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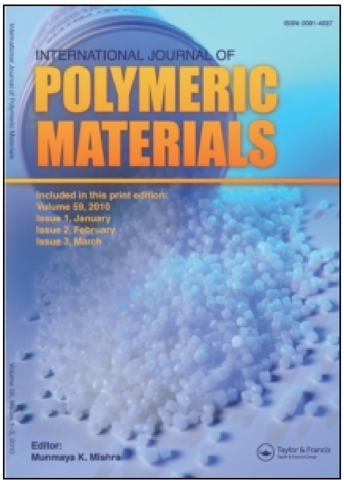

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Chelates of Poly (8-Hydroxyquinoline-Dimethylolurea)

T. B. Shah[a]; H. S. Patel[a]; R. B. Dixit[a]; B. C. Dixit[b]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India [b] Department of Chemistry, V. P. & R. P. T. P. Science College, Vallabh Vidyanagar, Gujarat State, India

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Chelates of Poly (8-Hydroxyquinoline-Dimethylolurea)

T. B. Shah
H. S. Patel
R. B. Dixit
Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar, Gujarat State, India

B. C. Dixit
Department of Chemistry, V. P. & R. P. T. P. Science College,
Vallabh Vidyanagar, Gujarat State, India

Novel polymeric chelates of a 8-hydroxyquinoline-based polymeric ligand (H_2L), namely 8-hydroxyquinoline-dimethylolurea (HQDMU), were prepared with the metal ions Zn(II), Cu(II), Ni(II), Co(II) and Mn(II). The novel 8-hydroxyquinoline-dimethylolurea (HQDMU) polymeric ligand (H_2L) was synthesized by condensation of N,N′-dimethylolurea (DMU) with 8-hydroxyquinoline in the presence of a base catalyst. All the polymeric chelates (ML_2) and the parent ligand (H_2L) were characterized by elemental analyses and IR spectral studies. The number-average molecular weight ($\overline{M}_n$) of the polymeric chelates and polymeric ligand (H_2L) was determined by non-aqueous conductometric titration. The thermal stability of polymeric ligand and chelates was investigated by thermogravimetric analysis (TGA). Thermogravimetric parameters such as T_0 (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 degradation process were calculated. Besides this, diffusion spectral studies of the polymeric chelates were characterized by determining their magnetic susceptibilities.

Keywords: DMU, HQDMU, IPDT, polymeric chelates, TGA

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Address correspondence to B. C. Dixit, Department of Chemistry, V. P. & R. P. T. P. Science College, Vallabh Vidyanagar 388120, Gujarat State, India. E-mail: dixits20002003@yahoo.co.in

INTRODUCTION

Perusal of the literature reveals that 8-hydroxyquinoline and its derivatives are widely used as bidentate ligands in chelate formation because of their enhanced chelating ability [1–2]. These bidentate ligands thus forming the chelates have many potential applications such as in waste water treatment for metal recovery, as water disinfectants, and for biological activity [3–4]. Manolova et al. published a series of papers on polymers and copolymers of 8-hydroxyquinoline either present as end group or as pendant groups with a view to study their complexing ability and biological activity [5–6]. On the basis of this, the present authors have made an attempt to synthesize a novel 8-hydroxyquinoline based polymeric ligand (H_2L) namely poly (8-hydroxyquinoline-dimethylolurea) (HQDMU), which have not been yet reported. In this polymeric ligand, the 5- and 7-positions of 8-hydroxyquinoline have been blocked by the condensation reaction of 8-hydroxyquinoline with dimethylolurea (DMU) with a view to render only the chelating sites of 8-hydroxyquinoline free. The polymeric metal chelates of such HQDMU polymeric ligand have been prepared with five different transition metal ions like Zn(II), Cu(II), Ni(II), Co(II), and Mn(II). Both preformed polymeric ligand (H_2L) and its polymeric metal chelates (ML_2) have been characterized further as discussed in the following section.

EXPERIMENTAL

Materials

All the chemicals used were of AR grade and were obtained from Chiti Chem Ltd. Baroda, India.

Procedure

Synthesis of 8-Hydroxyquinoline-Dimethylolurea (HQDMU) Polymeric Ligand

The polymeric ligand (H_2L) was prepared in two steps.

