Synthesis, Characterization, and Thermal Stability of Azomethine Oligomer and Its Metal Complexes

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ABSTRACT: The oxidative polycondensation reaction conditions of N,N'-bis[[(2-hydroxy-1-naphthyl)methylene]urea (2-HNMU) has been accomplished using NaOCl, H_2O_2, and air O_2 oxidants in an aqueous alkaline medium. The structures of the obtained monomer and oligomer were confirmed by FTIR, UV–vis, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The characterization was made by TG-DTA, size exclusion chromatography (SEC), and solubility tests. At the optimum reaction conditions, the yield of oligo-N,N'-bis[[(2-hydroxy-1-naphthyl)methylene]urea (O-2-HNMU) was found to be 95% (for air O_2 oxidant), 51% (for H_2O_2 oxidant), 96% (for NaOCl oxidant). According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index values of O-2-HNMU was found to be 1036, 1225 g/mol, and 1.182, respectively, using H_2O_2, and 765, 1080 g/mol, and 1.412, respectively, using air O_2, and 857, 1105 g/mol, and 1.289, respectively, using NaOCl. TG-DTA analyses showed that O-2-HNMU was more stable than 2-HNMU. According to TG analyses, the carbonaceous residue of 2-HNMU and O-2-HNMU was found to be 0.49% and 2.11% at 1000°C, respectively. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1356–1365, 2007

Key words: air O_2; H_2O_2; NaOCl; oligo-N,N'-bis[[(2-hydroxy-1-naphthyl)methylene]urea; oxidative polycondensation; thermal analysis

INTRODUCTION

Polymers containing metals have emerged as a new generation of material, with tremendous potential in fields like superconducting materials, ultrahigh-strength materials, liquid crystals, catalysts, and biocompatible polymers.[1–6] The structures of some polymer–metal ion complexes have been reported in the literature.[1,7–10] Also, polymer–metal complex compounds have useful properties such as thermal stability, ion selectivity, conductivity, and antimicrobial properties. Catalytic activity of styrene–allylchloride copolymer supported cobalt(II) Schiff base complex compound was studied by Gupta et al.[11] Conductivity properties of Cu(II) and Ni(II) complex compounds of poly(2-hydroxy-4-methacryloyloxybenzophenone) were studied by Kaliyappan et al.[12] Antimicrobial properties of oligophenols with Schiff base substitute and their oligomer–metal complex compounds were investigated by Kaya et al.[13,14] Thermal properties of polymer–metal complex compounds were investigated by Gad et al.,[15] Sebastian et al.,[16] Kaya and Gül,[17] and Thamizharasi et al.[18] More functional oligophenols may be used for the cleaning of poisonous heavy metals in the industrial waste waters. Also, Schiff base compounds had been used for the determination of transition metals in some natural food samples.[19] Therefore, the syntheses of these types of oligomer and oligomer–metal complexes are very important for analytical, environmental, and food chemistry. There are some significant advantages of this method because of using oxidants such as NaOCl, H_2O_2, and air O_2. For example, these types of oxidants are cheap and easy to provide. Phenols and Schiff base substitute phenols were easily polymerized using these oxidants.[8]

In this article, we have investigated the effects of different parameters such as temperature, times, and initial concentrations of NaOCl, H_2O_2 oxidants, and alkaline for the synthesis of oligo-N,N'-bis[[(2-hydroxy-1-naphthyl)methylene]urea (O-2-HNMU) in the alkaline medium. The structures of 2-HNMU and O-2-HNMU were confirmed by FTIR, UV–vis, ^{1}H NMR, ^{13}C NMR, elemental analysis, TG-DTA, and size exclusion chromatography (SEC) techniques. Also, O-2-HNMU-Cd, O-2-HNMU-Co, O-2-HNMU-Mn, O-2-HNMU-Ni, and O-2-HNMU-Cu were characterized by FTIR, elemental analysis, and TG-DTA techniques.

MATERIALS AND METHODS

Materials

Urea, 2-hydroxy-1-naphtaldehyde, methanol, ethanol, benzene, toluene, acetone, ethyl acetate, hexane,
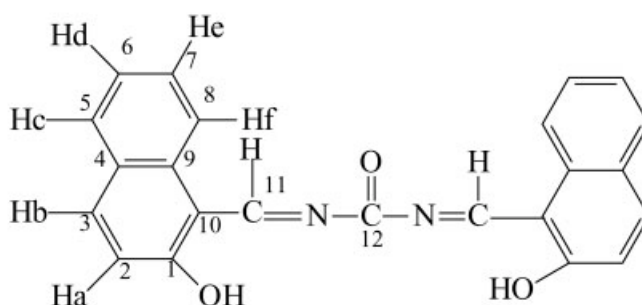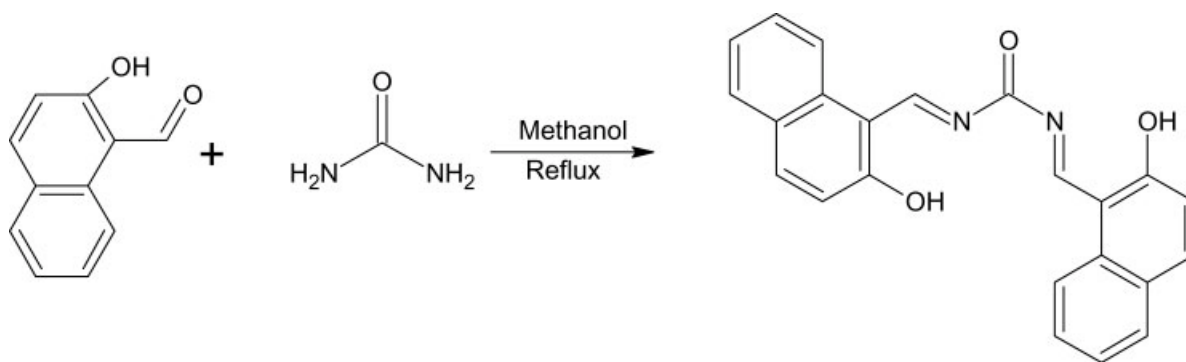
Scheme 1 Synthesis of N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.

