

# Synthesis and Characterization of Oligosalicylaldehyde-graft-oligoaniline and Its Beginning Oligomers

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**ABSTRACT:** Conjugate bonding oligosalicylaldehyde-graft-oligoaniline (OSA-graft-OA) was synthesized from the polycondensation reaction of oligosalicylaldehyde (OSA) with oligoaniline (OA). There were various functional groups such as —OH, —NH and —CH=N in the structure of the graft cooligomer. The physical properties of graft-cooligomers such as melting temperature and solubility were studied: number-average molecular weight, mass-average molecular weight, and a polydispersity index of OA, OSA, and fractions of the graft cooligomers [(OSA-graft-OA)-I] and [(OSA-graft-OA)-II] were found to be 740, 780 g mol<sup>-1</sup>, 1.05; 3700, 5990 g mol<sup>-1</sup>, 1.62; 990, 2770 g mol<sup>-1</sup>, 2.80 and 1300, 4100 g mol<sup>-1</sup>, 3.15, respectively. The FTIR and UV-Vis spectra of the graft cooligomer were compared with those of beginning oligomers. The spectral analyses results showed that the OSA-graft-OA synthesized from the polycondensation reaction of aromatic amine with aldehyde that have long oligophenol macromolecule bonded each other with an azomethine bridge through oligophenylamine side chains. The thermal stability of the graft cooligomer and oligomers were measured by thermogravimetric analysis (TG) under an air atmosphere. According to TG analyses, the carbonaceous residues of the [(OSA-graft-OA)-I] (soluble in ethanol) and (OSA-graft-OA)-II (soluble in toluene) were 23 and 40%, respectively, at 1000°C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 218–226, 2002

**Key words:** oligosalicylaldehyde-graft-oligoaniline; oligoaniline; oligosalicylaldehyde; synthesis and properties; thermogravimetric analysis

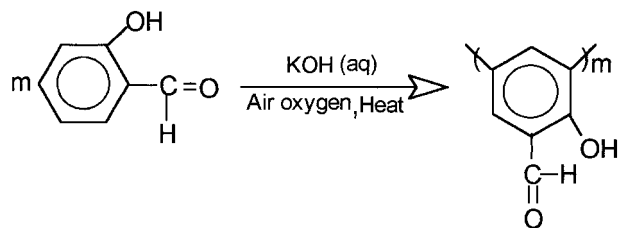
## INTRODUCTION

Synthesis of polymer-containing azomethine groups on a polymer chain has been a subject of considerable interest. Recently, so-called poly-Schiff bases have been prepared. Aromatic backbone units are more stable than aliphatic units, and they have significantly higher melting temperatures. Polymer-Schiff bases have higher thermal stabilities.<sup>1</sup> Because these contain functional

groups, poly- and oligoarylenes have important properties such as chemical reactivity, temperature and plasma resisting, and paramagnetism. Because of these properties, oligophenols and oligophenylamines were used to prepare active inhibitors, epoxy oligomers, and block copolymers,<sup>2,3</sup> semiconducting materials,<sup>4</sup> antistatic materials,<sup>5</sup> thermostabilizers,<sup>6</sup> accumulator detergents,<sup>7</sup> and photoresist by resistance to plasma.<sup>8</sup> Because of chemical and optical properties of oligosalicylaldehyde-graft-oligoaniline (OSA-graft-OA), it might be used to be an active complex formation and new polymer active dyes for textiles materials.

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Scheme 1

In this article, the preparation, characterization (FTIR, UV-Vis,  $^1\text{H-NMR}$ , element, HPLC, and TG) and some physical properties of OA, OSA, and their graft oligomers [(OSA-*graft*-OA)-I and (OSA-*graft*-OA)-II] have been described. The synthetic process for the preparation of the products are shown in Schemes 1, 2, and 3.

## MATERIALS AND METHODS

### Materials

Aniline, salicylaldehyde, 1,4-dioxane, ethanol, benzene, and toluene were supplied from Merck Chemical Co. as chromatographic grade, and they were used as received. Tetrahydrofuran (THF), dimethylformamide (DMF), acetone, hydrochloric acid (HCl), and sodiumhypochloride (NaOCl) (30% solution in water) were supplied from Carlo Erba Co. KOH was supplied from Analar BDH Chem Co.

