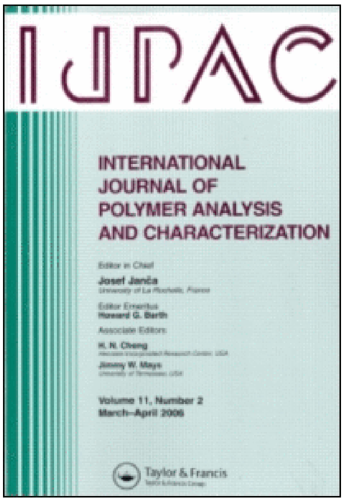

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Coordination Polymers of 1,8-Bis (8-Hydroxyquinolin-5-yl)-2,7-Dioxaoctane

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Coordination polymers of a novel bis(oxine) bidentate ligand, namely 1,8-bis(8-hydroxyquinolin-5-yl)-2,7-dioxaoctane (BQDO) (H_2L), have been prepared with the metal ions Cu(II), Co(II), Ni(II), Mn(II), and Zn(II). The novel bis(bidentate) ligand (H_2L) was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with butylene glycol in the presence of a base catalyst. All of these coordination polymers and the parent ligand were characterized by elemental analyses and IR spectral studies. The diffuse reflectance spectral studies of all of the coordination polymers also were performed. The number-average molecular weights (M_n) of all of the coordination polymers were determined by nonaqueous conductometric titrations. In order to determine thermal stability trend, thermogravimetric parameters, such as T_o (initial decomposition temperature), T_{10} (temperature for 10% weight loss), $T_{max.}$ (temperature of maximum rate of degradation), IPDT (integral procedural decomposition temperature), and the activation energy E_a of the thermodegradation process were calculated. All of the coordination polymers were also characterized by their magnetic susceptibilities.

Keywords: Bis(oxine); BQDO; Coordination polymers; Nonaqueous conductometric titration; IR spectral studies; TGA

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INTRODUCTION

In recent years there have been several reports in the literature on the coordination polymer 8-hydroxyquinoline and its derivatives, owing to their applications in various areas, such as in wastewater treatment for metal recovery and protective coatings, and in view of their biological activity[1–4]. Besides this, Manolova et al.[5] have also reported polymers bearing 8-hydroxyquinoline for their additional potential applications; for example, as water disinfectants, antifouling paints, antimicrobial surgical materials, disinfectants in solutions, and gels and ointments for medicinal uses[6–10]. Further, a promising method has been reported for the formation of coordination polymers of enhanced chelating ability by using a bidentate 8-hydroxyquinoline moiety, in which two 8-hydroxyquinolinyl end groups are joined by a linear aliphatic bridge, usually at the 5,5′-positions[11–13]. In this context, we have recently synthesized and characterized the coordination polymers based on a novel 8-hydroxyquinoline bis(bidentate) ligand containing a dimethylene oxide ($–CH_2–O–CH_2–$) aliphatic bridge[14]. This work has been further extended with a view to explore the chelating ability of an 8-hydroxyquinoline bis(bidentate) ligand by increasing the chain length of the aliphatic bridge between two 8-hydroxyquinoline moieties.

Accordingly, the present article describes the synthesis and characterization of a novel bis(oxine) ligand, namely 1,8-bis(8-hydroxyquinolin-5-yl)-2,7-dioxaoctane (BQDO) (H_2L), and its coordination polymers with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) metal ions. In this H_2L ligand the 5,5′-positions of two oxine units are linked with each other through a linear aliphatic chain of 2,7-dioxaoctane [$–CH_2–O–(–CH_2–)_4–O–CH_2–$] unit at its 1 and 8 carbon atoms as shown in Scheme 1.