The monomer N,N′-dimethylolurea (DMU) was prepared by the method reported in the literature with little changes in reaction conditions [7]. The procedure followed was: A mixture of urea (60 gm, 1 mole), formalin solution (2 mole, 162 ml) and 10 ml of 5% alcoholic KOH was refluxed at 100–110°C for 2 h. The reaction mixture was allowed to cool at room temperature, neutralized with formic acid, and excess water was removed by vacuum distillation. The monomer thus obtained was colorless thick liquid. The yield was 89%.

Polymeric Ligand of 8-Hydroxyquinoline with Dimethylolurea (HQDMU)

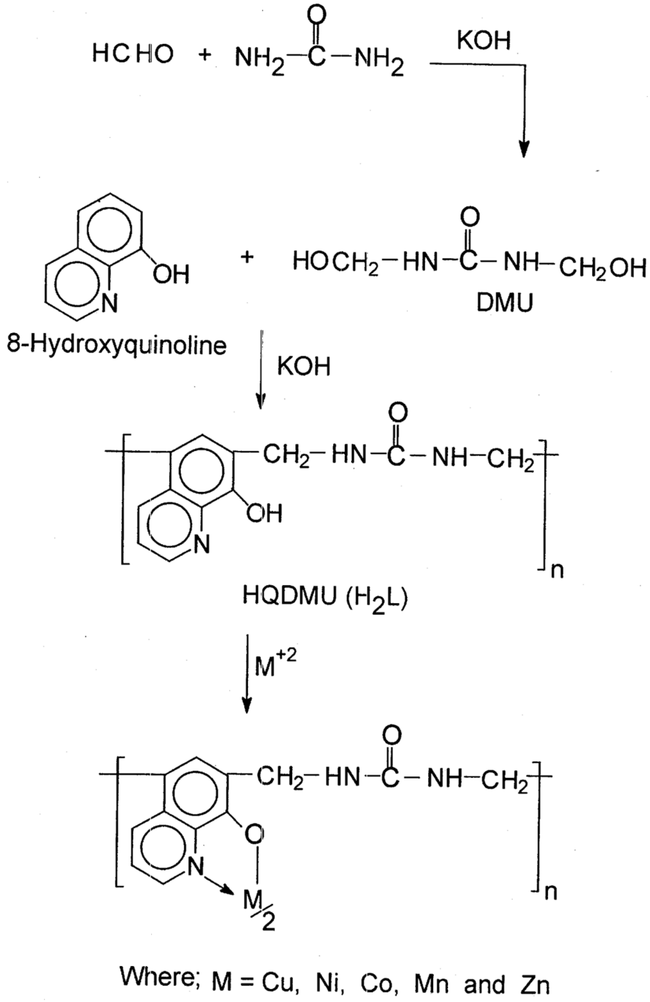
A mixture of dimethylolurea (4.4 gm, 0.05 mole), 8-hydroxyquinoline (7.25 gm, 0.052 mole), 30 ml methanol and 5 ml of 5% ethanolic solution of KOH was refluxed at 80–90°C for 10 h. The resultant reaction mixture was poured into water and neutralized with dilute HCI. Then the polymeric ligand was filtered off and washed with hot water followed by methanol to remove unreacted 8-hydroxyquinoline. The resulting product was air-dried and designated as HQDMU (8-hydroxyquinoline-dimethylolurea polymeric ligand). The yield of HQDMU was 82%. It was dark brown in color and not melted up to 300°C. The predicted structure and formation of polymeric ligand is shown in Scheme 1.

Preparation of Polymeric Chelates

All the polymeric chelates were synthesized by reaction of polymeric ligand with corresponding metal acetates. The detail procedure is as follows: A dried polymer sample (HQDMU) (2.29 gm, 0.01 mole) was dissolved in 200 ml aqueous solution of 20% formic acid and warmed on a waterbath for 10–15 min. To this solution, a warm solution of copper(II)acetate (0.995 gm, 0.005 mole) in 50% aqueous formic acid was added dropwise with constant stirring. The reaction mixture was made alkaline with dilute ammonia solution to precipitate out the polymeric chelate. The resultant mixture was further digested on waterbath for 1 h. Finally, the solid thus obtained was filtered off, washed with hot water followed by acetone and air-dried at room temperature. The polymeric chelates of HQDMU with Ni^{+2}, Co^{+2}, Mn^{+2}, and Zn^{+2} metal ions were prepared in a similar manner. The yields of all polymeric chelates were almost quantitative.