### The Synthesis of Oligosalicylaldehyde (OSA)<sup>9</sup>

Salicylaldehyde (24.4 g, 0.2 mol) and KOH (11.2 g, 0.2 mol) were mixed in 10 mL of water and the mixture was placed into a 500-mL three-necked round-bottomed flask. It was fit with a condenser, thermometer, stirrer, and placed in glass tubing over a condenser for sending air. The reaction mixture was stirred at 90°C for 25 h. The air was passed at a rate of 8.5 L/h during the course of the reaction. To have no loss of water in the reaction mixture and to deneutralize  $\text{CO}_2$  of air with KOH, air passed into 200 mL of an aqueous solution of KOH (20%) before sending into the reaction tub-

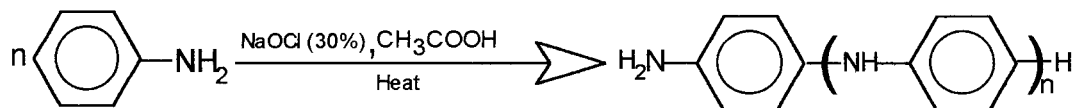
ing. It was cooled to room temperature, and then 0.2 mol of HCl (37%) was added to the reaction mixture. Unreacted salicylaldehyde was evaporated in a steam bath. The reaction product was separated into two fractions. The first fraction (OSA-I, 75% of product) was insoluble in water, and the second fraction (OSA-II, 25% of product) was soluble in water. The reaction product (OSA-I) was washed with water (50 mL  $\times$  3) and filtered and dried in an oven at 105°C (13.7 g, yield 56%). OSA was a black solid matter in powder form.

### The Synthesis of Oligoaniline (OA)<sup>9</sup>

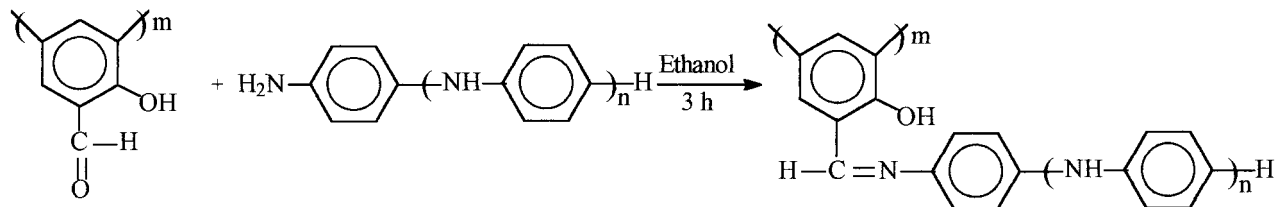
OA was synthesized by the oxidative polycondensation reaction of aniline (Scheme 2). Aniline (9.3 g, 0.1 mol) and acetic acid (10.5 g, 0.175 mol) were added to a 100-mL three-necked round-bottomed flask. It was fit with a condenser, thermometer, and added to a funnel containing 31 mL of an aqueous solution of NaOCl (30%, 0.125 mol). After heating at 30°C, for 15 min, NaOCl was added dropwise over 20 min, and the reaction continued for 2.5 h. The mixture was neutralized with NaOH (0.175 mol, 15 mL) and then unreacted aniline was evaporated on a steam bath. The reaction product (OA) was washed with water (50 mL  $\times$  3) and filtered and dried in the oven at 105°C (8.2 g, yield 88%). It was a dark black solid in powder form, and it melted at 209°C.

### The Synthesis of OSA-*graft*-OA

OSA-I (10 g, 0.084 mol  $\cdot$  unit) and OA (7.6 g, 0.084 mol  $\cdot$  unit) were dissolved in 100 mL of ethanol. and was placed into a 250-mL three-necked round-bottomed flask. It was fit with a condenser, thermometer, and stirrer. The reaction mixture was stirred for 3 h at 70°C (Scheme 3). The first fraction (OSA-*graft*-OA)-I that was soluble in ethanol was separated from the mixture by filtering. Ethanol was evaporated in a steam bath. The condensation product was dried in a vacuum oven at 80°C (product 3.04 g, 21%). The second fraction, that is (OSA-*graft*-OA)-II, was insoluble in ethanol. Thus, it



Scheme 2



Scheme 3

was dissolved in toluene and filtered. Toluene was distilled, and the product was dried in a vacuum oven at 80°C (OSA-graft-OA)-II, 11.66 g, 78%). (OSA-graft-OA)-I and II were melted at 110°C and 215–220°C, respectively, to be different from OSA and OA (209°C). The reason for melting the cooligomer fractions may be because of the plastic effect of the (OSA-graft-OA)-Is of the oligophenylamine branch.