CH_2Cl_2, CCl_4, $CHCl_3$, THF, DMF, DMSO, H_2SO_4 (98%), NaOH, KOH, H_2O_2 (30% aqueous solution), Co $(AcO)_2 \cdot 4H_2O$, Ni $(AcO)_2 \cdot 4H_2O$, Cu $(AcO)_2 \cdot 4H_2O$, $MnSO_4 \cdot H_2O$, Cd $(AcO)_2 \cdot 2H_2O$, and hydrochloric acid (HCl, 37%) were supplied from Merck Chemical (Germany) and they were used as received. Sodium hypochloride (NaOCl) (30% aqueous solution) was supplied from Paksoy Chemical (Turkey). 2-HNMU was synthesized by condensation reaction of 2-hydroxy-1-naphtaldehyde with urea and recrystallized in methanol.

Preparation of 2-HNMU

Urea (0.60 g, 0.01 mol) was dissolved in ethanol (25 mL) and then 2-hydroxy-1-naphtaldehyde (3.44 g,

0.02 mol) was added to this solution. The resulting mixture was refluxed and stirred at 70°C for 3 h (Scheme 1). The reaction mixture was cooled to room temperature and washed with cool ethanol. The product was recrystallized from methanol to give Schiff base 2-HNMU in 92% yield as yellow crystalline solid.

UV–vis (λ_{max}): 218, 236, 252, 316, 354 nm. ^{1}H NMR (DMSO): δ ppm, 12.10 (s, 1H, OH), 10.80 (s, 1H, —CH=N—), 7.24 (d, 1H, Ar-Ha), 8.15 (d, 1H, Ar-Hb), 7.90 (d, 1H, Ar-Hc), 7.43 (t, 1H, Ar-Hd), 7.62 (t, 1H, Ar-He), 8.95 (d, 1H, Ar-Hf). ^{13}C NMR (DMSO): ppm, 160.00 (C1-ipso-OH), 119.21 (C2-H), 132.81 (C3-H), 129.76 (C4-ipso), 129.30 (C5-H), 122.64 (C6-H), 128.04 (C7-H), 124.70 (C8-H), 138.87 (C9-ipso), 112.91 (C10-ipso), 164.34 (C11-H), 193.32 (C12-ipso).
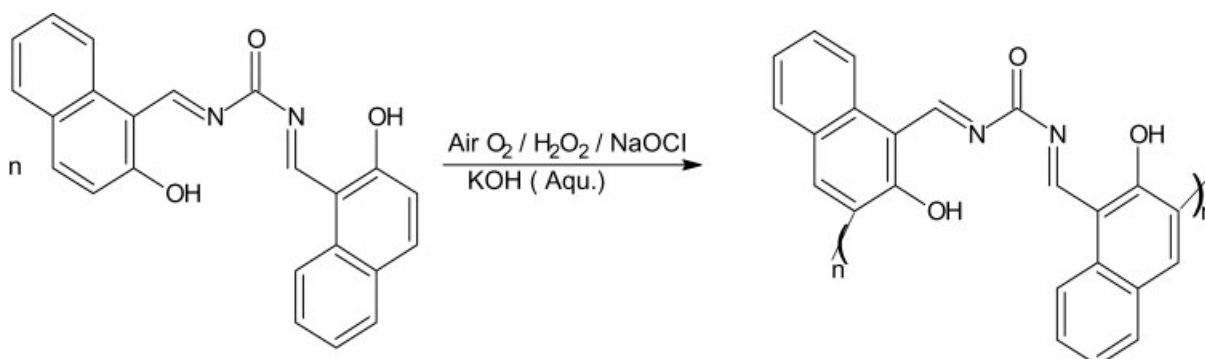
Scheme 2 Synthesis of oligo-N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.

TABLE I
The Oxidative Polycondensation Reaction Parameters of
N,N'-bis[(2-Hydroxy-1-naphthyl)methylene]urea[a] with
NaOCl in Aqueous KOH

Sample no.	$[KOH]_0$ (mol/L)	$[NaOCl]_0$ (mol/L)	Temp (°C)	Times (h)	Yield of O-2-HNMU (%)
1	0.1	0.1	50	3	73
2	0.1	0.1	60	3	81
3	0.1	0.1	70	3	76
4	0.1	0.1	80	3	63
5	0.1	0.1	90	3	60
6	0.1	0.1	60	5	94
7	0.1	0.1	60	10	95
8	0.1	0.1	60	15	92
9	0.1	0.1	60	25	90
10	0.2	0.1	50	3	44
11	0.2	0.1	60	3	50
12	0.2	0.1	70	3	52
13	0.2	0.1	80	3	47
14	0.2	0.1	90	3	40
15	0.2	0.1	70	5	58
16	0.2	0.1	70	10	61
17	0.2	0.1	70	15	60
18	0.2	0.1	60	25	60
19	0.1	0.2	50	3	86
20	0.1	0.2	60	3	87
21	0.1	0.2	70	3	91
22	0.1	0.2	80	3	87
23	0.1	0.2	90	3	80
24	0.1	0.2	70	5	94
25	0.1	0.2	70	10	96
26	0.1	0.2	70	25	89

[a] The initial concentration of 2-HNMU used was 0.1 mol/L.

TABLE II
The Oxidative Polycondensation Reaction Parameters of
N,N'-bis[(2-Hydroxy-1-naphthyl)methylene]urea[a] with
Air O_2 in Aqueous KOH

| Sample no.	$[KOH]_0$ (mol/L)	Air O_2 (L/h)	Temp (°C)	Times (h)	Yield of O-2-HNMU (%)
1	0.1	8.5	30	3	78
2	0.1	8.5	40	3	84
3	0.1	8.5	50	3	91
4	0.1	8.5	60	3	95
5	0.1	8.5	70	3	90
6	0.1	8.5	80	3	84
7	0.1	8.5	90	3	81
8	0.1	8.5	60	1	90
9	0.1	8.5	60	5	87
10	0.1	8.5	60	10	81
11	0.1	8.5	60	15	80
12	0.1	8.5	60	25	79

[a] The initial concentration of 2-HNMU used was 0.1 mol/L.

