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NOVEL POLYMERIC CHELATES OF 8-HYDROXYQUINOLINE-DIMETHYLOLACETONE

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A new chelating copolymer (HQDMA) has been synthesized through copolymerization of 8-hydroxyquinoline and dimethylolacetone monomers in the presence of base as a catalyst. This newly developed copolymer ligand (H_2L) has been used to prepare a series of five polymeric chelates (ML) by using Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) metal ions. Both the parent ligand and its metal chelates have been systemically investigated in detail to elucidate the chemical structure and thermal behaviour by elemental analyses, spectral (IR and electronic) characterization, number-average molecular mass ($\overline{M}_n$) determination and thermogravimetric analysis (TG). In addition to these, magnetic susceptibility measurements have also been carried out for studying geometry and metal-ligand stoichiometry of polymeric chelates.

The chemical structure of polychelates on the basis of elemental and IR characterization suggests that the bidentate ligand (H_2L) coordinates to metal ions through oxygen atom of the phenolic hydroxyl group by replacing hydrogen atom and nitrogen of the quinoline ring. The studies of magnetic moments and electronic spectra reveal that all polychelates with octahedral geometry are paramagnetic in nature except that of Zn(II) chelate, which is diamagnetic. The thermogravimetric analysis of parent ligand and its metal chelates have shown remarkable difference in mode of thermal decomposition and their thermal stabilities. The kinetic parameter, energy of activation (E_a) of thermal decomposition has also been estimated by Broido method.

Keywords: *DMA, HQDMA, integral procedural decomposition temperature, number average molecular mass, polymeric chelates, thermogravimetric analysis*

Introduction

The study of polymeric ligand, polychelates, metal complexes as well as of ionexchangers has attracted the attention of many researchers because of their versatile practical applications viz.; ion-exchangers in pollution control for separation of heavy metal ions, radio isotopes and in water treatment as well as for catalysis in organic synthesis and in bioinorganic chemistry. Such polymers have unique property profile that make them different from organic polymers with some characteristics like strong bond which resists cleavage reactions, multiple valences for attachment of wide variety of ligands, high thermal stability and ability to tailor made new polymeric structures with endless variations [1–3].

In this context, the interest in the coordination compounds of oxine has increased considerably in the last two decades. Most of the work has been done on the monomeric chelates and papers have also been published concerning polymeric ligands [4, 5]. Many of the workers in the field of polymeric chelating ligands have primarily interested in the synthesis of chelateing resins and determining selectivity of chelating polymer with various metal ions. Literature survey has revealed the proliferation in intensive developments of applications of coordination polymers and polymer chelates of 8-hydroxyquinoline and its derivatives in various areas of science and technology due to their versatile chelating ability. They are commonly used for their diversity of applications such as in waste water treatment for metal recovery, protective coatings, as water disinfectants, antifouling paints, antimicrobial, surgical materials, gels and ointment for medical uses, and biological activity [6–8] due to their high thermal stability.

Horrocks *et al.* [9] synthesized the first chelating polymers of oxine by polycondensation of oxine with formaldehyde using both acid and base catalysts and subsequently chelated with different metal ions like Zn(II), Cu(II), Ni(II), Co(II), Mn(II) in order to achieve the combination of properties of both coordination polymers and those of metal chelates crosslink's such as flexibility, thermal stability and ion exchange capacity. The study of thermal stability of parent ligands and their chelates carried out by TG, DSC, DTA and DTG methods. It is also reported that polymer chelates of oxine-formaldehyde resins gave polymeric chelates of better thermal stability by incorporation of aliphatic chain $(–CH_2–)_n$, directly attached to oxine at 5- or 7-position [10]. Manolova *et al.* [11, 12] have published a series of pa-

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pers of polymers and copolymers of 8-hydroxyquinoline either present as end groups or as pendent groups with a view to study their complexing ability and biological activity.

Recently, many research workers have reported the synthesis and characterization of various metal complexes 8-hydroxyquinoline and mixed ligand metal complexes. They have studied the structure-property relationship in terms of thermal stability [13–17]. Metal complexes of 8-hydroxyquinoline have also been reported for their antimicrobial activity [18] and for fluorescent sensors [19].

On the basis of this documentations, the present authors have made an attempt to synthesize a novel 8-hydroxyquinoline based copolymeric ligand (H_2L) namely 8-hydroxyquinoline-dimethylolacetone (HQDMA), which has yet not been reported. This polymeric ligand has been prepared by the copolymerization of 8-hydroxyquinoline with dimethylolacetone (DMA) in presence of base catalyst, such that 5- and 7-position of 8-hydroxyquinoline are blocked by dimethylolacetone and chelating sites of phenolic –OH and ring nitrogen are to be free.

The polymeric metal chelates of HQDMA copolymer ligand have been prepared with five different transition metal ions viz.; Zn(II), Cu(II), Ni(II), Co(II) and Mn(II). Both preformed copolymeric ligand (H_2L) and their polymeric metal chelates (ML) have been characterized further systematically as discussed in the following section.