Measurements

Elemental analyses for C, H, and N of HQDMU and its polymeric chelates were carried out on a Carlo Erba elemental analyzer (Italy). IR spectra of H_2L and the polymeric chelates were scanned on a Nicolet-400D FTIR spectrophotometer in KBr. The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA titration as reported in the literature [8]. Magnetic susceptibility measurements of all the polymeric chelates 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 polymeric chelates were recorded on a Beckman DK-2A



SCHEME 1 The proposed synthetic route for the polymeric chelates (ML_2).

spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Thermal stability studies of the HQDMU and its polymeric chelates 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 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) [9–10] and the activation energy E_a [11] 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 [9–10] the whole 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, that is, 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 rate of change of residual weight (dy) with respect to temperature (dT) versus temperature (T), found to be very useful for studying phenomena occurring closely in succession and in other cases for such gradual weight changes where the assignment of significant temperature is difficult. From this plot the IPDT can be obtained by using the following equation:

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

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

RESULTS AND DISCUSSION

The parent polymeric ligand (H_2L) is brown colored powder and did not melt up to 300°C. It is completely soluble in acidic and basic solvents like acetic acid, formic acid, DMF, pyridine, and so on as expected, and is partially soluble in chloroform, DMSO, and dioxane. The results of elemental analyses and number average molecular weight ($\overline{M}_n$) of the polymeric ligand (H_2L) are reported in Table 1. The data of elemental analysis are consistent with the predicted structure as shown in Scheme 1.

The IR spectra of polymeric ligand H_2L (HQDMU) comprise important bands due to the dimethylolurea and 8-hydroxyquinoline [12] moieties. A broad band in 3300–3600 $\mathrm{cm^{-1}}$ is observed due to phenolic hydroxyl and that of N−H stretching vibrations of amine. The absorption bands at 1420, 1470, 1580, and 1600 $\mathrm{cm^{-1}}$ are the characteristics of the 8-hydroxyquinoline moieties. The weak bands at 2940 and

TABLE 1 Analytical Data of the HQDMU (H_2L) and Its Polymeric Chelates (ML_2)

					Elemental analyses					
					% Found/(Calcd.)					
Compounds	Empirical formula of repeat unit of polymer	Formula weight of repeat unit of polymer	Yield (%)	Color	C	H	N	M	μ_{eff} (B.M.)	$\overline{M}_n$
H_2L	$C_{12}H_{11}N_3O_2$	229.00	78	Light brown	62.50 (62.88)	4.12 (4.80)	18.15 (6.16)	—	—	1717.50
$[CuL_2 \cdot (H_2O)_2]_n$	$Cu \cdot C_{24}H_{20}N_6O_4 \cdot H_2O$	537.54	81	Brown	53.07 (53.57)	3.62 (4.8709)	15.63 (15.62)	11.13 (11.82)	1.91	3464.85
$[CoL_2 \cdot (H_2O)_2]_n$	$Co \cdot C_{24}H_{20}N_6O_4 \cdot 2H_2O$	550.93	82	Brown	51.98 (52.27)	4.31 (4.35)	15.13 (15.24)	10.15 (10.69)	4.49	3372.50
$[NiL_2 \cdot (H_2O)_2]_n$	$Ni \cdot C_{24}H_{20}N_6O_4 \cdot 2H_2O$	550.71	85	Brown	52.13 (52.29)	4.29 (4.35)	15.09 (15.25)	10.32 (10.66)	3.35	3498.62
$[MnL_2 \cdot (H_2O)_2]_n$	$Mn \cdot C_{24}H_{20}N_6O_4 \cdot 2H_2O$	546.94	89	Light brown	52.25 (52.65)	4.207 (4.38)	15.15 (15.35)	9.77 (10.04)	5.42	3404.46
$[ZnL_2 \cdot (H_2O)_2]_n$	$Zn \cdot C_{24}H_{20}N_6O_4 \cdot 2H_2O$	557.37	88	Light brown	51.57 (51.67)	3.53 (3.58)	15.27 (15.07)	11.26 (11.53)	D	3413.18

2890 cm^{-1} are due to aliphatic stretching vibrations of methylene groups ($-CH_2-$), and the sharp bands at 1660 cm^{-1} and 1545 cm^{-1} may be attributed to the carbonyl group $(>C{=}O)$ and C–N stretching of amide group of dimethylolurea, confirming the predicted structure shown in Scheme 1. The presence of very small but distinct bands at 1050, 1100, and 1160 cm^{-1} may indicate the presence of 5,7,8-trisubstituted aromatic 8-hydroxyquinoline moieties as reported in literature [13].