UV-vis (λ_{max}): 220, 236, 252, 318, 360 nm. ^{1}H NMR
(DMSO): δ ppm, 12.00 (s, 1H, OH); 10.84 (s, 1H,
—CH=N—); 7.24 (d, 1H, end group Ar-Ha), 8.13 (d,
1H, Ar-Hb), 7.89 (d, 1H, Ar-Hc), 7.45 (t, 1H, Ar-Hd),
7.65 (t, 1H, Ar-He), 8.92 (d, 1H, Ar-Hf). ^{13}C NMR
(DMSO): ppm, 163.08 (C1-ipso-OH), 119.21 (C2-H),
128.05 (C3-H), 132.17 (C4-ipso), 129.77 (C5-H), 122.65
(C6-H), 129.30 (C7-H), 124.71 (C8-H), 138.89 (C9-
ipso), 112.92 (C10-ipso), 164.40 (C11-H), 193.33 (C12-
ipso), 127.08 (C2-ipso) (new peak of C—C coupling
system).

Synthesis of O-2-HNMU with NaOCl, air O_2, and H_2O_2 in aqueous alkaline medium

O-2-HNMU was synthesized through oxidative poly-
condensation of 2-HNMU with solution of NaOCl
(30%, in water), air O_2 and H_2O_2 (30%, in water) oxi-
dants, respectively (Scheme 2).[13] The 2-HNMU (3.68 g,
0.01 mol) was dissolved in an aqueous solution of
KOH (10%, 0.01 mol) and placed into a 50-mL three-
necked round-bottom flask. It was fitted with a con-
denser, thermometer, and stirrer and, in addition, a
funnel containing NaOCl or H_2O_2. After heating to
room temperature, NaOCl and H_2O_2 were added
drop by drop over about 30 min. The reaction mix-
tures were stirred at various temperatures and dura-
tions (Tables I–III). Air O_2 passed into an aqueous
solution of KOH (20%) before being sent through the
reaction tube to prevent water loss in the reaction
mixture and the neutralizing of CO_2 in the air to
KOH (Scheme 2). The mixture was neutralized with
0.01 mol of HCl (37%) at room temperature.
Unreacted monomer was separated from the reaction
products by washing with ethyl acetate. The mixture
was filtered and washed with hot water (3 × 25 mL)
for separating from mineral salts and then dried in
the oven at 110°C.

TABLE III
The Oxidative Polycondensation Reaction Parameters of
N,N'-bis[(2-Hydroxy-1-naphthyl)methylene]urea[a]
with H_2O_2 in Aqueous KOH

Sample no.	$[KOH]_0$ (mol/L)	$[H_2O_2]_0$ (mol/L)	Temp (°C)	Times (h)	Yield of O-2-HNMU (%)
1	0.1	0.1	50	3	36
2	0.1	0.1	60	3	41
3	0.1	0.1	70	3	44
4	0.1	0.1	80	3	45
5	0.1	0.1	90	3	43
6	0.1	0.1	80	5	48
7	0.1	0.1	80	10	50
8	0.1	0.1	80	15	50
9	0.1	0.1	80	25	48
10	0.2	0.1	50	3	31
11	0.2	0.1	60	3	39
12	0.2	0.1	70	3	40
13	0.2	0.1	80	3	44
14	0.2	0.1	90	3	33
15	0.2	0.1	80	5	51
16	0.2	0.1	80	10	49
17	0.2	0.1	80	15	41
18	0.2	0.1	80	25	33

[a] The initial concentration of 2-HNMU used was
0.1 mol/L.
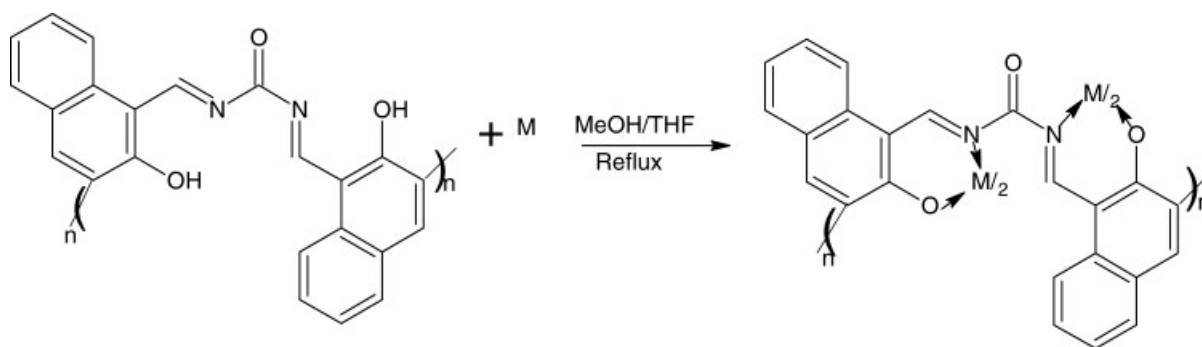
Scheme 3 Synthesis of oligo-*N,N'-bis*[(2-hydroxy-1-naphthyl)methylene]urea-metal complex compounds.

Synthesis of O-2-HNMU metal complexes

Solutions of Co (AcO)$_2$·4H$_2$O, Ni (AcO)$_2$·4H$_2$O, Cu (AcO)$_2$·4H$_2$O, MnSO$_4$·H$_2$O, and Cd (AcO)$_2$·2H$_2$O (1 mmol) in MeOH (10 mL) were added to a solution of O-2-HNMU (2 mmol/unit) in THF (20 mL). The mixture was stirred and heated at 70°C for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold MeOH/THF (1 : 1), and then dried in vacuum oven.

