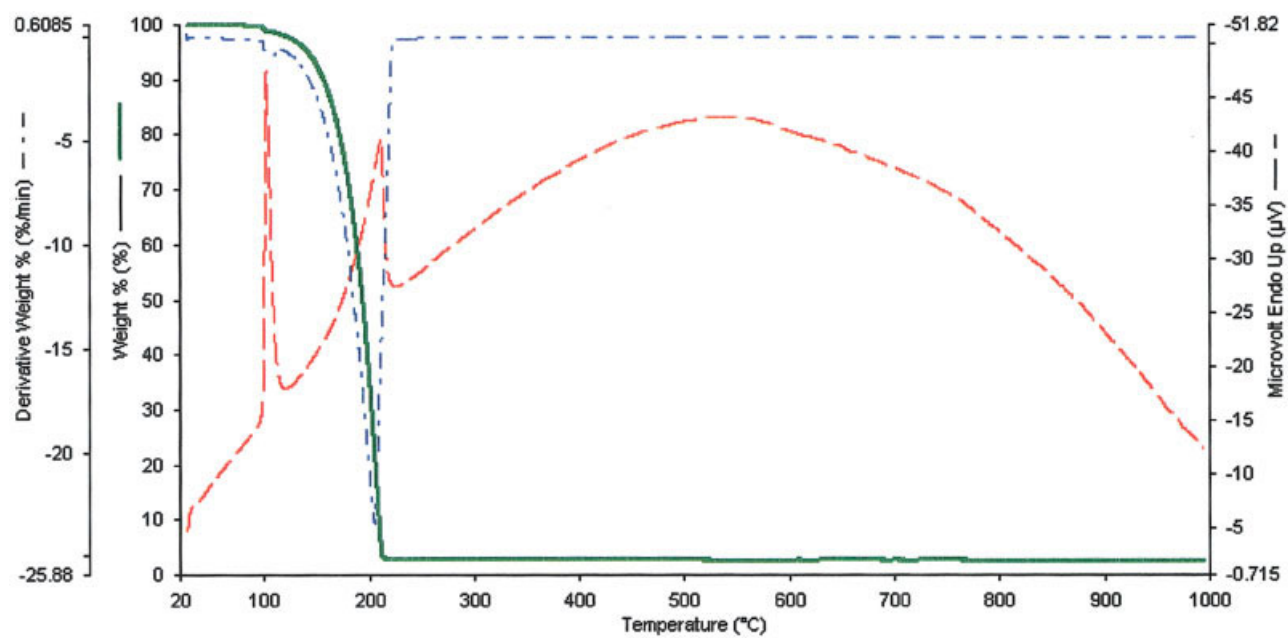
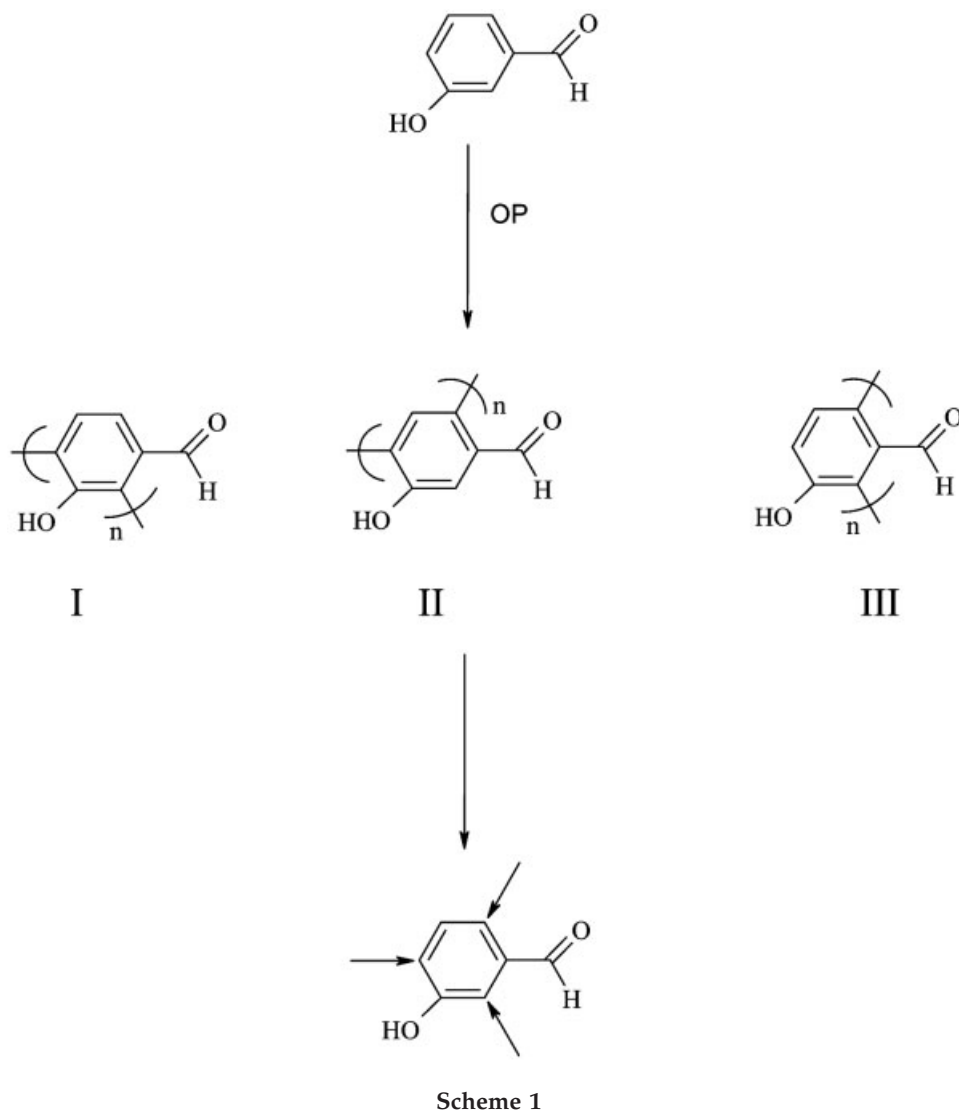


