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Synthesis and Characterization of Oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol and Oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol

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Oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol O-(2-HMPIMP) and oligo-2-[(2-hydroxymethylphenyl imino) methyl]-5-bromo-phenol O-(2-HMPIMBP) were synthesized by the oxidative polycondensation reaction using air as an oxidant in an aqueous alkaline medium at 70 °C. They were characterized by ¹H-NMR, FT-IR, UV-vis, TG, size exclusion chromatography (SEC) and elemental analysis. According to the SEC analyses, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of O-2-HMPIMBP and O-2-HMPIMP are 1100, 1600 g mol⁻¹ and 1.45; and 6000, 6250 g mol⁻¹ and 1.04, respectively. According to TG analyses, the weight losses of O-2-HMPIMP and O-2-HMPIMBP are 98.31% and 96.91%, respectively, at 900 °C.

Key Words: Oxidative polycondensation, oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol, oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol, thermal analyses, 2-aminobenzyl alcohol.

Introduction

Salicylaldehydes are very interesting materials biochemically and biophysically. Their coordination complexes are prototypes of pyridoxal and the B₆ vitamins. Isomeric Schiff bases derived from salicylaldehyde or 5-bromosalicylaldehyde with 2-aminobenzyl alcohol have been reported in the literature.¹⁻⁵ Schiff base ligands having phenolic oxygen, azomethine nitrogen and alcohol oxygen have been demonstrated to have dibasic tridentate (ONO) properties.⁶ The oligophenols and their derivatives have been used in various fields, because of their electronic structural properties. They have useful properties such as paramagnetism, semi-conductivity and use as an electrochemical cell and resistance to high energy. Because of these properties, they were used to prepare composites with resistance to high temperature, graphite materials, epoxy oligomer and block copolymers, photo resists and antistatic materials.⁷⁻¹⁵ The halogen derivatives of oligophenols

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were used to prepare composite materials enduring flame and specific detergents such as lead storing battery cathodes.¹⁴ These compounds can gain new properties when other functional groups are added to their structures. Their oligomer-metal complexes can be used to remove poisonous heavy metals from industrial wastewaters.

Polyaniline is a conducting polymer that presents good stability.¹⁶ Poly (2-aminobenzyl alcohol) and derivatives have electrical conductivity values in the semi-conducting range.¹⁷

In the present study, we synthesized oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol (O-2-HMPIMP) (**3**) and oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (O-2-HMPIMBP) (**4**) using air as an oxidant in an aqueous alkaline medium and characterized them by FT-IR, UV-vis, ¹H-NMR, elemental analysis, TGA and SEC techniques.

Materials and Methods

Materials

Salicylaldehyde, 5-bromo salicylaldehyde, 2-aminobenzyl alcohol and other organic solvents were obtained from Merck Chemical Co. and they were used as received.

Synthesis of 2-[(2-hydroxymethylphenylimino) methyl] phenol (**1**) and 2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (**2**)

A solution of salicylaldehyde (1 mmol) in absolute EtOH (25 mL) was added to a magnetically stirred solution of 2-aminobenzyl alcohol (1 mmol) in absolute ethanol (25 mL). The mixture was refluxed for 10 h on a water bath and kept for 1 day at room temperature. The solid product was filtered, washed with cold EtOH and Et₂O and then dried in vacuum (over P₄O₁₀). The product was recrystallized from methanol (yield 85%, mp 110 °C).

Anal. calcd. for 2-HMPIMP: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.73; H, 5.23; N, 6.20. UV-vis (λ_{max}): 221, 240, 271 and 343 nm. FT-IR (KBr, cm⁻¹): ν (O-H) 3385 s, ν (C-H aryl) 3074 m, ν (C=N) 1605 s, ν (C=C phenyl) 1581, 1497, 1459 s, (C-O phenolic) 1387 s, (C-O alcoholic) 1190 s. ¹H-NMR (DMSO): δ ppm, 8.66 (s, 1H, -CH=N-); 6.38-7.775 (m, 8H, Ar-H); 4.57 (s, 2H, CH₂); 5.10 (s, 1H, -CH₂-OH); 13.08 (s, 1H, -OH).