Solubility and characterization techniques

O-2-HNMU was dark brown in powder form and it was completely soluble in organic solvents such as DMF, THF, DMSO, methanol, and ethanol. O-2-HNMU was insoluble in hexane, benzene, toluene, ethyl acetate, CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$, and acetone. O-2-HNMU-Cd, O-2-HNMU-Co, O-2-HNMU-Cu, O-2-HNMU-Mn, and O-2-HNMU-Ni oligomer–metal complex compounds were insoluble in hexane, benzene, toluene, ethyl acetate, CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$, and acetone. These oligomer–metal complex compounds were partly soluble in DMSO and DMF.

The infrared and ultraviolet–visible spectra were measured by Perkin–Elmer FT-IR BX II and Perkin–Elmer Lamda 25, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FTIR spectra were recorded using KBr disc (4000–350 cm^{-1}).

UV–vis spectra of 2-HNMU and O-2-HNMU were determined using methanol and DMSO, respectively. 2-HNMU and O-2-HNMU were characterized by ^{1}H NMR and ^{13}C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded using deuterated DMSO-d_6 as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by a Perkin–Elmer Diamond Thermal Analysis system. The TG-DTA measurements were made between 15 and 1000°C (in N$_2$, rate 10°C/min). The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were determined by SEC techniques of Shimadzu. For SEC investigations, SGX (100 Å and 7-nm-diameter loading material) 3.3 mm i.d. × 300 mm columns, eluent: DMF (0.4 mL/min), and polystyrene standards were used. A refractive index detector was used to analyze the product at 25°C.

RESULTS AND DISCUSSION

Synthesis of O-2-HNMU

The optimum reaction conditions of 2-HNMU were investigated in aqueous alkaline medium using air oxygen, H$_2$O$_2$, and NaOCl oxidants. When 2-HNMU interacted with these oxidants in the alkaline medium, brown phenoxy radicals immediately precipi-

TABLE IV
The Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), Polydispersity Index (PDI) and % Values of Oxidative Polycondensation Products of O-2-HNMU

| | Molecular weight distribution parameters | | | | | | | | | | | | | | | |
| | Total | | | Fraction I | | | | Fraction II | | | | Fraction III | | | |
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
O-2-HNMU[a]	765	1080	1.412	1418	1628	1.148	9	1580	2120	1.343	86	16,154	18,195	1.126	5
O-2-HNMU[b]	857	1105	1.289	1674	1894	1.132	16	1720	2190	1.272	79	18,909	20,602	1.090	5
O-2-HNMU[c]	1036	1225	1.182	1560	2030	1.304	64	1698	1991	1.172	26	16,831	18,449	1.096	10

[a] Air O$_2$ oxidant.
[b] NaOCl oxidant.
[c] H$_2$O$_2$ oxidant.

TABLE V
Elemental Analyses Data and Yields of 2-HNMU, O-2-HNMU,
and Oligomer–Metal Complexes

Compounds	Calculated[a] (%)					Yield (%)
	C	H	N	Metal	μ_{eff}	
2-HNMU	75.00 (74.85)[b]	4.35 (4.18)	7.56 (7.45)	–	–	92
O-2-HNMU	75.41 (74.85)	3.83 (3.95)	7.65 (7.25)	–	–	96
O-2-HNMU-Cu	56.20 (55.40)	2.44 (2.55)	5.70 (5.45)	25.88 (22.00)	1.95	84
O-2-HNMU-Ni	57.34 (57.05)	2.49 (2.60)	5.82 (5.69)	24.38 (23.20)	3.50	82
O-2-HNMU-Co	57.28 (57.02)	2.49 (2.55)	5.81 (5.70)	24.46 (24.25)	5.40	89
O-2-HNMU-Cd	46.80 (46.43)	2.04 (1.96)	4.76 (4.65)	38.18 (34.65)	Diamag.	71
O-2-HNMU-Mn	58.24 (58.00)	2.53 (2.65)	5.91 (5.78)	23.19 (32.78)	5.41	64

[a] The theoretical calculations were made according to one unit of oligomer.
[b] Values within parentheses indicate the found values (in %).

tated in the solution medium. The oxidative poly-condensation reaction conditions of 2-HNMU with 30% NaOCl solution in aqueous alkaline medium are given in Table I. The yield of O-2-HNMU was 96% for NaOCl oxidant for 10 h at 70°C. It is seen that in Table I the yield of oligomer decreased in increasing of temperature, reaction times, and initial concentration of alkaline. At the same conditions, when molar amount of NaOCl oxidant increased in two coating, total yield of O-2-HNMU changed from 86 to 73%. The yield of O-2-HNMU was 94% at conditions such as $[2\text{-HNMU}]_0 = [KOH]_0 = 0.1$ and $[NaOCl]_0 = 0.2$ mol/L, at 70°C for 5 h.

The oxidative polycondensation reaction conditions of 2-HNMU with air O_2 solution in aqueous alkaline medium are given in Table II. At the oxidative polycondensation reaction of 2-HNMU, when air oxygen passed at 8.5 L/h rate into the reaction medium, at 60°C for 3 h, the yield of oligomer was 95%. The yield of O-2-HNMU was 79% at the reaction conditions such as $[2\text{-HNMU}]_0 = [KOH]_0 = 0.1$ mol/L and air O_2 (flow rate = 8.5 L/h), at 60°C for 25 h. At the same conditions, when temperatures and reaction times increased, total yield of O-2-HNMU decreased. When reaction temperatures increased from 30 to 90°C, the yield changed from 78 to 81%, respectively.