EXPERIMENTAL

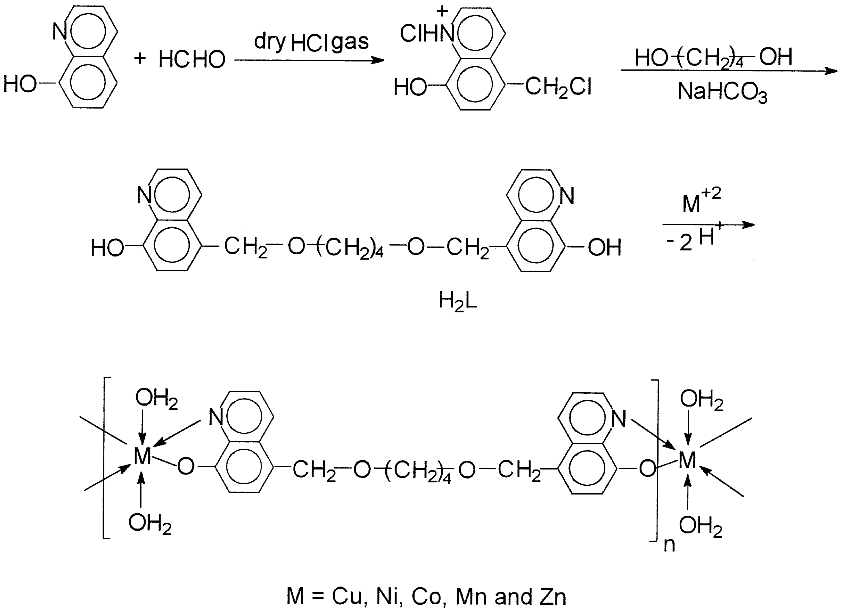
Materials

All the chemicals were of AR grade.

Procedure

Synthesis Of 1,8-Bis(8-Hydroxyquinolin-5-yl)-2, 7-Dioxaoctane (BQDO) (H_2L)

The precursor 5-chloromethyl-8-hydroxyquinoline hydrochloride was prepared by chloromethylation of 8-hydroxyquinoline according to



SCHEME 1 The proposed synthetic route for the coordination polymers.

Burckhalter and Leib[15]. It is a yellow-colored product with a melting point of 280°C.

H_2L was prepared by following a method reported for 5-alkoxymethylene-8-quinolinol[15]. According to this method, a mixture of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.1 mol), butylene glycol (4.43 mL, 0.05 mol) in tetrahydrofuran (THF), (30 mL), and sodium bicarbonate (8.4 g, 0.1 mol) was refluxed at 75°–80°C for 2.5 h with occasional shaking. The resulting solution was then made alkaline with dilute ammonia to precipitate out the BQDO ligand, which was then filtered and air dried. The yield of H_2L was 68%, and its melting point was 178°C.

Preparation of Coordination Polymers

All coordination polymers were synthesized by using metal acetates by the method described below.

A warm, clear solution of H_2L (4.04 g, 0.01 mol) in 20% aqueous formic acid (200 mL) was added to a solution of copper acetate (1.99 g, 0.01 mol) in 50% aqueous formic acid (50 mL) with constant stirring. After complete addition of the metal salt solution, the pH of the reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate thus separated out in the form of a suspension was digested on a water bath for 1 h and eventually filtered, washed with hot water followed by acetone and dimethyl formamide (DMF), and then dried in air at room temperature. The yields of all coordination polymers were almost quantitative.

Measurements

Elemental analyses for C, H, and N of H_2L and its coordination polymers were carried out on a Carlo Erba elemental analyzer (Italy). Infrared (IR) spectra of H_2L and the coordination polymers were scanned on a Nicolet-400D FTIR spectrophotometer in KBr. The metal content analyses of the coordination polymers were performed by decomposing a weighed amount of each coordination polymer followed by complexometric titration with EDTA (ethylene diaminetetra acetate)[16].

Although the number-average molecular weight (M_n) of a polymer is considered one of the prerequisite properties for end-use applications, no literature has appeared regarding the determination of M_n of coordination polymers. The reason may be due to either the insolubility or instability of the coordination polymers in acidic or basic media. However, we have made an attempt to determine M_n of coordination polymers under controlled experimental conditions by using nonaqueous conductometric titration of the phenolic hydroxyl end groups of polymers as reported in the literature[17–20]. The method is as described below.