### Characterization Techniques

The infrared and ultraviolet-visible spectra were measured by Shimadzu FTIR 8300 and UV-160, respectively. Elemental analysis was carried out by Carlo Erba 1106 models. UV-Vis spectra of cooligomer and beginning oligomers were determined by using ethanol and THF. OSA-graft-OA and its beginning oligomers were characterized by using a  $^1\text{H-NMR}$  spectra (Bruker AC FT-NMR 200 MHz spectrometer) recorded at 25°C by using deuteriated DMSO as solvent. TMS was used as internal standard. Thermal data were obtained by using a derivetograf MOM Q-1500D model instrument. The number-average molecular weight ( $M_n$ ), mass-average molecular weight ( $M_w$ ), and polydispersity index (PDI) were determined by high-pressure liquid chromatography (HPLC) from the Kovo Co. For HPLC investigations we used an SGX (100 Å and 7-mm diameter loading material) 3.3 i.d.  $\times$  150 mm columns. DMF (0.2 mL/min) was used as eluent. Refractometric detector (at 25°C) was used to analyze the product. Polystyrene was used as the standard column. The thermogravimetric measurements were made at both 20–500 and 500–1000°C at air medium (rate 5°C/min).

## RESULTS AND DISCUSSION

### The Solubility and Some Properties of (OSA-graft-OA)-I and II and Beginning Matters

The first section of the reaction product observed separating as precipitation after 20–25 min when

OA and OSA were heated in ethanol. According to solubility properties, the condensation product is different from the beginning oligomers. The condensation product is soluble in aromatic (benzene and toluene) and chloro-organic solvents such as  $\text{CHCl}_3$  and  $\text{CCl}_4$  to be different from OSA. OSA was soluble in the aqueous solution of alkaline, con.  $\text{H}_2\text{SO}_4$ , pyridine, THF, DMF, DMSO, and 1,4-dioxane, but it was insoluble in water, aromatic solvents, and chloro-organic solvents. OSA was poorly soluble in acetone, ethyl acetate, and ethanol. OA was soluble in aromatic (benzene and toluene), polar organic (ethanol, acetone, THF, and DMF), and chloro-organic solvents such as  $\text{CHCl}_3$  and  $\text{CCl}_4$ .

This result demonstrated formation of graft cooligomer, that is, of the azomethin group, to be the condensation product between the  $\text{NH}_2$  end group of OA with the aldehyde group of OSA. The graft cooligomer fractions formed various color



**Figure 1** The molecular weight distribution curves of the condensation product of (a) OA, (b) OSA, (c) OSA-graft-OA-I, and (d) OSA-graft-OA-II.

**Table I** The Number-Average Molecular Weight ( $M_n$ ), Mass Average Molecular Weight ( $M_w$ ) and Polydispersity Index (PDI) and % Yield of OSA, OA, and Graft-co-oligomers (OSA-graft-OA)-I and II

Oligomers	Low Molecular Weight Section							High Molecular Weight Section			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	Yield, %	$M_n$	$M_w$	PDI	Yield, %
OSA	3700	5990	1.62	560	660	1.18	25	6240	7820	1.25	75
OA	740	780	1.05	—	—	—	—	—	—	—	—
(OSA-graft-OA)-I	990	2770	2.80	815	1170	1.44	80	8100	9900	1.22	20
(OSA-graft-OA)-II	1300	4100	3.15	860	1200	1.40	64	7250	11100	1.53	36

complexes in normal conditions in ethyl acetate solvent by solid metal salts such as  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Sn}^{+2}$ .