A similar method was used for the preparation of 2-HMPIMBP (**2**) (yield 88%, mp 145 °C).

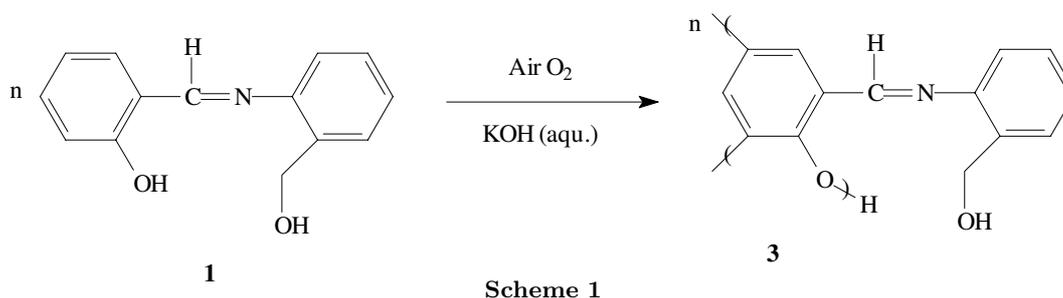
Anal. calcd. for 2-HMPIMBP: C, 54.92; H, 3.95; N, 4.40. Found: C, 54.56; H, 4.00; N, 4.58. UV-vis (λ_{max}): 240, 276 and 348 nm. FT-IR (KBr, cm⁻¹): ν (O-H) 3415 s, ν (C-H aryl) 3074 m, ν (C=N) 1608 s, ν (C=C phenyl) 1570, 1470 s, ν (C-Br) 817, 761 s, (C-O phenolic) 1380 s, (C-O alcoholic) 1200 s. ¹H-NMR (DMSO): δ ppm, 8.72 (s, 1H, -CH=N-); 13.08(s, 1H, -OH); 6.80-7.90 (m, 7H, Ar-H); 4.68 (s, 2H, CH₂); 4.89 (s, 1H, -CH₂-OH).

Synthesis of oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol (**3**)

2-HMPIMP (**1**) (1.50 g, 6.608 mmol) was dissolved in an aqueous solution of KOH (10%) (0.370 g, 6.608 mmol) and placed into a (50 mL) 3-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an air inlet.¹⁸ The reaction mixture was stirred at 70 °C for 10 h. Air was passed in at a rate

of 8.5 L/h during the course of the reaction. Air was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO₂ in the air O₂ (Scheme 1). The mixture was neutralized with 0.574 mL of HCl (37%) at room temperature.¹⁸ Then the mixture was filtered and washed with hot water (50 mL x 3) for separating mineral salts and unreacted monomer. The crude product was dried in the oven at 110 °C.

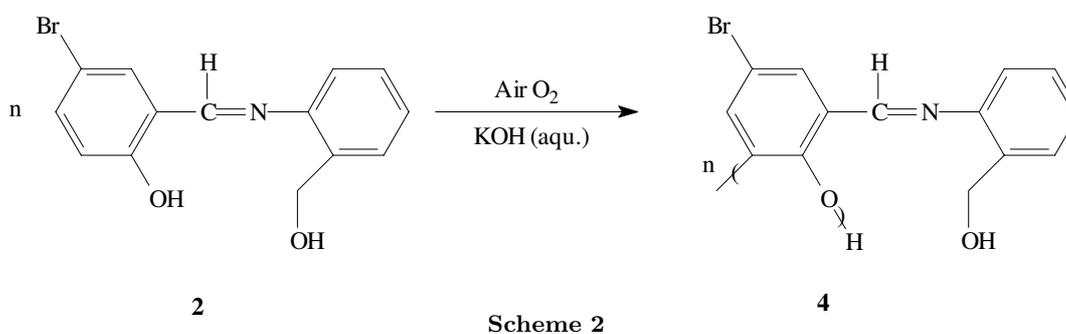
Anal. calcd. for O-2-HMPIMP: C, 74.66; H, 4.88; N, 6.22. Found: C, 74.00; H, 4.80; N, 6.00. UV-vis (λ_{max}): 221, 240, 271 and 343 nm. FT-IR (KBr, cm⁻¹): ν (O-H) 3397 s, ν (C-H aryl) 3074 m, ν (C=N) 1615 s, ν (C=C phenyl) 1581, 1497, 1459 s, ν (aliphatic C-H) 2926 s and ν (C-O) 1387 s. ¹H-NMR (DMSO): δ ppm, 8.80 (s, 1H, -CH=N-); 9.90 (s, 1H, -OH); 6.40-7.70 (m, 6H, Ar-H); 4.60 (s, 2H, CH₂); 5.20 (s, 1H, -CH₂-OH).