The oxidative polycondensation reaction conditions of 2-HNMU with 30% H_2O_2 solution in aqueous alkaline medium are given in Table III. The yield of O-2-HNMU was 51% at optimum conditions such as $[2\text{-HNMU}]_0 = [H_2O_2]_0 = 0.1$ mol/L and $[KOH]_0 = 0.2$ mol/L, at 80°C for 5 h. The yield of O-2-HNMU was 33% at the reaction conditions such as $[2\text{-HNMU}]_0 = [H_2O_2]_0 = 0.1$ mol/L and $[KOH]_0 = 0.2$ mol/L, at 80°C for 25 h. According to these values, high reaction times have not affected the yield of oligomer. As is seen from Tables I–III, the yields of these reactions were dependent upon temperature, reaction times, and initial concentrations of oxidants and alkaline. NaOCl and air O_2 were better oxidants than H_2O_2 at the same conditions for the yield of O-2-HNMU.

Structure of O-2-HNMU

According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of O-2-HNMU were calculated according to a polystyrene standard calibration curve and are given in Table IV.

The UV–vis spectra of 2-HNMU and O-2-HNMU were similar. However, at the spectra of 2-HNMU, K bands of phenol and C_6H_5—N= were observed at

TABLE VI
**FTIR Spectral Data of 2-HNMU, O-2-HNMU, and Oligomer–Metal Complexes**

Compounds	Wave number (cm^{-1})						
	—OH	—CH=N	—C=C	C=O	—C—O	Metal-O	Metal-N
2-HNMU	3335	1620	1589, 1520, 1464	1675	1312	–	–
O-2-HNMU	3305	1628	1595, 1512, 1465	1694	1315	–	–
O-2-HNMU-Cu	3400	1617	1602, 1584, 1538	1678	1186	520	585
O-2-HNMU-Ni	3310	1636	1609, 1591, 1540	1685	1187	560	658
O-2-HNMU-Co	3299	1634	1608, 1590, 1538	1680	1182	554	657
O-2-HNMU-Mn	3355	1636	1586, –, –	1689	1294	562	604
O-2-HNMU-Cd	3318	1613	1578, 1536, –	1690	1095	552	655
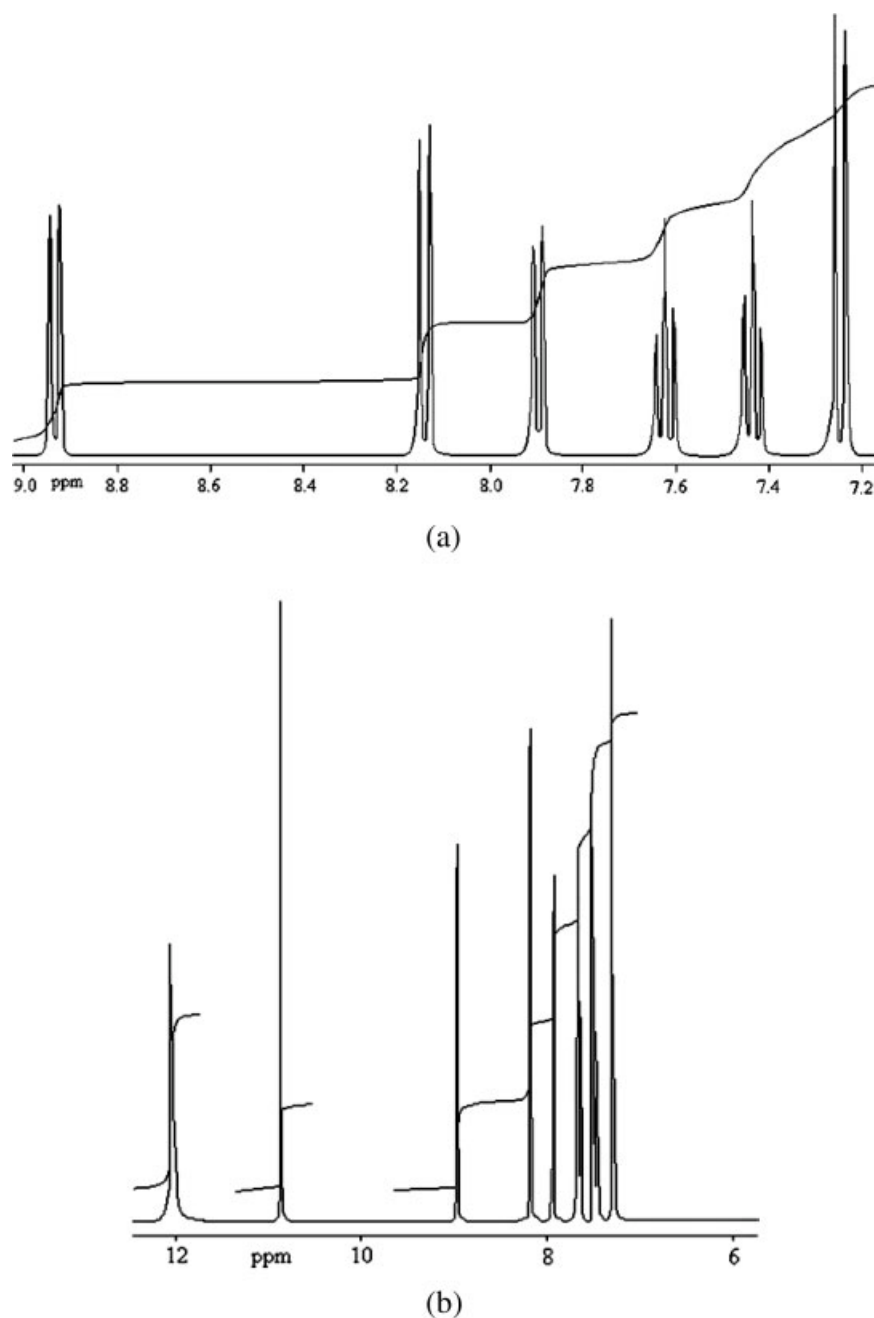
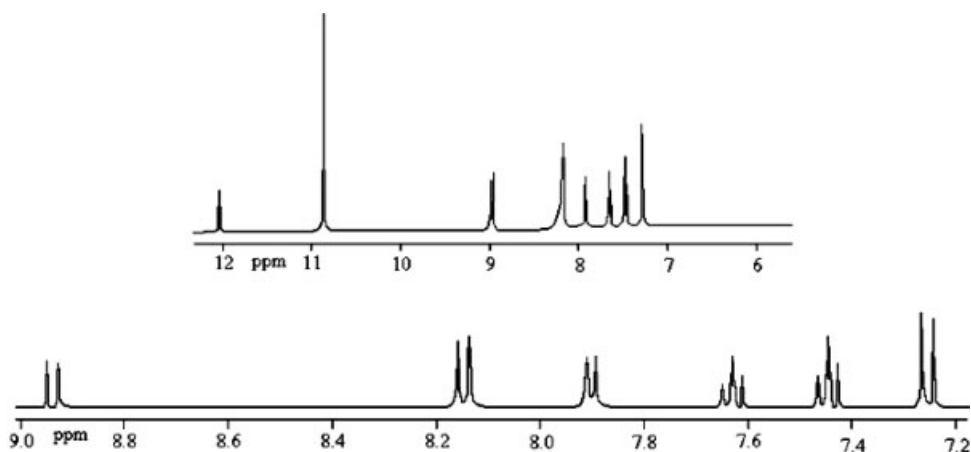**Figure 1** ^{1}H NMR spectrum of N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.