### Structure

The results of  $M_n$ ,  $M_w$ , and PDI analyses are shown in Figure 1 and Table I. OA is an octamer having very narrow PDI. The macromolecule of OSA is four to six times larger than the OA chain. The molecular weight of OSA is consistent with two different fractions. The first fraction was low molecule weight ( $M_n$ : 560 g mol<sup>-1</sup>,  $M_w$ : 660 g mol<sup>-1</sup>, PDI: 1.18). It formed 25% of OSA. But, the second fraction of OSA formed 75% of OSA, and it had a higher molecular weight ( $M_n$ : 6240 g mol<sup>-1</sup>,  $M_w$ : 7820 g mol<sup>-1</sup>) than the first fraction. PDI of this fraction was somewhat larger.

$M_n$  and  $M_w$  values of (OSA-graft-OA)-I and II were found to be 990 and 2770 g mol<sup>-1</sup>; and 1300 g mol<sup>-1</sup> and 4100 g mol<sup>-1</sup>, respectively. The graft-oligomer fractions are consistent with two different fractions (Fig. 1). In every two graft oligomers fractions there was a richer low molecular weight section. Low molecular weight sections of (OSA-graft-OA)-I and II were found to be 80 and 64%, respectively.

The high molecular weight values of (OSA-graft-OA)-I and II are found to be  $M_n$ : 8100 g mol<sup>-1</sup>,  $M_w$ : 9900 g mol<sup>-1</sup>, and  $M_n$ : 7850 g mol<sup>-1</sup>,

$M_w$ : 11,100 g mol<sup>-1</sup>, respectively.  $M_n$  and  $M_w$  values and PDI of every two fractions of cooligomers were completely different from the same parameters of OSA and OA. This resulted in a synthesized matter of a cooligomer.

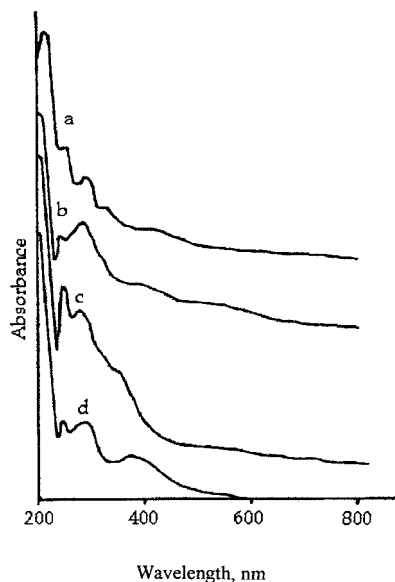
The results of elemental analyses of the products are given in Table II. These results showed that the second fraction contained more oligoaniline macromolecules (20%) than the first fraction. Because of these properties they are both different.

In the UV-Vis spectrum of oligoaniline, observing the R band in the 289-nm region, may convert to a formation of kinonimin (=C<sub>6</sub>H<sub>4</sub>=N-) groups that is one section of the structural units of the oligomer.<sup>8</sup> Kinonimin was absorbed in the wavelength that was the result of the passing away of the bi-radical form from the effect of the UV-Vis lights. Also, one section of bands belong to the structure of the beginning oligomer, and was observed at the UV-Vis spectra of the cooligomer.

The strong K band interested in the aromatic ring conjugate bands of OSA and the B band that belong to phenylamine units of OA were observed in 210 and 245-nm wave lengths, respectively. At the spectrum of the cooligomer, absorption of the CHO group was observed at 331 nm to be different from the spectrum of OSA. The B band at 281 nm of the OSA chains was wrapped with a new strong R band formation at 254 nm at the spec-

**Table II** Analytical Data of OA, OSA and (OSA-graft-OA)-I and II

Compound	Found (calcd., %)		
	C	H	N
OA	78.02 (79.10)	5.56 (5.50)	14.29 (15.39)
OSA	69.21 (70.00)	3.85 (3.33)	—
(OSA-graft-OA)-I	72.21 (73.46)	4.11 (4.26)	6.29 (6.63)
(OSA-graft-OA)-II	72.62 (73.46)	4.35 (4.26)	5.17 (6.63)