Figure 8. TG-DTA curve of 3-HBA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

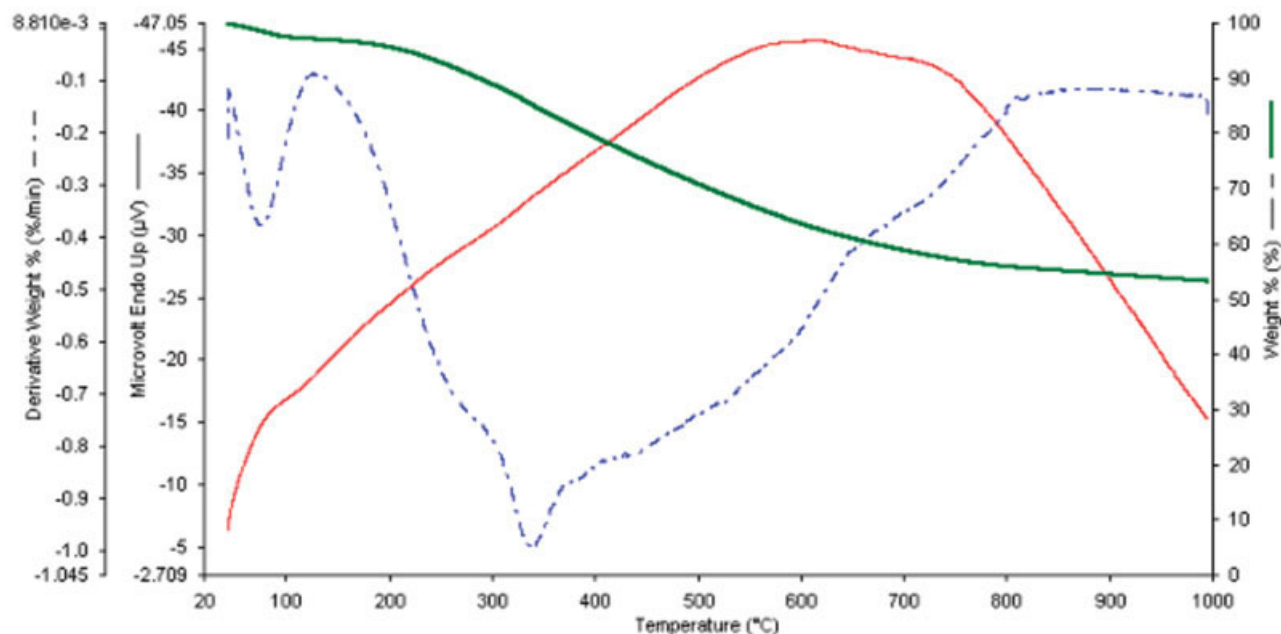


Figure 9. TG-DTA curve of O-3HBA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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