218 and 236 nm, respectively. Benzene band of 2-HNMU and strength R band of —CH=N— groups were observed at 252 and 354 nm, respectively. λ_{max} values of O-2-HNMU were observed in 220, 236, 252, 318, and 360 nm. At the UV–vis spectra of O-2-HNMU, K and R bands were observed at 236 and 360 nm, respectively. At the FTIR spectra of 2-HNMU and O-2-HNMU, bands of —OH and —CH=N groups were observed at 3335 and 1620 cm^{-1} and 3305 and 1628 cm^{-1}, respectively. The band of —CH=N groups of monomer and oligomer shifted from 1620 to 1628 cm^{-1}, respectively, forma-

tion of oligomeric units demonstrated at the structure of 2-HNMU. The peak strength of —OH group of oligomer was higher than that of monomer. The
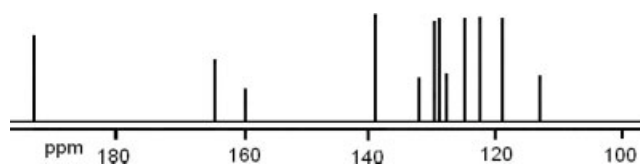
Figure 2 ^{13}C NMR spectrum of N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.

Figure 3 ^{1}H NMR spectrum of oligo-N,N′-bis[(2-hydroxy-1-naphthyl)methylene]urea.

stretching frequency was observed at 2743 and 2748 cm^{-1} for monomer and oligomer, respectively. These values show the presence of OH···N intramolecular hydrogen bond. Elemental analyses and FTIR data of monomer, oligomer, and oligomer–metal complex compounds are given in Tables V and VI, respectively. The bands of —OH and —CH=N groups were observed between 3400 and 3299 cm^{-1} and 1636 and 1613 cm^{-1}, respectively, at the FTIR spectra of oligomer–metal complex compounds.

The magnetic susceptibility measurement of 1.95 BM is an indicative of the appearance of the copper complex in a square planar geometry.[20] Magnetic moment values were 3.50 and 5.40 BM for Ni(II) and Co(II) complexes, respectively, which show consistent hexacoordinate configuration.[21] Cadmium complex is diamagnetic and is likely to be of tetrahedral structure.[20] Manganese complex has μ$_{eff}$ value 5.41 BM indicates the presence of four unpaired electrons Mn (II). This magnetic moment is in good agreement with Mn(II) in an octahedral configuration.[22] μ$_{eff}$ values of oligomer–metal complex compounds are given in Table V.

Other phenol derivatives were also polymerized, and the results reported in the literatures.[23–25] Crosslinking in polymer structure is expected in those cases where the *ortho* positions in the corresponding monomer structure are unsubstituted. ^{13}C NMR studies on O-2-HNMU indicate that the linkage between any two adjacent 2-hydroxy-1-naphthyl rings is largely at *ortho* positions. ^{1}H NMR and ^{13}C NMR spectra of the 2-HNMU and O-2-HNMU are given in Figures 1–4, respectively. At the ^{1}H NMR spectra of 2-HNMU and O-2-HNMU, the signals of —OH and —CH=N groups were observed at 12.10 and 12.00 ppm, and 10.80 and 10.84 ppm, respectively. According to ^{13}C NMR spectra, the peak values for C1 and C2 were observed at 160.00 and 119.21 ppm in the monomer and 163.08 and 127.08 ppm in the oligomer, respectively. It is seen from Figure 4 that

because of C—C coupling system a new peak is observed at 127.08 ppm. The ^{13}C NMR spectrum of O-2-HNMU has been demonstrated in C—C coupling systems.[24] Monomer and dimer interconversion combinations of radical units are proposed in the literature.[23] The SEC and ^{1}H-NMR and ^{13}C-NMR spectra data results of O-2-HNMU have supported together.