The polymeric chelates of H_2L (HQDMU) with the metal ions Zn(II), Cu(II), Ni(II), Co(II), and Mn(II) vary in color from light green to dark brown. They are completely insoluble in common organic solvents such as benzene, CCl_4, ethanol, DMF, THF, and so on.

On the basis of the proposed structure the molecular formula of the H_2L ligand is $C_{12}H_{11}N_3O_2$. Such two ligands coordinate with one central metal atom at four coordination sites in the formation of polymeric chelates along with two water molecules. Hence, the general molecular formula of the resulting polymeric chelates is $C_{28}H_{24}N_2O_4M.2H_2O$ ($ML_2 \cdot 2H_2O$). The results of elemental analyses of the polymeric chelates for C, H, and N reported in Table 1 are consistent with the predicted structure shown in Scheme 1.

The IR spectra of all the polymeric chelates of H_2L show that they resemble each other in their general shape. But the comparison of the IR spectrum of the parent ligand H_2L with those of its polymeric chelates has revealed certain characteristic differences.

One of the significant differences to be expected is the absence of a broad band in the region of 3300–3600 cm^{-1} due to O–H stretching vibration frequencies in IR spectrum of polymeric chelates as the oxygen of this O–H of parent ligand has formed bond with metal ions. However, this band has become broader in the IR spectrum of polymeric chelates. This is explained by the fact that water molecules might have strongly absorbed to the polymeric chelates during their 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 [12] is shifted toward higher frequency in the spectra of the polymeric chelates due to the formation of metal-oxygen bonds. This has been further confirmed by a weak band at 1105 cm^{-1} corresponding to C–O–M stretching [12] and the band around 740–760 cm^{-1} corresponds to the M–N vibration. Thus, all these characteristic features are in agreement with the predicted structure of the polymeric chelates. Examination of data of the metal content in each chelate (Table 1) revealed a 1:2 metal:ligand (M/L) stoichiometry with a variation of $\pm 1\%$ to that of theoretical values, predicting intermolecular coordination bond formation of metal ion with two repeat units of polymeric chelates.

The number average molecular weight ($\overline{M}_n$) of a polymeric ligand is considered as an important property. However, no literature report hitherto has appeared regarding the determination of $\overline{M}_n$ of polymeric chelates. The reason may be due to either the insolubility or unstability of the polymeric chelates in acidic or basic media. Therefore, we have made an attempt to determine $\overline{M}_n$ of polymeric chelates under controlled experimental conditions by using the non-aqueous conductometric titration of the phenolic –OH end groups of polymers as reported in the literature [14]. These data of $\overline{M}_n$ are reported in Table 1. A discernible single break corresponding to the free –OH group of the end 8-hydroxyquinoline moiety was observed in the titration curve. Examination of the results of number average molecular weight data has shown that there is not much variation in the number-average molecular weight ($\overline{M}_n$) of each chelate as expected from their structure.

Magnetic moments (μ_{eff}) of the polymeric chelates are given in Table 2. Examination of these data reveals that all polymeric chelates other than that of Zn(II) are paramagnetic, whereas that of Zn(II) is diamagnetic.

The diffuse electronic spectrum of the $[CuL_2 \cdot (H_2O)_2]$ polymeric chelates shows two broad bands at 15,570 and 25,950 cm^{-1} due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and charge transfer, respectively, suggesting a distorted octahedral structure for the $[CuL_2 \cdot (H_2O)_2]_n$ polymeric chelates and this is further confirmed by the higher value of μ_{eff} of the $[CuL_2.(H_2O)_2]_n$ polymeric chelates. The $[NiL_2 \cdot (H_2O)_2]_n$ and $[CoL_2 \cdot (H_2O)_2]_n$ polymers gave three absorption bands, respectively, at 9,025, 16,435, 26,250, and 8,757, 15,676, 22,125 cm^{-1} corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}(P)$, $^3A_{2g}(P) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions [15]. Thus, the absorption bands of the diffuse reflectance spectra and the values of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the $[NiL_2 \cdot (H_2O)_2]_n$ and $[CoL_2 \cdot (H_2O)_2]_n$ polymers [16]. The spectra of $[MnL_2 \cdot (H_2O)_2]_n$ show weak bands at 15,534, 18,585, and 22,375 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 $[MnL_2 \cdot (H_2O_2]_n$ polymer [17]. As the spectrum of the $[ZnL_2 \cdot (H_2O)_2]_n$ 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 polymeric chelates and their parent ligand was investigated by thermogravimetric analysis (TGA).