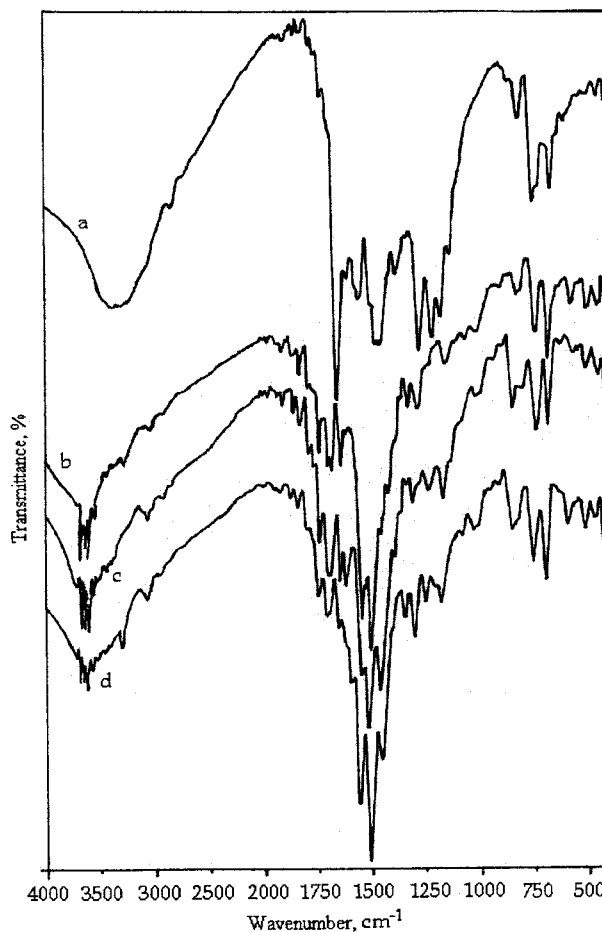
**Figure 2** The UV-Vis spectra of (a) OA, (b) OSA, (c) OSA-graft-OA-I, and (d) OSA-graft-OA-II.

trum of the cooligomer. The R band of the kinonimin and azomethine groups of (OSA-graft-OA)-I and II were formed together at 276 and 281 nm, respectively (Fig. 2).

New middle strength and extensive bands were observed at the 367 and 375-nm region in the UV-Vis spectra of the first and second fractions of the cooligomer, to be different from the spectrum of the beginning oligomers. The reason for this may be from the formation of the intramolecule  $\pi$  complexes between the NH groups in the side chain of the oligophenylimin with unreacted CHO groups in the main chain OSA of the cooligomer. These groups have strong complex formation properties. The cooligomer and beginning oligomers were observed to light in the visible region of the UV-Vis spectrum (300–750 nm) by the effect of the long conjugate bonding series. For this reason, ethylacetate solutions of OSA, OA, and cooligomer were green yellow, red, and red brown, respectively.

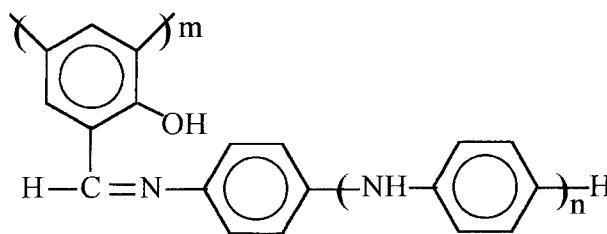
FTIR analyses were demonstrated to qualify for completely similar bands of the spectra of every two fractions of the cooligomer (Fig. 3). At the FTIR spectra, vibration bands of side-by-side three and four aromatic CH groups in which end rings of OSA and OA chains were observed at 692–752  $\text{cm}^{-1}$  and 832–856  $\text{cm}^{-1}$  regions, respectively.

Side-by-side middle strength four-piece bands were observed in the 1174–1340  $\text{cm}^{-1}$  region at

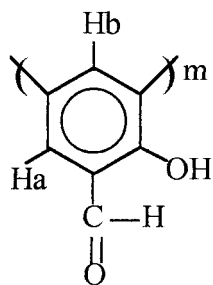


**Figure 3** The FTIR spectra of (a) OA, (b) OSA, (c) OSA-graft-OA-I, and (d) OSA-graft-OA-II.

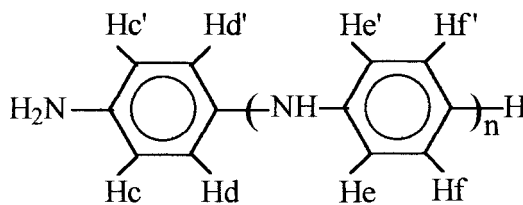
the spectrum of the cooligomer. These bands are attributed to (C—OH) stretching bands in the 1180 and 1221  $\text{cm}^{-1}$  regions in the spectra of OSA. All of these are in good agreement with the literature.<sup>10</sup> On the other hand, in the spectra of OA, bands between the 1294 and 1338  $\text{cm}^{-1}$  regions are assigned to the two aromatic amine groups, indicating these amine groups are bound to the unit structure of the OA macromolecules. Two valans vibrations of OH and NH groups of