The polymer sample dried at 60°C was finely powdered and used for conductometric titration. A weighed amount of this polymer sample (50 mg) was dissolved in 40 mL anhydrous pyridine. The solution was allowed to stand overnight for complete dissolution. This polymer solution was transferred to a conductance cell and it was then stirred magnetically. The base sodium methoxide was added to the conductance cell at regular intervals of 0.1 mL of titrant beyond the stage of equivalence.

Magnetic susceptibility measurements of all the coordination polymers were carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate(II), $Hg[Co(NCS)_4]$, was used as a calibrant. The diffuse reflectance spectra of the solid coordination polymers were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Thermal stability studies of the coordination polymers were carried out by TGA on a DuPont 950 thermogravimetric analyzer at a heating rate of 10°C/min in an air atmosphere. In order to determine the thermal stability trend, thermogravimetric parameters, such as T_0 (initial decomposition temperature), T_{10} (temperature for 10% weight loss), $T_{max.}$ (temperature of maximum rate of degradation), PDT (deferential procedural decomposition temperature), IPDT (integral procedural decomposition temperature)[21,22], and the activation energy E_a[23] of the degradation process were calculated by the method reported in the literature. T_0 and T_{10} are the main criteria used to indicate the heat stability of polymers. Higher values of T_0 and T_{10} suggest higher thermal stability of polymers.

According to Doyel[21,22] the entire shape of the thermogram was taken into account for determining the total area of the thermogram, and the area of the thermogram representing decomposition was integrated in order to sum up all the variations in the thermogram. The PDT was determined from the normalized data record of a thermogram, i.e., the temperature for maximum rate of polymer degradation. The IPDT was estimated by the comparison of the area under the transition to the total area of the normalized curve obtained from the thermogram data records. Thus the normalized curve represents the plot of the rate of change of residual weight (dy) with respect to temperature (dT) versus temperature (T). This procedure was useful for studying phenomena occurring closely in succession and for gradual weight changes where the assignment of the temperature is difficult. From this plot the IPDT can be obtained by using following equation:

$$\mathrm{IPDT} = T_0 + \frac{\text{Area under the thermogram}}{\text{Total area of thermogram}}(T_f - T_0)$$

where T_0 and T_f are, respectively, the initial and final temperatures of the thermal degradation process.

RESULTS AND DISCUSSION

The parent ligand BQDO (H_2L) is a light green powder, soluble in organic solvents such as dioxane, DMSO (dimethyl sulfoxide), and DMF. The results of elemental analyses of the ligand reported in Table I are consistent with the predicted structure as shown in Scheme 1.

The IR spectrum of H_2L shows a broad band at 3300–3550 cm^{-1} due to a phenolic hydroxyl group, and the characteristic IR frequencies for 8-hydroxyquinoline moiety appear at 1420, 1480, 1588, and 1600 cm^{-1} as expected[24]. The weak bands at 2932 cm^{-1} are attributed to aliphatic stretching vibrations of methylene groups ($–CH_2–$) and the band at 1080 and 1145 cm^{-1} indicates C–O stretching of the ether groups of the 2,7-dioxaoctane bridge. In addition to these bands, the IR spectrum of H_2L has many characteristic absorption bands common to those that occurred in 5,5′-methylenebis(8-hydroxyquinoline)[11], further confirming the predicted structure shown in Scheme 1.