Synthesis of Oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (4)

2-HMPIMBP (2) (2.02 g, 6.608 mmol) was dissolved in an aqueous solution of KOH (10%) (0.370 g, 6.608 mmol) and placed into a (50 mL) 3-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an air inlet.¹⁸ The reaction mixture was stirred at 70 °C for 10 h. Air was passed in at a rate of 8.5 L/h during the course of the reaction. Air was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO₂ in the air O₂ (Scheme 2). The mixture was neutralized with 0.574 mL of HCl (37%) at room temperature.¹⁸ Then the mixture was filtered and washed with hot water (50 mL x 3) for separating mineral salts and unreacted monomer. The crude product was dried in the oven at 110 °C.

Anal. calcd. for O-2-HMPIMBP: C, 55.08; H, 3.60; N, 4.59. Found: C, 54.85; H, 3.00; N, 4.17. UV-vis (λ_{max}): 240, 276 and 348 nm. FT-IR (KBr, cm⁻¹): ν (O-H) 3430 s, ν (C-H aryl) 3074 m, ν (C=N) 1616 s, ν (C=C phenyl) 1570, 1470 s, ν (aliphatic C-H) 2926 s, ν (C-Br) 817, 761 s and ν (C-O) 1387 s. ¹H-NMR (DMSO): δ ppm, 8.86 (s, 1H, -CH=N-); 10.10 (s, 1H, -OH); 6.60-8.00 (m, 6H, Ar-H); 4.60 (s, 2H, CH₂); 5.80 (s, 1H, -CH₂-OH).



Characterization Techniques

Elemental analysis was carried out with a Carlo Erba 1106. The infrared and ultraviolet-visible spectra were measured by Perkin-Elmer FT-IR BX and Shimadzu UV-1208, respectively. UV-vis spectra of 2-HMPIMP, 2-HMPIMBP, O-2-HMPIMP and O-2-HMPIMBP were recorded in DMSO. 2-HMPIMP, 2-HMPIMBP, O-2-HMPIMP and O-2-HMPIMBP were characterized using $^1\text{H-NMR}$ spectra (Bruker AC FT-NMR 400 MHz spectrometer) recorded at 25 °C by using deuterated DMSO as a solvent. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using Perkin-Elmer thermal analyzer. The thermogravimetric measurements were obtained between 20 and 900 °C (in air, rate 10 °C/min). GPC analyses were performed at 30 °C using DMF as eluent at a flow rate of 0.4 mL/min. A refractive index detector was used as a detector. The instrument (Shimadzu GPC-SEC system) was calibrated with a mixture of polystyrene standards using GPC software for the determination of the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of the copolymer sample. Polystyrene standards were supplied by Polymer Laboratories Co., Germany, and their M_w values were 162, 580, 925, 1260, 2350, 3370, 4920, 8450, 12,970 and 19,880 g mol $^{-1}$.