Experimental

Materials

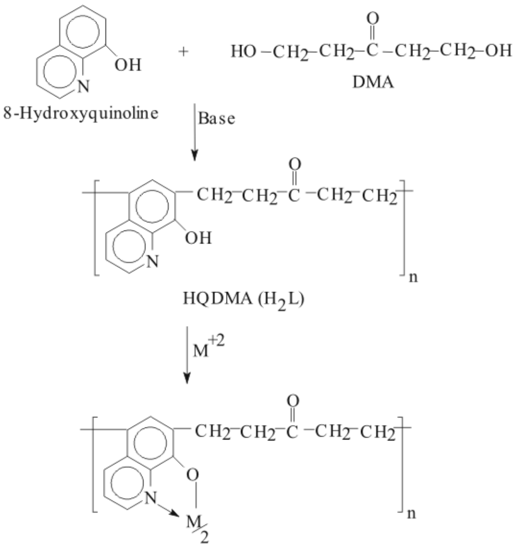
All the chemicals used were of AR grade and were obtained from Chiti Chem Corporation Baroda, India and were purified when and where required.

Synthesis of DMA monomer

The monomer α, α′-dimethylolacetone (DMA) was prepared by the method reported in the patent literature with little changes in reaction conditions [20]. The procedure followed was: a mixture of acetone (1 mol, 60 mL), paraformaldehyde (0.66 mol, 60 g) and 10 mL of 5% alcoholic KOH was heated at 40±2°C with continuous stirring for 10–15 min and allowed it to cool at room temperature. The resulting solution obtained was neutralized with formic acid, giving colorless thick liquid. The yield was 96%.

Synthesis of HQDMA copolymer

Copolymerization of 8-hydroxyquinoline (0.05 mol, 7.25 g) with dimethylolacetone (0.05 mol, 5.9 g) in 30 mL methanol was carried out in presence of alcoholic solution of KOH (5 mL, 3.5% based on mass of 8-hydroxyquinoline) by refluxing at 80–900° for 8 h. The colour of reaction mixture changes from yellow to dark red and then to green. The reaction mixture was poured into water and neutralized with dilute acid. The resulting copolymer was filtered off and washed several times with hot water followed by methanol in order to remove unreacted 8-hydroxyquinoline. It was then air-dried and the yield was 88%. 8-hydroxyquinoline-dimethylolac- etone copolymer was designated as HQDMA. The synthetic protocol for the copolymerization is shown in Scheme 1.



Scheme 1 Synthetic protocol for the formation of ligand (H_2L) and its polymeric metal chelates (ML)

Synthesis of polymeric metal chelates (ML)

Polymeric chelates were prepared by the following method.

A dried copolymeric ligand (HQDMA) (2.27 g, 0.01 mol) was dissolved in 200 mL aqueous solution of formic acid (20%) and warmed in the temperature range of 60–80°C on a water bath for 10–15 min. To this solution, a warm solution of metal acetate (0.005 mol) of each of the metal ion in aqueous formic acid (50%) was added dropwise with constant stirring. The reaction mixture was made alkaline with dilute ammonia solution and further digested on water bath for an hour. Finally, the solid thus obtained was filtered off, washed with hot water followed by acetone, DMF and air dried at room temperature. The yields of all polymeric metal chelates were almost quantitative.

Methods

Elemental analyses for C, H and N were carried out on a Carlo Erba Elemental Analyzer (Italy). The metal content of the polymeric chelates was carried by decomposing a weighed amount of each polymeric chelates with concentrated acid followed by standard EDTA titration method [21]. Number average molecular mass ($\overline{M}_n$) of ligand and its chelates was determined by non-aqueous conductometric titration method using sodium methoxide as titrant base and pyridine as solvent.

IR spectra of H_2L and the polymeric chelates were scanned on a Nicolet-400D FTIR Spectrophotometer in KBr. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method using mercury tetrathiocyanatocobaltate(II) $Hg[Co(NCS)_4]$ as a calibrant. The electronic spectra of the solid polymeric chelates were recorded on a Beckman DK-2A Spectrophotometer using MgO as reference.

Thermal behaviour of parent ligand and its metal chelates were studied by TG on a DuPont 950 Thermogravimetric Analyzer in presence of air at the heating rate of 10°C min^{-1}.

Results and discussion

Characterization of HQDMA copolymer ligand (H_2L) and its metal chelates

The physical and analytical data of HQDMA copolymeric ligand and its metal chelates are furnished in Table 1. The parent ligand (H_2L) is a brown colored powder and not melted upto 300°C. It is soluble in acidic and basic solvents like acetic acid, formic acid, DMF, pyridine, etc. as expected and, are partially soluble in chloroform, DMSO and dioxane. The polymeric chelates of H_2L (HQDMA) with the metal ions Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) vary in color from light green to dark brown. It is completely insoluble in common organic solvents such as benzene, CCl_4, ethanol, DMF, THF, etc.