TABLE I Analytical data of the coordination polymers of BQDO (H_2L)

					Elemental analyses						
					% Found/(Calcd.)						
Compound	Empirical formula	Formula weight	Yield (%)	Color	C	H	N	M	μ_{eff}[a] (B.M.)	M_n	DP[b]
H_2L	$C_{24}H_{24}N_2O_4$	404.00	68	Light green	71.0 (71.28)	5.1 (5.94)	6.1 (6.93)	—	—	—	—
$[CuL(H_2O)_2]_n$	$Cu.C_{24}H_{22}N_2O_4.H_2O$	483.54	86	Green	59.3 (59.56)	4.7 (4.96)	5.5 (5.79)	12.2 (13.14)	2.0	2869	6
$[CoL(H_2O)_2]_n$	$Co.C_{24}H_{22}N_2O_4.2H_2O$	496.93	84	Brown	57.6 (57.95)	5.3 (5.23)	5.4 (5.63)	11.2 (11.85)	3.8	2697	5
$[NiL(H_2O)_2]_n$	$Ni.C_{24}H_{22}N_2O_4.2H_2O$	496.71	90	Green	57.1 (57.17)	5.4 (5.97)	5.6 (5.80)	11.3 (11.85)	3.3	2681	5
$[MnL(H_2O)_2]_n$	$Mn.C_{24}H_{22}N_2O_4.2H_2O$	492.94	85	Light green	58.2 (58.42)	5.1 (5.27)	5.3 (5.68)	10.9 (11.14)	5.9	2784	6
$[ZnL(H_2O)_2]_n$	$Zn.C_{24}H_{22}N_2O_4.2H_2O$	503.37	92	Pale yellow	57.0 (57.25)	4.1 (4.37)	5.1 (5.56)	12.2 (12.92)	D	2890	6

[a] Magnetic moment; D is diamagnetic.
[b] Number-average degree of polymerization.

The coordination polymers of H_2L with metal ions Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) vary in color from light green to brown. On the basis of the proposed structure shown in Scheme 1, the molecular formula of the H_2L ligand is $C_{24}H_{24}N_2O_4$, which, upon chelation coordinates with one central metal atom at four coordination sites and with two water molecules. Therefore, the general molecular formula of the resulting coordination polymer is given by $C_{24}H_{22}N_2O_4M.2H_2O$ as shown in Scheme 1. This has been confirmed by the results of elemental analyses of all of the five coordination polymers and their parent ligand. The data of elemental analyses reported in Table I are in agreement with the calculated values of C, H, and N based on the above-mentioned molecular formula of parent ligand as well as coordination polymers. The IR spectra of all of the coordination polymers of H_2L are similar to each other in their general shape, but the comparison of the IR spectrum of the parent ligand H_2L with those of its coordination polymers has revealed certain characteristic differences.

One of the significant differences to be expected between the IR spectrum of the parent ligand and that of its metal coordinated polymers is the presence of much broader bands in the region of 3000–3600 cm^{-1} for the coordination polymer, as the oxygen of the O–H group of the ligand forms a coordination bond with the metal ions. This is explained by the fact that water molecules could have strongly absorbed to the polymer sample during its formation. Another noticeable difference is that the band due to the C=N stretching vibration of 8-hydroxyquinoline at 1600 cm^{-1} in the IR spectrum of H_2L is shifted to lower frequency, whereas the band at 1420 cm^{-1} in the IR spectrum of H_2L assigned to in-plane –OH deformation[24] is shifted toward higher frequency in the spectra of the coordination polymers. This may be due to chelation of metal with 8-hydroxyquinoline. This feature has been further confirmed by a weak band at 1110 cm^{-1} corresponding to C–O–M stretching[24] and the band around 780 and 640 cm^{-1} corresponding to the M–N vibration in coordination polymers. Thus, all of these characteristic features of the IR studies suggest the structure of the coordination polymer shown in Scheme 1. Examination of data of the metal content in each polymer (Table I) revealed a 1:1 metal:ligand (M/L) stoichiometry in all of the coordination polymers.

