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The synthesis and properties of oligosalicylaldehyde and its Schiff base oligomers

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Abstract

The products and oxidative polycondensation reaction conditions of salicylaldehyde (SA) with air oxygen and sodium hypochloride (NaOCl) were studied. In this reaction, NaOCl was observed to be more active than O_2 and their optimum reaction conditions were determined. Oligosalicylaldehyde (OSA) was synthesized from the oxidative polycondensation of SA with air and NaOCl in an aqueous alkaline medium between 85 and 100°C. The products were characterized by ^{1}H-NMR, FT-IR, UV–Vis and elemental analysis. The number average molecular weight, mass average molecular weight and polydispersity index values of OSA synthesized at medium NaOCl and O_2 were found to be 3700, 5990 g mol^{-1}, 1.62 and 1690, 5150 g mol^{-1}, 3.05, respectively. At the optimum reaction conditions, the yield of the reaction products were found to be 65.5% (O_2) and 71.4% (NaOCl). About 80% SA was converted to OSA. TG analyses showed OSA to be resistant to thermo-oxidative decomposition. The weight loss of OSA were found to be 5, 50 and 89% at 217, 587 and 1000°C, respectively. Also, new oligomeric Schiff bases were synthesized from condensation of OSA with aniline, *p*-toluidine and *p*-nitroaniline and their the structures and properties were determined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Salicylaldehyde; Oligosalicylaldehyde; Oxidative polycondensation

1. Introduction

Oligophenols and their derivatives have been used in various fields because of their electron structure properties. They have useful properties such as paramagnetism, semiconductivity, electrochemical cell and resistance to high energy. Because of these properties, oligophenols were used to prepare inhibitors with resistance at high temperature, thermostabilizers [1,2], graphite materials [3], epoxy oligomer and block copolymers [4,5], adhesives [6], photoresistors [7] and antistatic materials [8]. Halogen and sulfur derivatives of the oligophenols were used to prepare flame-resistant composite materials of specific detergents such as lead collecting battery cathodes [9]. Nowadays, despite these advantages, use of bi-functional oligophenols is very limited. The Schiff bases derived from the salicylaldehydes (SAs) are well-known polydentate ligands, coordinating in deprotonated or neutral forms. Oligosalicylaldehyde (OSA) and its Schiff base oligomers can form polymer–metal

complexes with metal salts. Therefore, they can be used to remove heavy metals from industrial waste waters.

In the first part of this paper the effects of different parameters such as temperature, flow rate of air, beginning concentration of SA, sodium hypochloride (NaOCl) and alkaline medium on OSA were investigated. In the second part, the new Schiff base oligomers were synthesized from OSA with aniline, *p*-toluidine and *p*-nitroaniline; then OSA and its Schiff base oligomers were characterized using FT-IR, UV–Vis, ^{1}H-NMR, element analysis, thermogravimetric analyses (TGA) and size exclusion chromatography (SEC) techniques.

2. Experimental

2.1. Materials

Aniline, *p*-toluidine, *p*-nitroaniline, SA, 1,4-dioxane, ethanol, benzene, acetone, ethyl acetate, pyridine, tetrahydrofuran, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4 and toluene were from Merck Chemical Co. in chromatographic grade and they were used as received. Hydrochloride acid (HCl) and NaOCl (30% solution in water)

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were supplied from Carlo Erba Co. and Paksoy Co., respectively. KOH was supplied from Analar BDH Chem. Co.