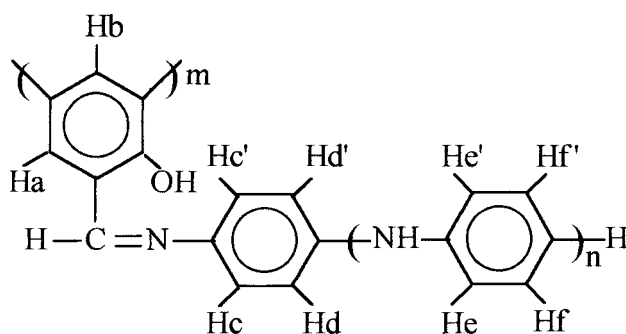
**Scheme 4**



OSA



OA



### OSA-graft-OA

#### Scheme 5

cooligomer were observed to be weak strength bands in the  $3364$  and  $3286\text{ cm}^{-1}$  regions, respectively.

At the spectrum (Fig. 3), although OH groups of OSA demonstrated an extensive and strengthening band in the  $3200\text{--}3450\text{ cm}^{-1}$  region, the OH group of the cooligomer was observed as a very weak band at  $3564\text{ cm}^{-1}$ . The reason for this may be a breaking down association of hydrogen bonding between the OH groups due to a stereo-obstacle of the oligophenylimin side chain of the cooligomer.

For cooligomer fractions, CH vibration bands of the aromatic ring and C=C bands were observed in the  $1448\text{--}1510$  and  $1550\text{--}1553\text{ cm}^{-1}$  regions, respectively. At the spectrum of the cooligomer fractions, bands of the benzene ring and C=N group were found at a weak strength in the  $1618$  and  $1622\text{ cm}^{-1}$  regions, respectively. The band of CH bonding of the unreacted CHO group was

observed at a very weak strength at  $2860$  and  $2928\text{ cm}^{-1}$ . At the spectrum of the graft cooligomer fractions, the band of the unreacted CHO group was observed at  $1637$  and  $1647\text{ cm}^{-1}$ . This band was observed in good strength at  $1654\text{ cm}^{-1}$  at the spectrum of OSA. The vibration band of the aromatic CH groups was observed at  $3060\text{ cm}^{-1}$  (Fig. 3).

Chromatographic curves, UV-Vis, and FTIR spectral analyses of the newly synthesized cooligomer proved that the product of polycondensation reaction between the CHO group of OSA with NH end groups of OA have a structure like oligosalicylaldehyde-graft-oligoaniline (Scheme 4). To identify the structures of OSA, OA, and OSA-graft-OA (Scheme 5), the  $^1\text{H-NMR}$  spectra were recorded in  $\text{DMSO-d}_6$ . The  $^1\text{H-NMR}$  assignments are also given in Table III. The FTIR spectral data of the OSA, OA, and OSA-graft-OA oligomers confirm the results of the  $^1\text{H-NMR}$  spectra.

Table III The <sup>1</sup>H-NMR Spectral Data of the OSA, OA, and OSA-graft-OA-I and II (DMSO; δ, ppm; Me<sub>4</sub>Si as Internal Standard)

Compound	OH	CHO	NH <sub>2</sub>	NH	CH=N	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>	H <sub>ec'ad'</sub>	H <sub>ec'ff'</sub>
OSA	4.24 (s, 1H)	10.05 (s, 1H)	—	—	—	7.15 (s, 1H)	8.26 (s, 1H)	—	—	—	—
OA	—	—	5.45 (s, 2H)	6.05 (s, 1H)	—	—	—	6.90 (d, 2H)	7.20 (d, 2H)	—	6.94–7.30 (m, 4H)
OSA-graft-OA-I	13.2 (s, 1H)	—	—	6.20 (s, 1H)	8.90 (s, 1H)	7.00 (s, 1H)	7.66 (s, 1H)	—	—	7.42–7.48 (m, 4H)	7.00–7.40 (m, 4H)
OSA-graft-OA-II	13.2 (s, 1H)	—	—	6.20 (s, 1H)	8.90 (s, 1H)	7.00 (s, 1H)	7.66 (s, 1H)	—	—	7.42–7.48 (m, 4H)	7.00–7.40 (m, 4H)