The M_n values determined by nonaqueous conductometric titration are shown in Table I. The method is reported by Chatterjee et al.[17–20]. These authors carried out good deal of the work for M_n determination of functional oligomers. One of the present authors has also determined M_n of amino-terminated polymers as well as carboxy-functional polymers [25–26]. Although coordination polymers might be unstable and insoluble in acidic or alkaline medium, the author kept it aside for 24 h in the pyridine medium in which the titration could be carried out. It was observed that the sample was relatively intact in the pyridine medium. The samples required only a small amount of alkali to neutralize terminal –OH groups, which were also relatively intact after the titration was completed. Thus, on the basis of these results, the M_n values were calculated. The results of the nonaqueous conductometric titrations reveal that there was not much variation in each coordination polymer as expected from their suggested structure.

Magnetic moments (μ_{eff}) of the coordination polymers are given in Table I. Examination of these data reveals that all coordination polymers other than that of Zn(II) are paramagnetic while that of Zn(II) is diamagnetic.

The diffuse electronic spectrum of the $[CuL(H_2O)_2]$ coordination polymer shows two broad bands at 15,873 and 22,691 cm^{-1} due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and charge transfer, respectively, suggesting a distorted octahedral structure for the $[CuL(H_2O)_2]$ polymer, which is further confirmed by the higher value of μ_{eff} of the $[CuL(H_2O)_2]$ polymer[27,28]. The $[NiL(H_2O)_2]$ coordination polymer gave two absorption bands, respectively, at 15,503 and 22,988 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). The $[CoL(H_2O)_2]$ polymer shows two absorption bands, at 15,384, 18,518, and 22,727 cm^{-1} corresponding to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, respectively[13]. Thus, the absorption bands of the diffuse reflectance spectra and the values of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the $[NiL(H_2O)_2]$ and $[CoL(H_2O)_2]$ polymers[29,30]. The spectra of $[MnL(H_2O)_2]$ show weak bands at 15,384, 17,695, and 22,955 cm^{-1} assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(4G)$, and $^6A_{1g} \rightarrow {}^4A_{1g} \cdot {}^4E_g$ respectively, suggesting an octahedral structure for the $[MnL(H_2O)_2]$ polymer[29]. As the spectrum of the $[ZnL(H_2O)_2]$ polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

The thermal behavior of the coordination polymers and parent ligand was investigated by thermogravimetric analysis (TGA). The TGA data of all the samples are presented in Table II and the thermograms are shown in Figure 1. The initial degradation temperature of the coordination polymers, as well as the non-chelated bis ligand, is about 25–50°C (T_0). A very slight decrease in weight loss (3–4%) depicted from the thermogram in the temperature range 25–150°C for the parent ligand may be attributed to loosely bonded moisture. However, the gradual weight loss that initially occurred below 150°C in all of the coordination polymers may be due to the removal of hydrated water, where the loss obtained in the range of 150°–200°C might be due to metal-coordinated water molecules[31]. The rate of decomposition for the entire coordination polymer is initially low up to 150°C and gradually increases to a maximum in the range of 240°–400°C at which almost 83–88% loss in weight occurred. The remarkable difference is observed in the thermal degradation of the parent ligand and its coordination polymer. The bis(bidentate) ligand follows a two-step mode as compared to a single-step thermal

TABLE II TGA data and thermal parameters of BQDO coordination polymers

Compounds	Percentage weight loss at different temperatures (°C)											T_0°C	T_{10}°C	PDT[a]	IPDT[b]	Activation energy (E_a) Kcal/mol
	100	150	200	250	300	350	400	450	500	550	650					
H_2L	2.50	4.00	7.80	8.60	10.5	13.8	25.0	33.0	39.0	73	98	25	350	560	569	10.2
$[CuL(H_2O)_2]_n$	6.58	7.11	7.50	50.86	81.5	82.0	—	—	—	—	—	25	210	250	253.25	7.0
$[CoL(H_2O)_2]_n$	7.00	10.5	11.5	16.5	50.0	63.25	82.08	83.5	85.5	—	—	25	230	350	355.55	8.5
$[NiL(H_2O)_2]_n$	8.00	11.6	14.1	21.1	47.6	84.0	87.51	88.0	—	—	—	25	220	325	350.80	8.4
$[MnL(H_2O)_2]_n$	7.49	8.16	8.94	10.21	13.61	14.86	76.20	83.0	85.5	85.5	—	25	255	425	450.55	9.0
$[ZnL(H_2O)_2]_n$	12.0	13.5	14.0	16.2	50.0	56.5	73.0	83.0	88.5	—	—	25	250	400	420.25	8.9

[a] Temperature for maximum rate of thermal degradation.