Thermal analysis

The thermal degradations of monomer, oligomer, and oligomer–metal complex compounds were studied by TG-DTA analyses in N$_2$ medium, and the curves and data of these analyses are given in Figures 5–9 and Table VII, respectively. The initial degradation temperature and the temperature after 99.51% weight loss of 2-HNMU were found to be 135 and 1000°C, respectively. The initial degradation temperature and the temperature after 97.89% weight loss of O-2-HNMU were found to be 172 and 1000°C, respectively. This oligomer formed carbines residue in low amount (2.11%) at 1000°C. Because of long conjugated band systems, oligomer demonstrated higher resist against high temperature than monomer. According to TG analysis, O-2-HNMU was more stable than monomer to temperature and thermal decomposition. The high
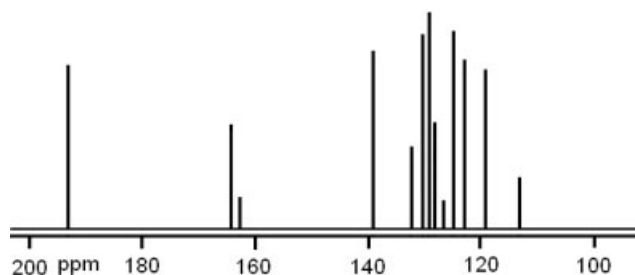
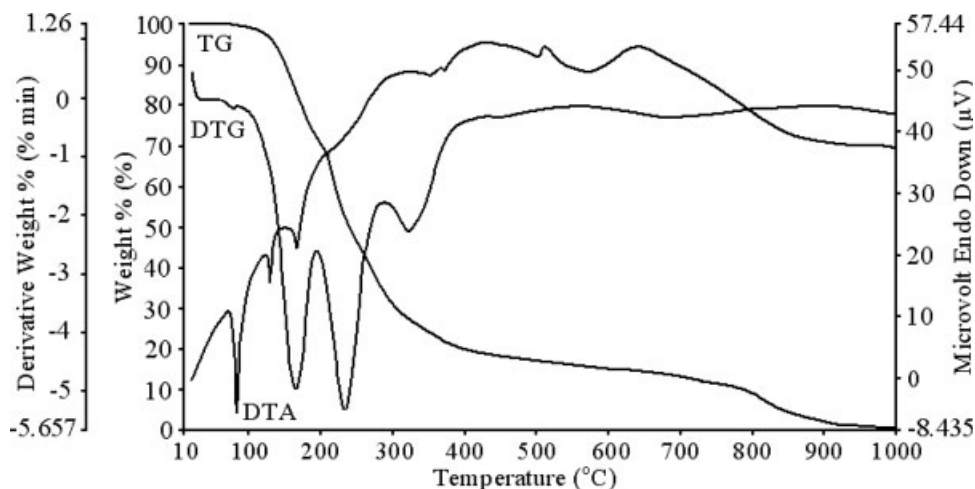**Figure 4** ^{13}C NMR spectrum of oligo-N,N′-bis[(2-hydroxy-1-naphthyl)methylene]urea.

Figure 5 TG-DTG-DTA curves of N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.
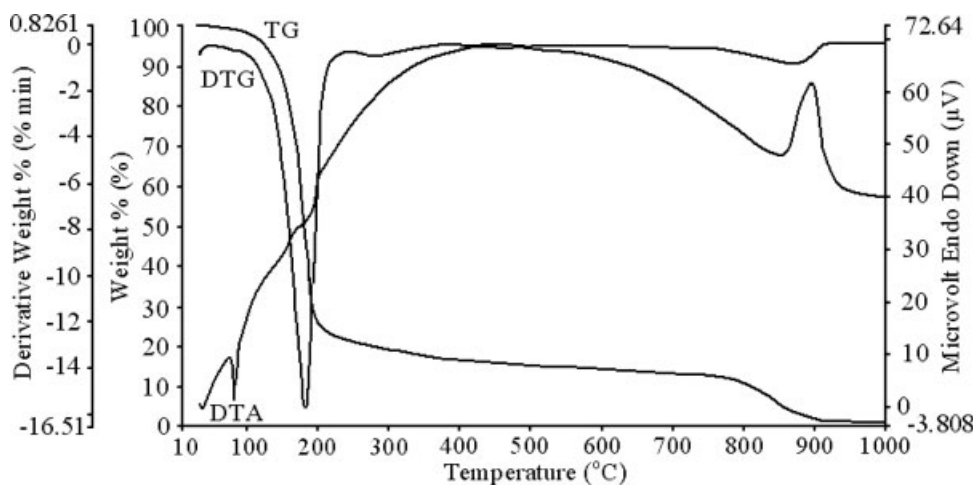

Figure 6 TG-DTG-DTA curves of oligo-N,N'-bis[(2-hydroxy-1-naphthyl)methylene]urea.

thermal stability of O-2-HNMU is demonstrated to be formed by C—C coupling system. O-2-HNMU-Mn compound demonstrated higher thermal stability among oligomer–metal complex compounds. The initial degradation temperature and the temperature after 53.82% weight loss of O-2-HNMU-Mn compound
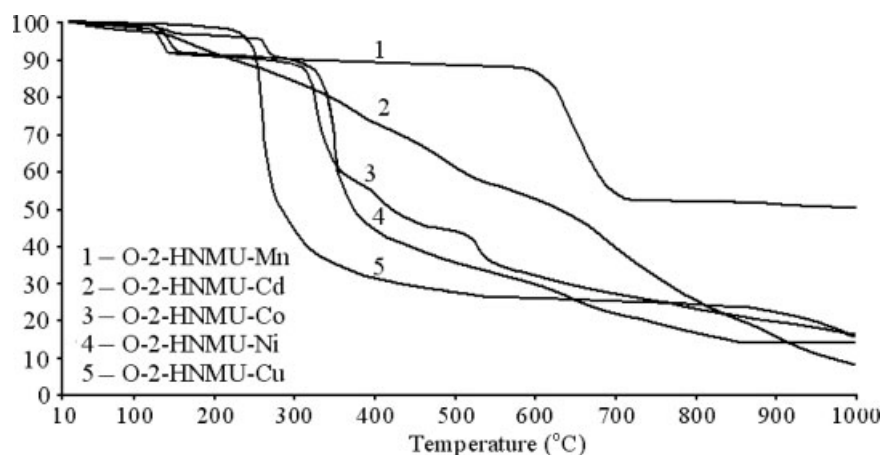