### Thermal Analyses of OSA-graft-OA Oligomers and Beginning Oligomers

The thermal degradations of the new graft cooligomer and beginning oligomers were studied by TG analyses at the air medium. The results of these analyses are given in Table IV and Figure 4. The thermo-oxidative degradation of OSA was formed in two steps (Fig. 4).

The first step was started at 115°C, and OSA lost 5% of weight at 190°C. Thermal degradation was obtained at a weak speed at 287°C (0.43 mg/min). The total weight loss was 11.5% at the first step of thermo-oxidative degradation (at 115–287°C). At the first step, the reason for the relatively high thermal resistance demonstration of OSA might be due to molecular weight. The second step was started at 287°C, and OSA was degraded with a high speed (1.45 mg/min) at 500°C. Half of the oligomer weight was lost at 435°C. Mainly more weak groups such as OH and CHO of OSA were brought into at the violent degradation period.

This time is interesting, together with a break in graftification and formation of the three-dimensional structure belonging to the aromatic conjugate bonding orderly macromolecules in OSA macromolecules.<sup>11</sup> For this reason, OSA had been formed to 27% carbene residue at 1000°C. OA demonstrated more thermal resistance than OSA. The thermo-oxidative degradation of OA was formed in two steps. The thermo-oxidative degradation of OA started at 150°C and OA lost 5% of weight at 208°C. In the first step, degradation of OA (1.9 mg/min) proceeded with a higher speed than OSA. But, in the second step total weight loss was 14% at 238°C. In this step di- and trimers of OA were broken, and the fraction started to vaporize. In the second step (238–500°C), the degradation of OA proceeded with a lower speed than the first step.

The half degradation temperature ( $T_{50\%}$ , at 856°C) of OA had very high values, and the carbene residue of OA was 40% at 1000°C. This result showed that OA chains have high thermic resistance. It had a structure formed from phenylimin units and was inclined to have a higher aromatization and graftification at the thermo-oxidative degradation process.

The thermo-oxidative degradation of the first fraction of the graft cooligomer (OSA-graft-OA)-I proceeded at the three step, which is different from the tested oligomers. (OSA-graft-OA)-I started degradation at 125°C and lost 5% of its

**Table IV** The Some Parameters of Thermo-oxidative Degradation of OSA, OA, and OSA-graft-OA-I, II at the Air Medium (at a Heating Rate 5°C/min)

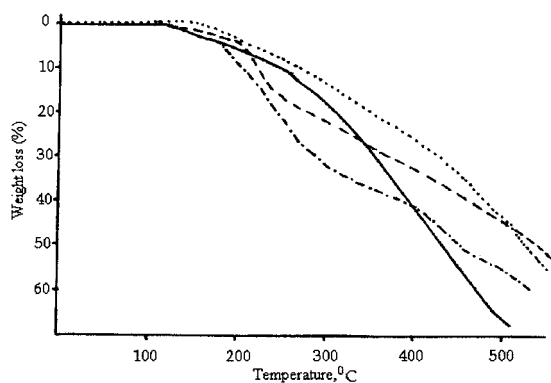
Oligomers	$T_{5\%}$	$T_{50\%}$	First Step			Second Step			Third Step			$\Delta m, \% 1000^\circ\text{C}$
			$T, ^\circ\text{C}$	$W_{\max}$ mg/min	$\Delta m, \%$	$T, ^\circ\text{C}$	$W_{\max}$ mg/min	$\Delta m, \%$	$T, ^\circ\text{C}$	$W_{\max}$ mg/min	$\Delta m, \%$	
OSA	190	435	115–287	0.43	15	287–500	1.45	51	—	—	—	73
OA	208	856	150–238	1.90	14	238–500	0.55	30	—	—	—	60
OSA-graft-OA-I	175	450	125–287	1.30	30	287–410	0.50	12.5	410–500	1.25	20.5	77
OSA-graft-OA-II	211	690	150–425	0.50	29	425–500	0.95	12.5	—	—	—	60