[b] Integral procedural decomposition temperature.

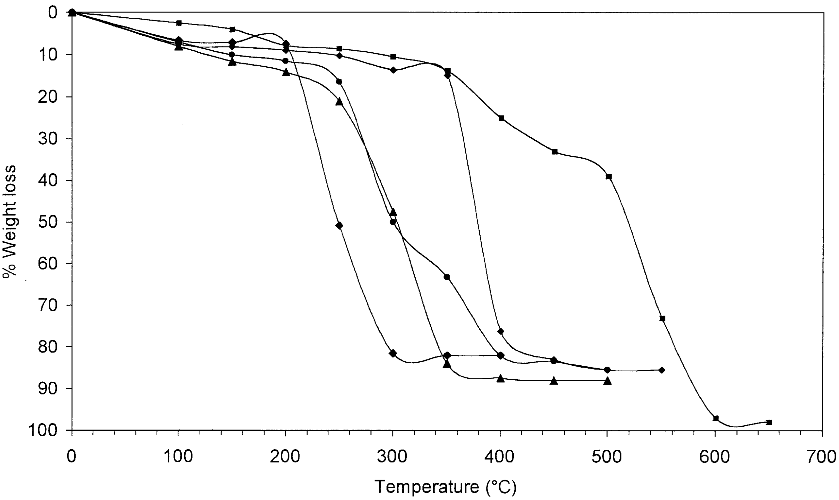


FIGURE 1 Thermograms of: —◆— Cu–BQDO —▲— Ni–BQDO —●— Co–BQDO —◆— Mn–BQDO —■— BQDO.

degradation of the five coordination polymers. The two steps of thermal degradation in parent bis(bidentate) ligand can be explained as follows:

- The first slow step of thermal degradation in the range of 340°–480°C may be due to the decomposition of a more labile aliphatic bridge present between the two 8-hydroxyquinoline units as compared to the aromatic nature of oxine.
- The second step of thermal degradation may be in the 8-hydroxyquinoline, initiated at 500°C, with a rapid weight loss at around 550°C and completed at 650°C.

Examination of the percentage weight loss as a function of temperature in all coordination polymers reveals that they all decompose in a single step and have an almost similar mode of decomposition, indicating that the thermal decomposition reactions in these coordination polymers are independent of the nature of the metal ion present. However, the rate of thermal decomposition in each of the samples is remarkably different, indicating that the thermal degradation is also dependent on an efficiency of a central metal atom to act as a catalyst in the thermal decomposition. On the basis of these criteria, the order of thermal stability predicted among these five coordination polymers is Mn–BQDO > Zn–BQDO > Co–BQDO ≅ Ni–BQDO > Cu–BQDO.

Thus, the non-chelated bis(bidentate) ligand and coordination polymers begin to decompose almost at the same temperature, but in the polymer chelates this decomposition is propagated very fast compared to that of the parent ligand. Consequently, the ligand is thermally more stable than its coordination polymer. This thermal behavior can be explained by the fact that the decomposition in metal-coordinated polymers was catalytically induced by the metal ions[32] and/or the introduction of the metal ion into the polymer backbone chain may develop a considerably greater strain in the coordination polymer of the bis(bidentate) ligand than the strain of the free bis(bidentate) ligand molecule.