TABLE 2 TGA Data and Thermal Parameters of HQDMU (H_2L) and Its Polymeric Chelates (ML_2)

Compounds	Percentage weight loss at different temperature (°C)													
	100	200	300	350	400	450	500	600	650	T_0°C	T_{10}°C	PDT	IPDT	Activation energy (E_a) Kcal/mol
H_2L	1.65	3.29	6.57	11.48	34.43	38.53	49.19	88.55	97.00	25	350	550	553.25	12.0
$[CuL_2 \cdot (H_2O)_2]_n$	11.06	12.11	80.21	82.11	—	—	—	—	—	25	195	250	310.00	8.2
$[CoL_2 \cdot (H_2O)_2]_n$	7.50	9.50	17.25	39.56	77.20	83.50	—	—	—	25	260	350	370.00	8.5
$[NiL_2 \cdot (H_2O)_2]_n$	7.51	10.22	14.31	25.18	77.44	80.96	—	—	—	25	200	400	405.00	8.5
$[MnL_2 \cdot (H_2O)_2]_n$	3.82	11.00	17.05	25.00	31.50	46.70	70.50	81.00	—	25	290	450	470.99	9.5
$[ZnL_2 \cdot (H_2O)_2]_n$	4.15	9.10	16.43	21.38	25.47	40.23	65.64	82.5	—	25	300	450	466.25	9.0

PDT = Temperature for maximum rate of thermal degradation.
IPDT = Integral procedural decomposition temperature.

The TGA data of all the samples are presented in Table 2 and the thermograms are shown in Figure 1. Scrutiny of these thermograms reveals that the polymeric ligand follows a two steps thermal degradation as compared to a single step thermal degradation occurring in each of the five polymeric chelates. The two steps of thermal degradation in parent polymeric ligand can be explained as:

The first slow step of thermal degradation in the temperature range of 300–400°C may be due to decomposition of a more labile aliphatic bridge of dimethylolurea [–HN–CO–NH–] present between the two 8-hydroxyquinoline units as compared to the aromatic nature of 8-hydroxyquinoline.

The second step of thermal degradation may be in 8-hydroxyquinoline, initiated at the temperature of 400°C and then weight loss rapidly around 550°C reaching about 97% weight loss at 650–700°C.

Further, the thermal degradation in parent polymeric ligand has initiated with a very slight decrease in weight loss (2–4%) in the temperature range of 25–150°C and it may be due to loosely held moisture present in the polymeric ligand. On the other hand the gradual weight loss initially occurred below 150°C in thermal degradation of all of the polymeric chelates may be due to removal of uncoordinated water whereas weight loss (about 7%) obtained in the temperature range 150–200°C might be due to presence of two coordinated water molecules [18].

The rate of decomposition for the entire polymeric chelates is initially low up to 100°C. Eventually the maximum rate of decomposition with 80–84% weight loss was observed in the temperature range of 300–450°C for polymeric chelates of Cu^{+2}, Ni^{+2}, and Co^{+2} metal ions and that of 81–83% weight loss was observed in the temperature range of 350–600°C for polymeric chelates of Mn^{+2} and Zn^{+2} metal ions.

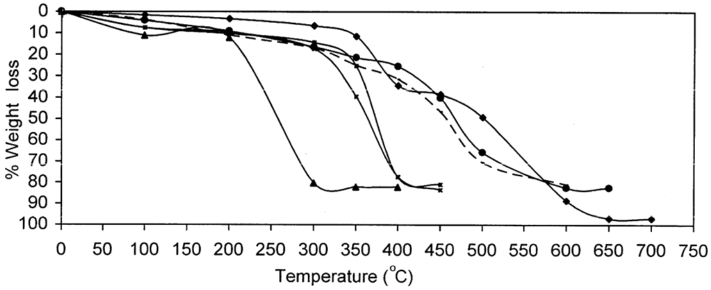


FIGURE 1 Thermograms of: —◆—HQDMU, —●—Zn-HQDMU, —▲—Cu-HQDMU, —▪—Co-HQDMU, —■—Ni-HQDMU, ---Mn-HQDMU.

There is a remarkable difference in the mode of thermal degradation for parent polymeric ligand and its polymeric chelates.