Results and Discussion

Synthesis Conditions of O-2-HMPIMP and O-2-HMPIMBP

The oxidative polycondensation reaction of 2-HMPIMP and 2-HMPIMBP with air as oxidant was investigated in an aqueous alkaline medium. The oxidative polycondensation reactions of 2-HMPIMP and 2-HMPIMBP immediately occurred in an aqueous alkaline solution and the solution turned brown after the addition of air. The yield of O-2-HMPIMP was 24% under the reaction conditions $[2\text{-HMPIMP}]_0 = [\text{KOH}]_0 = 0.015$ mol/L and air (flow rate = 8.5 L/h), at 70 °C for 10 h. The yield of O-2-HMPIMBP was 42% under the reaction conditions $[2\text{-HMPIMBP}]_0 = [\text{KOH}]_0 = 0.010$ mol/L and air (flow rate = 8.5 L/h), at 70 °C for 10 h. The oxidative polycondensation reactions of 2-HMPIMP and 2-HMPIMBP did not work with H_2O_2 and NaOCl as oxidants under the same conditions.

Solubility

O-2-HMPIMP was dark brown in powder form and it was completely soluble in organic solvents such as DMF and DMSO but it was sparingly soluble in acetone, methanol, 1-butanol, ethanol, acetonitrile, ethyl acetate, aqueous alkaline solution, conc. H_2SO_4 , toluene, CHCl_3 and CCl_4 . O-2-HMPIMBP was dark brown in powder forms and it was completely soluble in organic solvents such as DMF, THF, DMSO, acetone, methanol, 1-butanol, ethanol, acetonitrile, ethyl acetate, aqueous alkaline solution and conc. H_2SO_4 but it was sparingly soluble in toluene, CHCl_3 and CCl_4 . Both O-2-HMPIMP and O-2-HMPIMBP were insoluble in heptane and dioxane.

Structure of O-2-HMPIMP and O-2-HMPIMBP

The UV-vis spectra of O-2-HMPIMP showed the same bands at 221, 240, 271 and 343 nm. K bands belong to -OH and azomethine groups of O-2-HMPIMP were observed at 240 and 271 nm, respectively. The R band of the $\text{CH}=\text{N}$ group of O-2-HMPIMP was observed at 343 nm. The UV-vis spectra of O-2-HMPIMBP showed the same bands at 240, 276 and 348 nm. K bands belonging to -OH and azomethine groups of

O-2-HMPIMBP were observed at 240 and 276 nm, respectively. The R band of the CH=N group of O-2-HMPIMBP was observed at 348 nm.

The $^1\text{H-NMR}$ spectra of the O-2-HMPIMP and O-2-HMPIMBP are given in Figures 1 and 2, respectively. In the $^1\text{H-NMR}$ spectrum of O-2-HMPIMP, the characteristic peaks of the functional groups were observed: phenyl-OH and $-\text{CH}_2\text{-OH}$ groups at 9.90 and 5.20 ppm and the azomethine ($-\text{CH}=\text{N}$) group at 8.80 ppm. In the $^1\text{H-NMR}$ spectrum of O-2-HMPIMBP, the characteristic peaks of the functional groups were observed: phenyl-OH and $-\text{CH}_2\text{-OH}$ groups at 10.10 and 5.80 ppm and the azomethine ($-\text{CH}=\text{N}$) group at 8.86 ppm (Scheme 3). The FT-IR spectral data of the O-2-HMPIMP and O-2-HMPIMBP confirm the results of the $^1\text{H-NMR}$ spectra. Oligophenols with Schiff base substitute were synthesized by Kaya and co-workers and characterized using some instrumental techniques.^{19–21} In the oxidative polymerization of phenol and phenol derivatives, it is known that the 2 types of linkage between the monomer units, the C-C and C-O-C bonds, can be formed during the polymerization. The reaction mechanism on the coupling selectivity has been studied by Ayyagari et al.²² The reaction mechanism on the coupling selectivity has been studied by Kaya and co-workers²³ and 3 possible reaction mechanisms for the C-C and C-O-C coupling systems have been proposed:¹⁸ (i) coupling of Schiff base substitute free phenoxy radicals resulting from one-electron-oxidation of Schiff base monomers, (ii) coupling of phenoxy radicals coordinated to each other *ortho* or *para* positions by using oxidants such as NaOCl, H_2O_2 and air, and (iii) coupling through phenoxonium anion formed by using KOH. C-C and C-O-C coupling systems were found in the polymerization of some specific phenols and Schiff base monomers. Monomer and dimer interconversion combinations of radical units are proposed in the literature.¹⁸