2.2. The oxidative polycondensation of SA with air in an aqueous alkaline medium

SA (3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10%) (0.025 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 glass tubing over the condenser for sending air. The reaction mixture was stirred at 90°C for 25 h (Scheme 1). The air was passed at a rate of $8.5 \, l \, h^{-1}$ during the course of the reaction. To prevent the loss of water in the reaction mixture and to deneutralize CO_2 in air with KOH, air was passed through 200 ml of an aqueous solution of KOH (20%) before passing through the reaction mixture. It was cooled to room temperature, then 0.2 mol of HCl (37%) was added to the reaction mixture. Unreacted SA was removed by steam distillation. The crude product was separated into two fractions by solubility differences in water. The first fraction (OSA-I, 75% of product) was insoluble in water and the second fraction (OSA-II, 25% of product) was soluble in water. The reaction product (the first fraction) was washed with water (50 ml × 3), filtered and dried in the oven at 105°C (13.7 g, yield 56%).
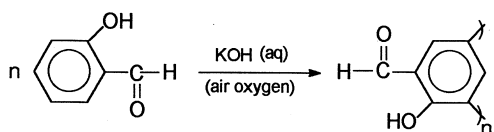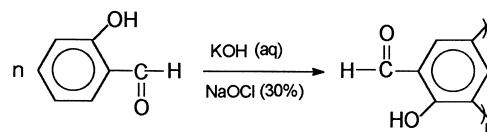

Scheme 1.

FT-IR (KBr; cm^{-1}): 2500–3355 (phenol-OH); 1654 (CHO); 2854–2925 (aldehyde C–H); 3030 (aromatic C–H); 1658 (Ar-COOH). Anal. calcd. for OSA: C, 70.00; H, 3.33. Found for OSA-I and OSA-II: C, 69.21; H, 3.85; and C, 67.06; H, 3.60, respectively.

2.3. The oxidative polycondensation of SA with NaOCl

OSA was synthesized through the oxidative polycondensation of SA with aqueous solution of NaOCl (30%). The SA (3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10%, 0.025 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 NaOCl. After heating to 60°C, NaOCl was added dropwise over about 20 min. The reaction mixture was stirred at 90°C for 25 h (Scheme 2). The mixture was neutralized with 3 ml HCl (37%) at room temperature. Then, unreacted SA was removed by steam distillation. The crude product was washed with water (50 ml × 3), filtered and dried in an oven at 105°C.

Scheme 2.

### 2.4. The syntheses of Schiff bases of OSA

OSA-I (the first fraction, insoluble in water) (3.00 g, 0.025 mol unit^{-1}) and aniline (2.56 g, 0.0275 mol) were dissolved in 1,4-dioxane (25 ml) and placed into a 50 ml two-necked round-bottomed flask (Scheme 3). It was fitted with a condenser and a thermometer. The mixture was stirred magnetically on a water bath at 100°C for 5 h. Then, 1,4-dioxane and unreacted aniline were separated from the condensation product by distillation and dried in an oven at 105°C (4 g, 82% yield).

FT-IR (KBr; cm^{-1}): 1620 (CH=N); 3418 (Ar-OH); 3060 (olefinic –CH). Anal. calcd. for oligophenylazomethinephenol (OPAP): N, 7.18. Found for OPAP: N, 5.62.

OSA-I (the first fraction, insoluble in water) (3.00 g, 0.025 mol unit^{-1}) and p-toluidine (2.94 g, 0.0275 mol) were dissolved in ethanol and placed into a 50 ml two-necked round-bottomed flask (Scheme 3). It was fitted with a condenser and a thermometer. The mixture was stirred magnetically on a water bath at 80°C for 5 h. Then ethanol was separated from the condensation product by distillation. The condensation product was extracted by hot toluene for 15 h and dried in an oven at 105°C (4 g, 77% yield).

FT-IR (KBr; cm^{-1}): 1614 (CH=N); 3385 (Ar-OH); 3080 (olefinic –CH); 2860–2920 (Ar-CH$_3$). Anal. calcd. for oligophenylazomethinephenol (OTAP): N, 6.70. Found for OTAP: N, 5.25.

OSA-I (the first fraction, insoluble in water) (3.00 g, 0.025 mol unit^{-1}) and p-nitroaniline (3.80 g, 0.0275 mol) were dissolved in 1,4-dioxane and placed into a 50 ml

R=H   R=CH₃   R=NO₂
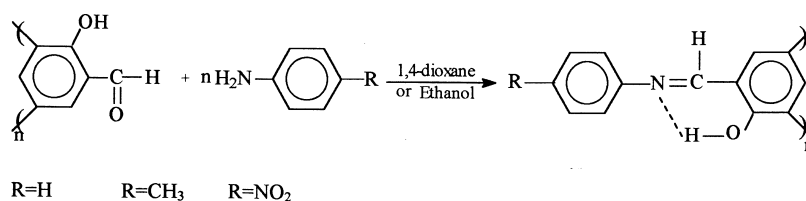
Scheme 3.

two-necked round-bottomed flask (Scheme 3). It was fitted with a condenser and a thermometer. The mixture was stirred magnetically on a water bath at 80°C for 5 h. Then 1,4-dioxane was separated from the condensation product by distillation. The condensation product was extracted by hot toluene for 15 h and dried in an oven at 105°C (4.4 g, 70% yield).