Examination of the percentage weight loss as a function of temperature in all polymeric chelates reveals that they all decompose in a single step and have similar mode of decomposition indicating that the thermal decomposition reactions in these polymeric chelates are independent of the nature of the metal ion present. However, the rate of thermal decomposition in each sample is remarkably different indicating that the thermal degradation is 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 among these five polymeric chelates is;

$$\text{Zn-HQDMU} > \text{Mn-HQDMU} > \text{Co-HQDMU} \\ \cong \text{Ni-HQDMU} > \text{Cu-HQDMU}$$

Thus, the TGA studies of HQDMU ligand and its polymeric chelates have shown that the decomposition in polymeric chelates propagated very fast as compared to its parent ligand, even though their decomposition begins almost at the same temperature. Consequently, one may conclude that the polymeric ligand is thermally more stable than its polymeric chelates. These results of thermal behavior can be explicable by the fact that the decomposition in polymeric chelates was catalytically induced by the metal ions [19] and/or the introduction of the metal ion between two polymer backbone chains may develop a considerable strain in the polymeric chelates of polymeric ligand larger than that of the free polymer molecule.

A comparative study of thermal stability of polymeric chelates has also been carried out with a view to examine structure-property relationship. For this purpose the thermal parameters such as T_0, T_{10}, PDT, IPDT are estimated using Doyel method [9–10] and are furnished in Table 2. A significant difference is observed for the temperatures corresponding to T_{10}, PDT, and IPDT. The values of these temperatures are higher in the case of polymeric ligand than those of the metal polymeric chelates, further confirming that parent polymeric ligand is thermally more stable than its polymeric chelates. The selected normalized thermograms of HQDMU and Zn-HQDMU polymeric chelates are shown in Figure 2. Securitization of PDT and IPDT values of polymeric chelates have indicated that the Cu-HQDMU polymeric chelate is least thermally stable and Zn-HQDMU is most stable.

The energy of activation for the thermal decomposition of HQDMU polymeric ligand and its chelates was estimated by Broido [11]

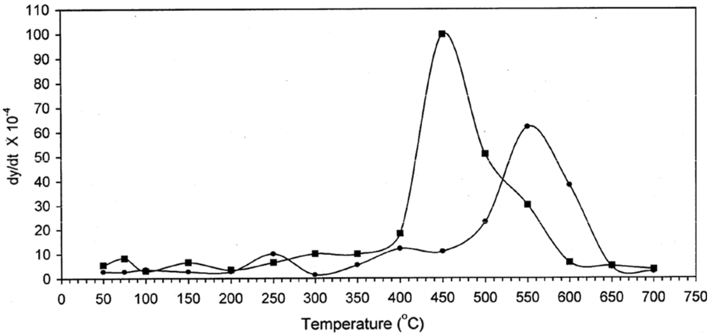


FIGURE 2 Normalized thermograms of: —●—HQDMU, —■—Zn-HQDMU.

method. The equation followed is:

$$\text{In } [\text{In}(1/y)] = (E_a/RT_m + 1) \text{ In } T + \text{constant}.$$

The energy of activation E_a is computed from the slope of the plot of ln(ln 1/y) versus (I/T) and reported in Table 2.

$$\text{Slope} = -E_a/R \qquad \text{where, } R = 1.987 \text{ kcal/mole}.$$

and it is 12 Kcal/mole for polymeric ligand while the activation energy observed for polymeric chelates are in the range of 8.2–9.5 kcal/mole.

CONCLUSIONS

The investigation described in the present article reveals the following conclusions:

Polycondensation of 8-hydroxyquinoline with N,N′-dimethylolurea (DMU) in the presence of a base catalyst yielded a novel 8-hydroxyquinoline-dimethylolurea (HQDMU) polymeric ligand. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ions indicating that the HQDMU polymeric ligand has good chelating property and high thermal stability.

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, Cu-HQDMU chelates is least stable, whereas Zn-HQDMU polymeric chelate is the most stable having a thermal stability comparable to that of parent polymeric ligand (HQDMU). Therefore, Zn-HQDMU polymeric chelates may be used as heat resistant material up to 350°C. The polymeric ligand follows a two steps thermal degradation whereas polymeric chelates follow a single step thermal degradation.

A comparison of the thermal stability of the present polymeric chelates with those of epoxy based polyester containing 8-hydroxyquinoline as pendent groups polymeric chelates [20] reveals that the HQDMU polymeric chelates are thermally more stable. Finally, the magnetic susceptibility results indicate that polymeric chelates of Cu^{+2}, Ni^{+2}, and Co^{+2} are paramagnetic, whereas that of Zn^{+2} is diamagnetic in nature.

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