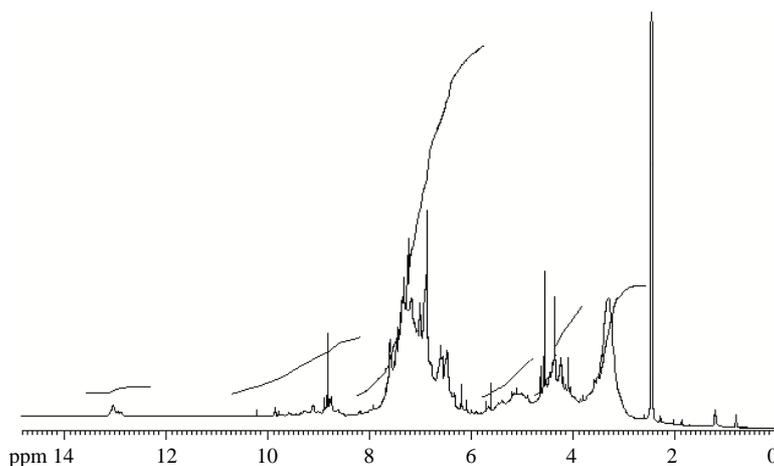


Figure 1. $^1\text{H-NMR}$ spectrum of oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol (3).

In the FT-IR spectra of 2-HMPIMP and 2-HMPIMBP, the bands of the azomethine and phenolic hydroxyl groups were observed at 1605 and 1608 cm^{-1} , and 3397 and 3430 cm^{-1} , respectively. The fields' downshifting of azomethine and phenolic hydroxyl bands have demonstrated the formation of oligomer units. In the FT-IR spectrum of O-2-HMPIMP and O-2-HMPIMBP (Figures 3 and 4), the characteristic peaks of the functional groups were observed: phenyl-OH group at 3397 and 3430 cm^{-1} , aromatic $-\text{CH}$ groups at 3074 and 3074 cm^{-1} , the azomethine ($-\text{CH}=\text{N}$) group at 1615 and 1616 cm^{-1} and $-\text{C}=\text{C}$ double bonds at 1581 , 1497 , 1459 and 1570 , 1470 cm^{-1} , respectively.

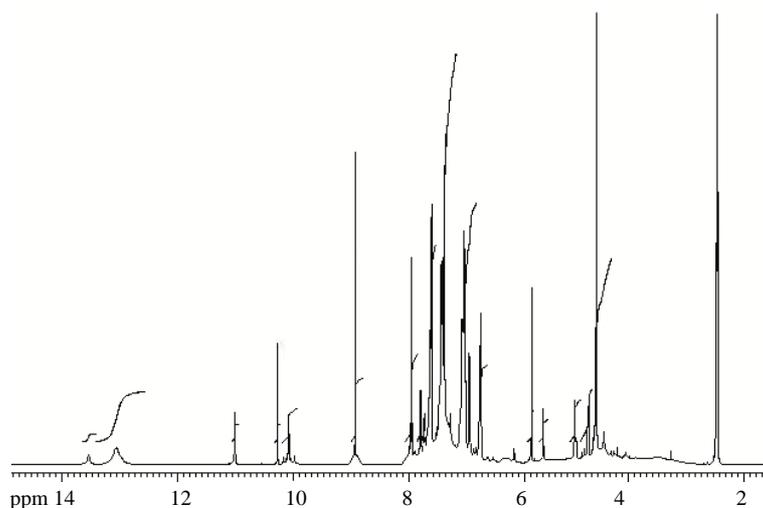
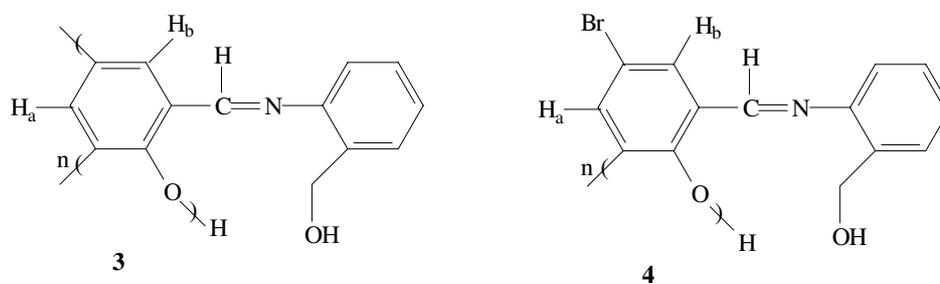