FT-IR (KBr; cm^{-1}): 1627 (CH=N); 3362 (Ar-OH); 3076 (olefinic –CH). Anal. calcd. for oligonitrophenylazomethinephenol (ONPAP): N, 11.70. Found for ONPAP: N, 8.98.

2.5. Characterization techniques

The infrared and UV–Vis spectra were measured by Shimadzu FT-IR 8300 and UV-160, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}). UV–Vis spectra of OPAP, OTAP, ONPAP and OSA oligomers were determined by using ethanol and THF. OSA and its Schiff base oligomers were characterized using ^{1}H-NMR spectra (Bruker AC FT-NMR 200 MHz spectrometer) recorded at 25°C using deuterated DMSO as solvent. TMS was used as internal standard. Thermal data were obtained using a derivatograph MOM Q-1500D of Kovo Co. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by SEC of Kovo Co. For SEC investigations SGX (100 Å and 7 mm diameter loading material) 3.3 mm i.d. × 150 mm columns were used; eluent: DMF (0.2 ml min^{-1}), polystyrene standards. A refractometric detector (at 25°C) was used to analyze the product. The thermogravimetric measurements were made between 20 and 1000°C (in air, rate 5°C min^{-1}).

3. Results and discussion

3.1. The investigation of synthesis conditions of OSA

The conditions for oxidative polycondensation reaction of SA with O$_2$ solution in aqueous alkaline medium are given in Table 1. No reaction was observed in THF and acetic acid. SA was soluble in aqueous NaOH but no reaction was observed when heated at 80°C for 5 h. However, the oxidative polycondensation reaction of SA immediately formed in an aqueous solution and a solution that turned into dark brown upon addition of oxidants such as NaOCl and H$_2$O$_2$ and air oxygen. When $[SA]_0 = [KOH]_0 = 1.25$ mol l^{-1}, the conversion of the SA oligomer by air oxygen at 85°C for 6 h was 9.8% (see Table 1).

As is seen from Table 1, in these reactions, the yield of the oligomer was dependent upon temperature and time factors. The maximum yield (50.4%) of OSA-I formed at high concentrations of SA (3.75 mol l^{-1}) at 90°C for 25 h. The yield of OSA-I increased from 41.7 to 50.4% in the case of 3 × $[SA]_0$ under the same conditions (Table 1). Also, the yield of the oligomer was affected by the increase in rate of air passing through the reaction mixture. SA is known to be relatively less active than phenols during oxidative polycondensation. It should be because of the attracting electron density from OH of electron-acceptor CHO groups [10].

The conditions of oxidative polycondensation reaction of SA with 34% NaOCl solution in aqueous alkaline medium are given in Table 2. As is seen in Table 2, the products SA formed in the presence of NaOCl which is a better oxidant than air oxygen. The conversion of SA was 71.4% at optimum conditions such as $[SA]_0 = [KOH]_0 = 1.01$ mol l^{-1}, $[NaOCl]_0 = 2.02$ mol l^{-1}, at 100°C for 25 h. The product yields of OSA-I and OSA-II were 38.9 and 32.5%, respectively. It is observed in Table 2 that under the same conditions the yield of OSA-I was higher than that of OSA-II. The various conditions for OSA are given in Table 2.