A comparative study of thermal stability of coordination polymers has also been carried out with a view to examine structure-property relationships. For this purpose the thermal parameters, such as T_0, T_{10}, PDT, and IPDT, are estimated and are furnished in Table II. The values of these temperatures are higher in the case of the non-chelated bis(bidentate) ligand as compared to those of its metal coordination polymers, indicating that the parent bis(bidentate) ligand is thermally more stable than its coordination polymers. The selected normalized thermograms of BQDO and Mn–BQDO coordination polymers are shown in Figure 2. PDT and IPDT values of coordination polymers have indicated that the Cu-coordinated polymer has the least thermal stability, while that of the Mn-coordination polymer is the most stable. Therefore, the Mn–BQDO coordination polymer may be used as heat resistant material up to 300°C.

The Broido method was used for estimating the energy of activation of thermal decomposition of all samples[23]. The energy of activation E_a is computed from the slope of the plot of ln(ln 1/y) versus (1/T) and reported in Table II (where y is the weight fraction of residue,

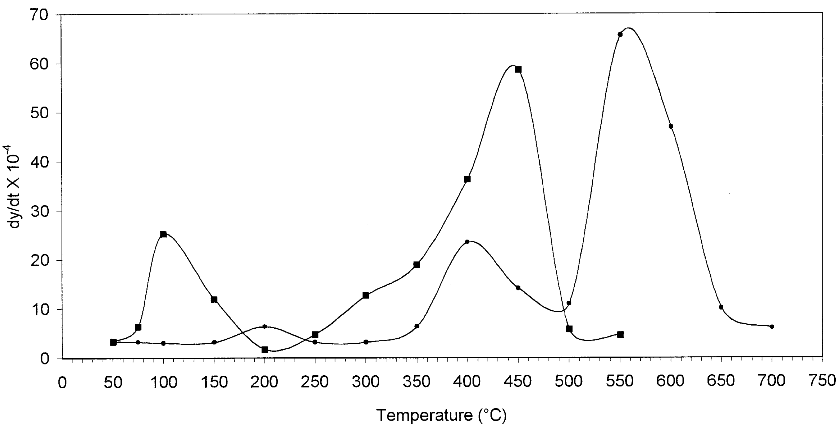


FIGURE 2 Normalized thermograms of: —●— BQDO —■— Mn–BQDO.

i.e., y = weight of residue at time (t) or temperature (T)/initial weight of the polymer sample:

$$\text{slope} = -E_a/R$$

where R = 1.987 kcal/mol and 10.2 kcal/mol for the bis ligand, while the coordination polymers are in the range of 7–9 kcal/mol.

CONCLUSIONS

A comparison of the thermal stability of the present coordination polymers with the reported thermal stability of coordination polymers having bis(8-hydroxyquinolinyl)methane (MBQ)[11] and bis(8-hydroxyquinolin-5-yl-methylene)ether (BHQE)[14] reveals that the polymers of this study containing $-CH_2-O-(CH_2)_4-O-CH_2-$ bridges are thermally less stable than those containing methylene ($-CH_2-$) or dimethylene oxide ($-CH_2-O-CH_2-$) bridges. This effect may be due to the higher aliphatic character of the bridge $-CH_2-O-(CH_2)_4-O-CH_2-$ containing two ether oxygen atoms, making it more labile.

REFERENCES

[1] Geckeler, K. E. and Z. Rongnong. (1994) *Chem. Abstr.*, **121**, 10302.

[2] Purohit, R. and S. Devi. (1991) *Analyst.*, **116**, 825–832.

[3] Pittman, C. U., K. S. Ramachandran Jr., and K. R. Lowyer. (1982) *J. Coat. Technol.*, **54**, 27–40.

[4] Albert, E. (1979). In *Selective Toxicity*. Chapman and Hall, London.

[5] Manolova, N., M. Ignatova, and I. Rashkov. (1998) *Eur. Polym. J.*, **34(8)**, 1133–1141.

[6] Bankova, M., N. Manolova, and I. Rashkov. (1994) *Eur. Polym. J.*, **30(10)**, 1179–1185.