Figure 2. $^1\text{H-NMR}$ spectrum of oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (4).



Scheme 3



Figure 3. FT-IR spectrum of oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol (3).

According to SEC analyses, the molecular weights and molecular weight distributions of O-2-HMPIMP and O-2-HMPIMBP were as follows: according to air O_2 , M_n , M_w and PDI values of O-2-HMPIMP were 1100, 1600 g mol^{-1} and 1.45, respectively. When air was used as oxidant, M_n , M_w and PDI values of O-2-HMPIMBP were 6250, 6000 g mol^{-1} and 1.04, respectively. In the molecular weight distribution of O-2-HMPIMBP, 2 peaks were observed. Fifty-two percent of the mass of O-2-HMPIMBP was low molecular weight (for the first fraction: M_n , 1555; M_w , 1900 g mol^{-1} ; PDI, 1.22) but 48% of its weight was high molecular weight (for the second fraction: M_n , 8290; M_w , 8300 g mol^{-1} ; PDI, 1.00).

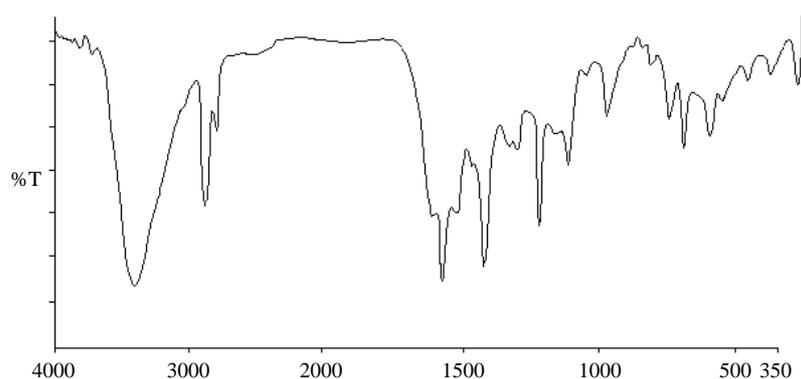


Figure 4. FT-IR spectrum of oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (4).

Thermal analysis of O-2-HMPIMP (3) and O-2-HMPIMBP (4)

TGA and DTG curves of O-2-HMPIMP and O-2-HMPIMBP are given in Figures 5 and 6. The initial degradation temperature and 50% weight losses of O-2-HMPIMP and O-2-HMPIMBP were 155 and 170, and 535 and 520 °C, respectively. The weight losses of O-2-HMPIMP and O-2-HMPIMBP were found to be 98.31% and 96.91%, respectively, at 900 °C. O-2-HMPIMP and O-2-HMPIMBP formed carbine residue in low amounts such as 1.69% and 3.09% at 900 °C. Because of the long conjugated band systems, the oligomer demonstrated higher resistance against high temperature than the monomer. Although 2-HMPIMP and 2-HMPIMBP lost 75% of their mass at 345 and 330 °C, O-2-HMPIMP and O-2-HMPIMBP lost 50% of their masses at 535 and 520 °C, respectively. According to TG analyses, O-2-HMPIMP and O-2-HMPIMBP were more stable than 2-HMPIMP and 2-HMPIMBP against high temperature and thermal decomposition. The highest weight losses were observed at 450-670 and 500-700 °C, respectively, in DTG curves of O-2-HMPIMP and O-2-HMPIMBP. The presence of water can be seen in the TGA curves of O-2-HMPIMP and O-2-HMPIMBP compounds (Figures 5 and 6), showing between 3.55 and 9.29% wt losses in the 50-150 and 50-190 °C ranges, respectively, and corresponding to the loss of water of crystallization (50-150 °C) and coordination water (150-200 °C).²⁴