3.2. Solubility

The oxidative polycondensation products of SA with air oxygen and NaOCl in aqueous alkaline medium were black solid powders. The first (OSA-I) and the second fractions (OSA-II) were soluble in aqueous NaOH, H$_2$SO$_4$, pyridine, tetrahydrofuran, dimethylformamide, DMSO and 1,4-dioxane. However, the first fraction (OSA-I) was poorly soluble in acetone, ethyl acetate and ethanol, and insoluble in water,

Table 1
The oxidative polycondensation of SA with air oxygen in aqueous KOH

Sample number	$[SA]_0$ (mol l^{-1})	$[KOH]_0$ (mol l^{-1})	V_{air} (l h^{-1})	T (°C)	Time (h)	Conversion of SA, %	Reaction products, %	
							(OSA-I)	(OSA-II)
1	1.25	1.25	8.5	85	6	9.8	7.5	2.3
2	1.25	1.25	8.5	90	6	4.3	11.8	3.5
3	1.25	1.25	8.5	90	15	28.6	22.0	6.6
4	1.25	1.25	8.5	90	20	35.5	27.2	8.3
5	1.25	1.25	8.5	90	25	54.2	41.7	12.5
6	1.25	2.50	8.5	90	25	55.0	42.5	12.5
7	2.50	2.50	8.5	90	25	63.2	48.6	14.6
8	3.75	3.75	8.5	90	25	65.5	50.4	15.1
9	1.25	1.25	6.0	90	15	21.7	4.5	6.2
10	1.25	1.25	10.5	90	15	36.9	24.4	12.5

Table 2
The oxidative polycondensation of SA with NaOCl in aqueous KOH

Sample number	$[SA]_0$ (mol l^{-1})	$[KOH]_0$ (mol l^{-1})	$[NaOCl]_0$ (mol l^{-1})	T (°C)	Time (h)	Convers. of SA, %	Reaction products, %	
							(OSA-I)	(OSA-II)
1	1.01	1.01	1.01	90	5	8.2	6.2	2.0
2	1.01	1.01	2.02	90	5	14.4	10.8	3.6
3	1.01	1.01	3.03	90	5	23.8	18.4	5.4
4	1.01	1.01	2.02	90	10	33.5	24.1	8.8
5	1.01	1.01	2.02	90	15	39.5	30.5	9.0
6	1.01	1.01	2.02	90	25	66.6	50.2	16.4
7	1.01	1.01	2.02	95	25	69.4	37.6	31.8
8	1.01	1.01	2.02	100	25	71.4	38.9	32.5
9	0.50	0.50	1.00	90	15	23.6	17.8	5.8

aromatic solvents and chlorinated solvents, such as $CHCl_3$ and CCl_4.

3.3. Structure of OSA

According to SEC analysis, the number average molecular weight (M_n), mass average molecular weight (M_w) and PDI values of the polycondensation product (OSA-I) of SA with NaOCl and air O_2 were found to be 3700, 5990 g mol^{-1}, 1.62 and 1690, 5150 g mol^{-1}, 3.05, respectively, (Fig. 1 and Table 3).
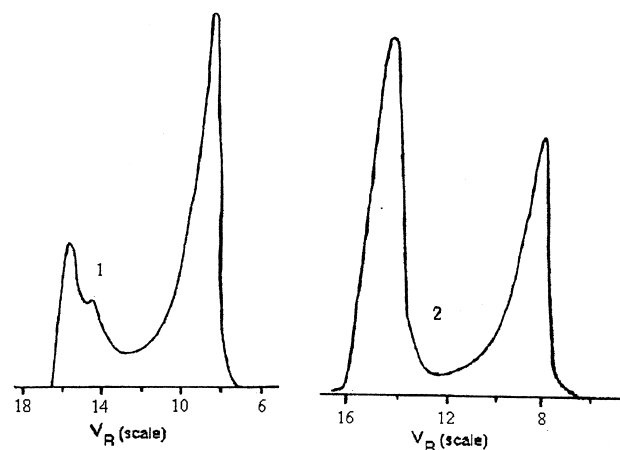

Fig. 1. The molecular weight distribution curves of the oxidative polycondensation products (OSA-I) of SA with: (1) NaOCl; and (2) air oxygen.

The oxidative polycondensation product of SA was completely soluble in aqueous NaOH. The oligomer was again precipitated when it is neutralized with CO_2. These properties showed phenolic hydroxy (–OH) groups in the structure of the oligomer by FT-IR and ^{1}H-NMR analyses. The Schiff bases of SA with aromatic amines such as aniline, *p*-toluidine and *p*-nitroaniline were insoluble in ethanol.