1 — O-2-HNMU-Mn
2 — O-2-HNMU-Cd
3 — O-2-HNMU-Co
4 — O-2-HNMU-Ni
5 — O-2-HNMU-Cu

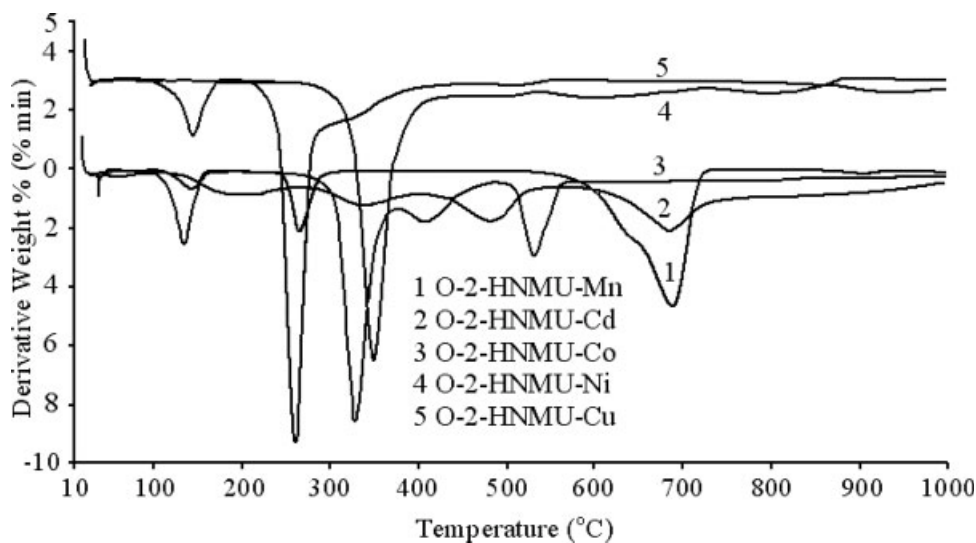**Figure 7** TG curves of O-2-HNMU-metal complex compounds.

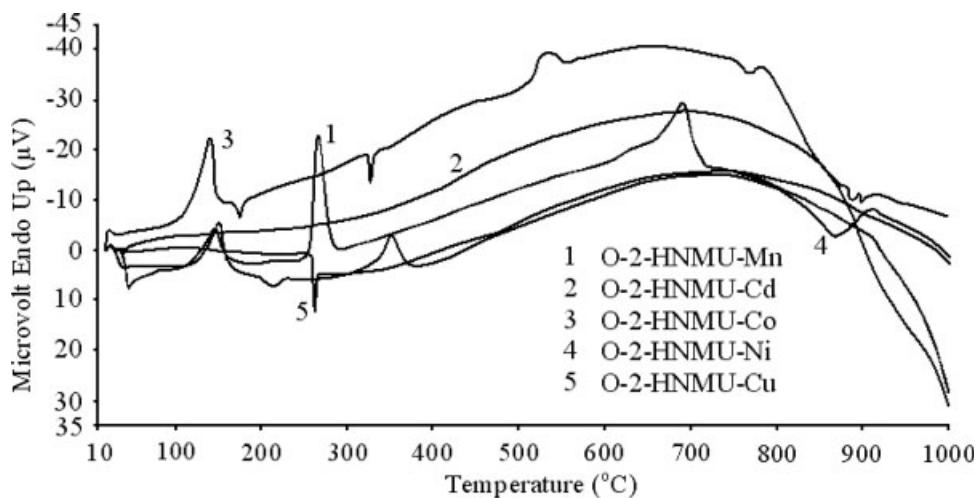**Figure 8** DTG curves of O-2-HNMU-metal complex compounds.

Figure 9 DTA curves of O-2-HNMU-metal complex compounds.

were found to be 257 and 1000°C, respectively. According to TG curves, high thermal stability of oligomer–metal complex compounds may indicate the formation of metal–oxygen valance and metal–nitrogen coordination bond between oligomer–metal ions. The presence of water can be seen in TGA curves of

TABLE VII
Thermal Degradation Values of 2-HNMU, O-2-HNMU, and Oligomer–Metal Complex Compounds

Compounds	$T_{on}{}^{a}$	$W_{max}T^{b}$	20 wt % loss	% Carbines residue at 1000°C	DTA Exo	Endo
2-HNMU	135	168, 232, 317	167	0.49	82, 126, 162, 752	–
O-2-HNMU	172	213	183	2.11	581, 786	–
O-2-HNMU-Cu	254	734	257	15.83	–	263
O-2-HNMU-Ni	332	360	343	23.31	151, 154, 697, 917	216
O-2-HNMU-Co	314	655	325	25.18	140, 534	176, 328
O-2-HNMU-Mn	257	264, 687	645	53.82	146, 268, 692	–
O-2-HNMU-Cd	160	707	365	16.00	–	–

^a The onset temperature.
^b Maximum weight temperature.

[a] The onset temperature.
[b] Maximum weight temperature.

O-2-HNMU-Cd and O-2-HNMU-Mn compounds (Fig. 7), showing between 5 and 3.47 wt % losses in the 50–150°C and 50–190°C range, respectively, and corresponding to the loss of water of crystallization (50–150°C) and coordination water (150–200°C).[25,26]

CONCLUSIONS

O-2-HNMU was synthesized using oxidants such as air oxygen, H_2O_2, and NaOCl in an aqueous alkaline medium. The maximum yield of O-2-HNMU was determined for air O_2 and NaOCl oxidants. The M_n, M_w, and PDI values of O-2-HNMU were found to be 1036, 1225 g/mol, and 1.182, using H_2O_2, and 765, 1080 g/mol, and 1.412, using air O_2, and 857, 1105 g/mol, and 1.289, using NaOCl, respectively. At the oxidative polycondensation reaction of 2-HNMU, H_2O_2 demonstrated less activity than NaOCl and air O_2. The spectral analyses such as FTIR, ^{1}H and ^{13}C NMR have demonstrated to unite from *ortho* of 2-hydroxy-1-naphthyl ring each other of oligomer formation from oxidative polycondensation of 2-HNMU. The carbines residue of this oligomer was in low amount such as 2.11% at 1000°C. According to TG-DTA analyses, 2-HNMU and O-2-HNMU were less stable than oligomer–metal complex compounds against thermal degradation.

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