$W_{\max}$ : maxima weight loss (mg/min),  $\Delta m$ : Total weight loss (%).  $T_{5\%}$ : Temperature to be of 5% weight loss,  $T_{50\%}$ : Temperature to be of 50% weight loss.

weight at 175°C, and at the end of the first step (287°C) weight loss was 30%. In this step, small molecular weight cooligomers and their functional groups were broken. In the second step, because of low breaking speed of the graft-oligomer (0.5 mg/min), its weight loss was 12.5% at 410°C. In the first step, thermic resistance of the graft cooligomer rises. It is possible to explain formation of a more stationary three-dimensional macromolecular structure to add to radical active center formation from oxidation of the NH and OH groups. As a result, in the third step, breaking speed (410–500°C) of (OSA-graft-OA)-I was raised to 1.25 mg/min values. Half of the weight of (OSA-graft-OA)-I was lost at 450°C, and formed 23% carbene residue at 1000°C.

The high molecular weight (OSA-graft-OA)-II was demonstrated to be resistant to a higher temperature than OSA. According to these properties, (OSA-graft-OA)-II was very close to OSA. (OSA-graft-OA)-II started degradation at 150°C,

and its weight loss was very low at 0.5 mg/min and a constant speed at 425°C. In the first step, total weight loss of (OSA-graft-OA)-II was 29%. In the second step (at 425°C) thermo-oxidative degradation speed of (OSA-graft-OA)-II raised to approximately two times (0.95 mg/min). Half of the breaking temperature of (OSA-graft-OA)-II was 690°C, and carbene residue was at very high values such as 40%. The reason for high thermal resistance exhibited by (OSA-graft-OA)-II may be explained by its thermo-oxidative breaking process of the graft cooligomer. It had high molecular weight and richer oligophenylimin chains, and had a high inclination for graftification and formation of the network structure. Because of some properties of (OSA-graft-OA)-I and II such as high temperature resistance, polyfunction, and chemical activity, they may be used for thermostabilizers, inhibitors, antistatic dopants and composite components, and epoxy resins and complex formation.



**Figure 4** TGA curves of (---) OA, (—) OSA, (- · - · - · -) OSA-graft-OA-I, and (· · · ·) OSA-graft-OA-II (at air medium, at a heating rate of 5°C/min).

## CONCLUSION

First, we synthesized a conjugate bonding cooligoanilineazomethinphenol that is an orderly graft cooligomer containing three functional groups by using mol · units of OSA ( $M_n$ : 3700 g mol<sup>-1</sup>,  $M_w$ : 5990 g mol<sup>-1</sup>) and OA ( $M_n$ : 740 g mol<sup>-1</sup>,  $M_w$ : 780 g mol<sup>-1</sup>). It was separated into two fractions at the point of solubility in ethanol (OSA-graft-OA)-I and toluene (OSA-graft-OA)-II. Both graft-cooligomer and OSA and OA have been made by analyses such as melting temperatures, solubility, and colored in various solvents, average molecular weight. The  $M_n$  and  $M_w$  values of (OSA-graft-OA)-I and II were found to be 990 g mol<sup>-1</sup> and



1300 g mol<sup>-1</sup>; 2770 g mol<sup>-1</sup> and 4100 g mol<sup>-1</sup>, respectively. To be different from the beginning oligomers with this property, the new synthesized matter was demonstrated to be a cooligomer.

According to <sup>1</sup>H-NMR, FTIR and UV-Vis spectral analyses, the product has been determined to have a structure of side oligophenylimin chains bonded by bridge azomethine to long oligophenol macromolecules of a graft cooligomer enduring defined reaction between aldehyde with aromatic amine groups.

According to TG analyses, despite the difference of molecular weight of (OSA-graft-OA)-I and II, the first fraction, (OSA-graft-OA)-I, and second fraction, (OSA-graft-OA)-II, have demonstrated resistance to temperature close to OSA and OA, respectively. *T*<sub>50%</sub> weight loss values of (OSA-graft-OA)-I and II were determined to be 450 and 690°C, respectively, and carbine residues of them were found to be 23 and 40%, respectively.

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