It is seen that in UV–Vis spectra of SA and its oligomer (Fig. 2) high intensive K, less intensive B and less intensive
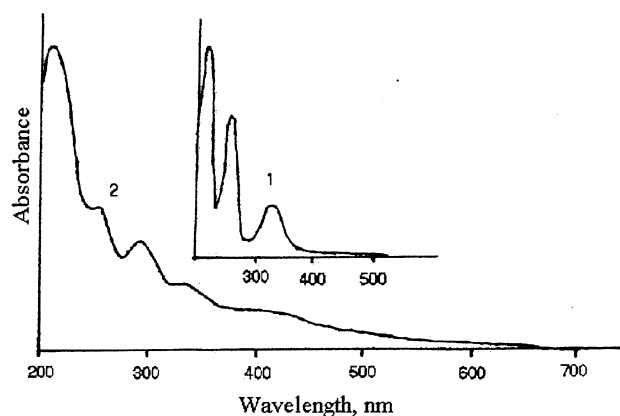

Fig. 2. The UV–Vis spectra of: (1) SA; and (2) OSA-I.

Table 3
The number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index (PDI) and % yield of OSA-I (NaOCl), OSA-I (air O_2) and OSA-II (air O_2)

Oligomers	M_n	M_w	PDI	Low molecular weight section				High molecular weight section			
				M_n	M_w	PDI	Yield (%)	M_n	M_w	PDI	Yield (%)
OSA-I (NaOCl)	3700	5990	1.62	560	660	1.18	25	6240	7820	1.25	75
OSA-I (air O_2)	1690	5150	3.05	550	640	1.16	54	7600	10300	1.36	46
OSA-II (air O_2)	3950	6260	1.58	–	–	–	–	–	–	–	–

Table 4
The ^{1}H-NMR spectral data of the OSA and its Schiff base oligomers (DMSO; (δ, ppm; Me$_4$Si as internal standard))

Compounds	R	–OH	–CHO	–CH=N–	a	b	cc'	dd'	dd'e
OSA (1)	–	4.24 (s, 1H)	10.05 (s, 1H)	–	7.15 (s, 1H)	8.26 (s, 1H)	–	–	–
OPAP (2)	H	13.10 (s, 1H)	–	8.90 (s, 1H)	7.10 (s, 1H)	7.65 (s, 1H)	7.35 (m, 2H)	–	6.92–7.26 (m, 3H)
OTAP (3)	CH$_3$	13.14 (s, 1H)	–	8.93 (s, 1H)	7.00 (s, 1H)	7.64 (s, 1H)	7.00–7.28 (m, 4H)	–	
ONPAP (4)	NO$_2$	12.72 (s, 1H)	–	9.10 (s, 1H)	7.40 (s, 1H)	6.73 (s, 1H)	6.53–7.90 (m, 4H)	–	

R bands were observed in 210, 254 and 331 nm, respectively. The R band of the CHO group of the oligomer was observed in a lower field (bathochromic), such as 5 nm, than the same band of SA. The difference in the visible region (400–740 nm) of spectrum between SA and its oligomer depends on the shifting of the B band. The mesomeric and inductive effects of the OH and CHO groups of the monomer and oligomer showed the structural similarity. As a result, the UV–Vis spectra of oligomers synthesized from SA in the air O_2 and NaOCl medium were similar.

When the FT-IR spectra of SA and its oligomers are compared, both have similar bands. In the structures of oligomers, the vibration bands of phenol OH groups were observed to be intense with wide bands in 2500–3355 cm^{-1}. Whereas the CHO band was observed at 1654 cm^{-1}. As a shoulder of the OH band, the weak vibration bands of the aldehyde C–H and aromatic C–H groups were observed at 2854–2925 and 3030 cm^{-1}, respectively. The band of the carboxylic acid group was observed at 1658 cm^{-1} at the OSA-I synthesized from the oxidative polycondensation reaction of SA with NaOCl. The ^{1}H-NMR and FT-IR results showed the formation of oligomeric macromolecules from the SA unit by polymerization in the C_3 and C_5 positions (Scheme 4).
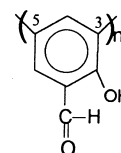
Scheme 4.