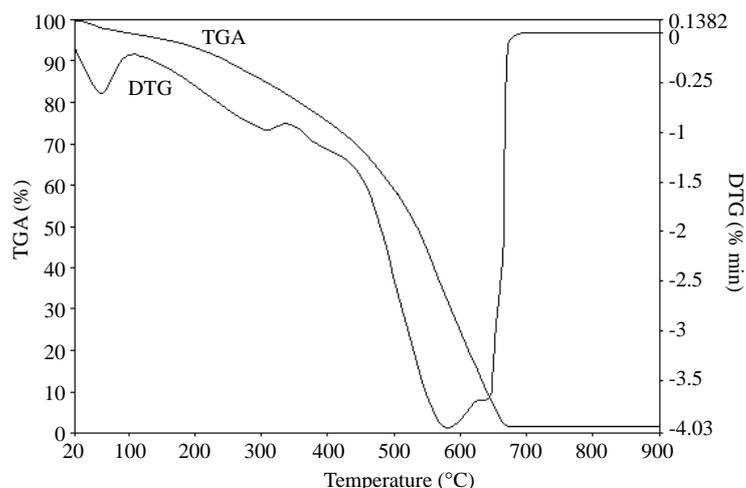


Figure 5. TGA and DTG curves of oligo-2-[(2-hydroxymethylphenylimino) methyl] phenol (3).

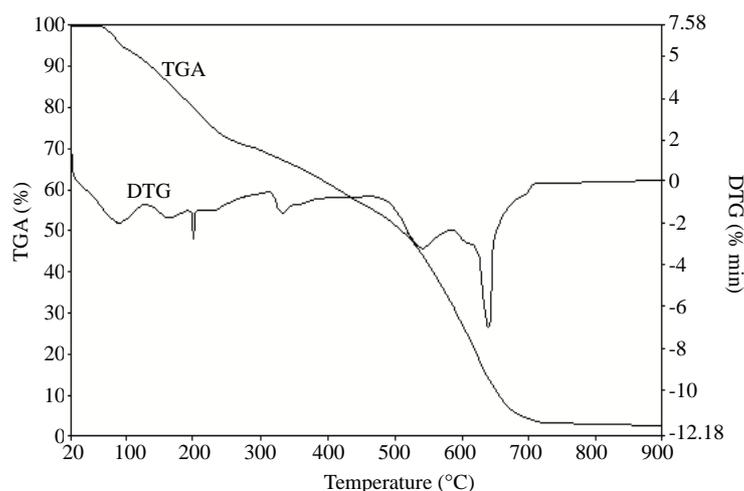


Figure 6. TGA and DTG curves of oligo-2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol (4).

Conclusion

2-HMPIMP and 2-HMPIMBP were converted to oligomers by an oxidant such as air in an aqueous alkaline medium. The yields of O-2-HMPIMP and O-2-HMPIMBP were between 24% and 42%, respectively, at 70 °C for 10 h. In the oxidative polycondensation reaction of 2-HMPIMP and 2-HMPIMBP, air was shown to be the better choice. The M_n , M_w and PDI values of O-2-HMPIMBP and O-2-HMPIMP were 1100, 1600 g mol⁻¹ and 1.45, and 6250, 6000 g mol⁻¹ and 1.04, respectively. The oligomer units were formed from *ortho* and *para*-carbons of the phenol ring from oxidative polycondensation of 2-HMPIMP. The oligomer units were formed from *ortho*-carbons of the phenol ring from oxidative polycondensation of 2-HMPIMBP. As a result, synthesized oligophenols showed sufficient resistance to thermal degradation. Half of the O-2-HMPIMP and O-2-HMPIMBP weights were lost at 535 and 520 °C, respectively.

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