[7] Angelova, N., N. Manolova, I. Rashkov. (1995) *Eur. Polym. J.*, **31(8)**, 741–748.

[8] Bankova, M., T. Petrova, N. Manolova, and I. Rashkov. (1996) 5-Chloro-8-quinolinyl acrylate and N-vinyl-2-pyrrolidone copolymers: Synthesis, characterization and complexes with poly(methacrylic acid). *Eur. Polym. J.*, **32(3)**, 325–330.

[9] Bankova, M., T. Petrova, N. Manolova, and I. Rashkov. (1996) *Eur. Polym. J.*, **32(5)**, 569–578.

[10] Bankova, M., N. Manolova, N. Markova, T. Radoucheva, K. Dilova, and I. Rashkov. (1999) *Eur. Polym. J.*, **34(2)**, 247–253.

[11] Horowitz, E. and T. P. Perros. (1964) *J. Inorg. Nucl. Chem.*, **26**, 139–159.

[12] Bailer, Jr., J. C., M. L. Judd, and M. J. McLean. (1959) *Coordination Polymers.* WADC Technical Reports, 58–51, Part II, 116–145.

[13] Patel, R. D., S. R. Patel, and H. S. Patel. (1987) *Eur. Polym. J.*, **23(3)**, 229–232.

[14] Shah, T. B., H. S. Patel, and R. B. Dixit. (1999) *Orient. J. Chem.*, **15(1)**, 107–112.

[15] Burckhalter, J. H. and R. I. Leib. (1961) *J. Org. Chem.*, **26**, 4078–4083.

[16] Vogel, A. I. (1961) *A Text Book of Quantitative Inorganic Analysis*, 3rd ed., Longman, London, 433.

[17] Chatterjee, S. K. and R. P. Mitra. (1963, 1964, 1969) *Indian J. Chem.*, **1**, 62–67; **2**, 85–91; **7**, 605–610.

[18] Chatterjee, S. K. and V. B. Agrawal. (1971) *J. Polym. Sci. Part A 1*, **9**, 3225–3232.

[19] Chatterjee, S. K. and N. D. Gupta. (1973) *J. Polym. Sci. Polym. Chem. Ed.*, **11(6)**, 1261–1270.

[20] Chatterjee, S. K. and N. D. Gupta. (1974) *J. Macromol. Sci. Chem., A*, **8(2)**, 451–457.

[21] Doyel, C. D. (1961) *Anal. Chem.*, **33**, 77–79.

[22] Doyel, C. D. (1969) *Quantitative Calculations in Thermogravimetric Analysis*. Marcel Dekker, New York.

[23] Broido, A. (1969) *J. Polym. Sci. Part A* 2, **7**, 1761–1773.

[24] Charles, R. G., H. F. Freiser, R. Priedel, L. E. Hilliand, R. D. Johnston. (1956) *Spectrochem. Acta*, **8**, 1–8.

[25] Patel, H. S., S. R. Patel, and R. N. Patel. (1982) *Angew. Makromomol. Chem.*, **99**, 125–130.

[26] Patel, H. S. and S. R. Patel. (1982) *J. Makromol. Sci. Chem.*, **17**, 1383–1389.

[27] Patel, D. C. and P. K. Bhattacharya. (1972) *J. Indian Chem. Soc.*, **49**, 1041–1043.

[28] Oza, D., K. N. Kaul, and R. K. Mehta. (1996) *Indian J. Chem.*, **7**, 927–928.

[29] Papplardo, R. (1960) *J. Chem. Phys.*, **33**, 613–614.

[30] Lewis, J. and R. S. Wilkins. (1960) *Modern Coordination Chemistry*, Interscience, New York, 290.

[31] Nikolaev, A. V., V. A. Logvinenko, and L. T. Myachina. (1960) *Thermal Analysis*, Academic Press, New York, 779.

[32] DeGeiso, R. C., L. G. Donaruma, and E. A. Tomic. (1965) *J. Appl. Polym. Sci.*, **9(2)**, 411–420.