3.4. Structure of the Schiff base derivatives of OSA

The condensation products of OSA with aniline, *p*-tolui-dine and *p*-nitroaniline, i.e. OPAP, OTAP and ONPAP, respectively, were all dark black powders and insoluble in ethanol. They have higher softening temperatures (T_g) than that of OSA. These oligomers are infusible at 220°C similar to OSA.

It is supposed that polymeric Schiff bases can only be prepared from the condensation of aromatic anilines with electron-acceptor substituents. Fundamental differences were observed in the UV–Vis spectra of Schiff bases formed from condensation of SA with aniline and *p*-tolui-dine (Fig. 3). The K band of Schiff base oligomers was divided into two peaks (208 and 222 nm). The reason for this is the conjugation between benzene ring and non-bonding electrons of nitrogen in the azomethine group.
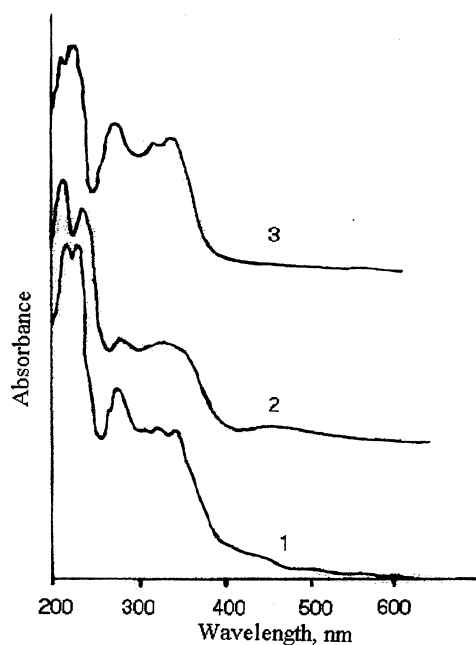
Fig. 3. The UV–Vis spectra of the oxidative polycondensation products of OSA-I with: (1) aniline; (2) *p*-toluidine; and (3) *p*-nitroaniline.

B and R bands of CH=N groups were observed in 269 and 339 nm, respectively, in the spectrum of OPAP.

After the oxidative polycondensation reaction, the benzene bands of electron-acceptors such as CHO and NH_2 turned into electron-donor phenylazomethine bands. Similarly, the UV–Vis spectrum of OPAP, which was synthesized by oxidative polycondensation reaction in air was completely identical to the UV–Vis spectrum of an oligomer obtained by the condensation of OSA-I with aniline. The benzene band of C_6H_5–N= shifted from 221 to 229 nm due to the CH_3 group in the UV–Vis spectrum of OTAP rather than that of OPAP.

The CH=N absorption bands are observed at 1620, 1614 and 1627 cm^{-1} for compounds OPAP, OTAP and ONPAP, respectively. The stretching frequency observed at 2740, 2752 and 2704 cm^{-1} for OPAP, OTAP and ONPAP shows the presence of O–H···N intramolecular hydrogen bond, which is in agreement with the reported values in the literature [11].

In order to identify the structures of OSA and its Schiff base oligomers (Scheme 5), the ^{1}H-NMR spectra were

recorded in DMSO-d_6. The ^{1}H-NMR assignments are also given in Table 4. The FT-IR spectral data of the OSA and its Schiff base oligomers confirm the results of the ^{1}H-NMR spectra. The OH signals in the Schiff base derivatives (OPAP, OTAP and ONPAP) appeared at a much lower field because of intramolecular H-bonding (Scheme 5). This case is also supported by the FT-IR bands at 2740–2760 cm^{-1}.
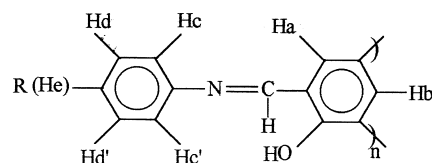
OPAP (2)   OTAP (3)   ONPAP (4)

R=H   R=CH₃   R=NO₂

Scheme 5.

3.5. Thermal analyses of OSA and its Schiff base oligomers

TGA of the prepared OSA and its Schiff base oligomers were measured under air atmosphere in the temperature ranges 20–1000°C in order to investigate the thermal stability. The TG data are illustrated in Table 5 for OSA and its Schiff base oligomers and Fig. 4 shows the TG traces for the OSA and its Schiff base oligomers. According to the TG traces, OSA and its Schiff base oligomers started to degrade at 121 and 127–159°C (Table 5, Fig. 4). The TG data in Table 5 and Fig. 4 indicate that the OSA and its Schiff base oligomers decomposed at high temperatures. Although they are resistant enough to thermooxidative degradation, they are less stable than oligophenols [10].

4. Conclusions

Thus, we determined the optimum conditions of the oxidative polycondensation reaction of SA with air oxygen and NaOCl, and described new synthesis methods for OSA. We synthesized for the first time condensation products of OSA with aniline, *p*-toluidine and *p*-nitroaniline, and determined their structure and chemical and physical properties. In this reaction, NaOCl found to be more active than O_2 and gave SA with a conversion yield of 80%. The M_n and M_w values of OSA synthesized with NaOCl and O_2 were found to be 3700, 5990 g mol^{-1} and 1690, 5150 g mol^{-1}, respectively. According to TG, OSA and its Schiff base oligomers were resistant enough to thermo-oxidative degradation, and the carbonaceous residue values of OSA, OPAP, OTAP and ONPAP were found to be 11, 9.5, 11.5 and 16%, respectively, at 1000°C.

Table 5
The thermo-oxidative degradation parameters of OSA and its Schiff bases

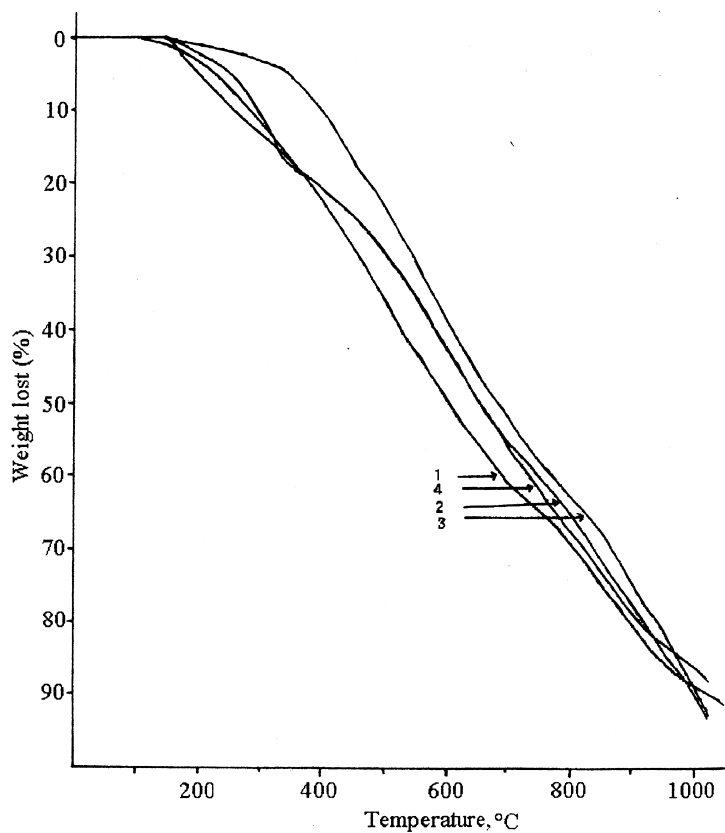| Oligomers	$T_{initial}$ (°C)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Carb. residue % at 1000°C
OSA-I	121	217	587	11.0
OPAP	127	196	666	9.5
OTAP	159	337	677	11.5
ONPAP	130	250	670	16.0

Fig. 4. TGA curves of: (1) OSA-I and its oligomers with (2) aniline; (3) *p*-toluidine; and (4) *p*-nitroaniline at air medium (at a heating rate of $5°C \, min^{-1}$).

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