The results of elemental analyses of the HQDMA copolymeric ligand (H_2L) are given in Table 1 and are consistent with the proposed structure shown in Scheme 1 with the molecular formula $C_{14}H_{13}NO_2$. Examination of the metal content in each polymeric chelates (Table 1) indicated metal to ligand (M/L) stoichiometry ratio as 1:2 suggesting that in the formation of polymeric metal chelates two ligands coordinate with central metal atom at four coordination sites and two water molecules at two coordination sites. Hence, the general molecular formula of the resulting polymeric chelates is $C_{28}H_{24}N_2O_4M{\cdot}2H_2O$. The data of elemental analyses reported in Table 1 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 polymeric chelates.

Non-aqueous conductometric titration of H_2L copolymeric ligand and its polymeric metal chelates was carried out in pyridine against standard sodium methoxide in pyridine as titrant. The $\overline{M}_n$ of each sample was calculated according to method reported in literature [22] and data are reported in Table 1. The degree of polymerization in the H_2L ligand was estimated to about 8.

Infrared spectra

The IR spectra of copolymeric ligand (HQDMA) and all of its polymeric metal chelates show that they resemble each other in their general shape. Comparison of the IR spectra of copolymeric ligand (HQDMA) and its polymeric metal chelates have shown some important characteristic differences (Table 2).

The four characteristic fundamental frequencies of 8-hydroxyquinoline ring in ligand are observed at 1650, 1565, 1500 and 1460 cm^{-1} as expected on the basis of literature reports [23]. A broad band at 3335–3550 cm^{-1} and a medium band at 1420 cm^{-1} are attributed to –OH stretching and bending vibration of phenolic group of 8-hydroxyquinoline. One of the significant difference that have been observed in the IR spectrum of the parent ligand and that of its polymeric metal chelates is the presence of more broadened bands in the region of 3300–3600 cm^{-1} in the IR spectra polymeric chelates because of the formation of a coordination bonds with the metal ions through oxygen atom of phenolic group of 8-hydroxyquinoline as well as may be due to coordination of water molecule. Another noticeable difference is that the band due to the C–N stretching vibration of 8-hydroxyquinoline at 1580 cm^{-1} in the IR spectrum of H_2L is shifted to a lower frequency i.e. 1572–1560 cm^{-1}. A weak band at 1110 cm^{-1} corresponding to C–O–M stretching, and the two bands around 770 and 650 cm^{-1} correspond to the M–N vibration. Another medium band at 1420 cm^{-1} in the spectrum of the copolymeric ligand (HQDMA) is due to the O–H inplane bending vibration of phenolic group [23]. This band was appeared at 1408–1400 cm^{-1} in the IR spectra of polymeric metal chelates indicating a negative shift of 10–15 cm^{-1} with decreased intensity supporting the coordination of metal ion with oxygen atom. Further, the appearance of two sharp new bands at 1110 and 502 cm^{-1} corresponding to the stretching vibration of C–O–M bond and M–O bond [23] formed in chelation and the coordination of ligand with metal through nitrogen atom of the quinolinol ring can be evident from the negative shift (5–20 cm^{-1}) in characteristic stretching frequency of C=C/C=N at 1630 and 1580 cm^{-1}, respectively in the IR spectra of chelates.

Table 1 Physical and analytical data of the ligand (H_2L) and its polymeric metal chelates (ML)

Compound	Empirical formula of repeat unit of polymer	Formula mass of repeat unit of polymer	Yield/%	Colour	Elemental analyses/% found (calcd.) C	H	N	M	$\overline{M}_n$
H_2L	$C_{14}H_{13}NO_2$	227.00	72	light brown	74.15 (74.44)	5.12 (5.72)	6.05 (6.16)	–	1877.00
$[CuL(H_2O)_2]_n$	$Cu{:}C_{28}H_{24}N_2O_4{\cdot}2H_2O$	533.54	84	brown	62.17 (62.97)	4.42 (4.87)	5.13 (5.24)	11.13 (11.90)	4264.85
$[CoL(H_2O)_2]_n$	$Co{:}C_{28}H_{24}N_2O_4{\cdot}2H_2O$	546.93	85	brown	61.28 (61.43)	5.01 (5.11)	5.03 (5.11)	10.15 (10.77)	4376.50
$[NiL(H_2O)_2]_n$	$Ni{:}C_{28}H_{24}N_2O_4{\cdot}2H_2O$	546.71	92	brown	61.13 (61.45)	5.10 (5.12)	5.19 (5.12)	10.12 (10.73)	4368.62
$[MnL(H_2O)_2]_n$	$Mn{:}C_{28}H_{24}N_2O_4{\cdot}2H_2O$	542.94	81	light brown	61.21 (61.88)	5.07 (5.15)	5.05 (5.15)	10.07 (10.11)	4344.46
$[ZnL(H_2O)_2]_n$	$Zn{:}C_{28}H_{24}N_2O_4{\cdot}2H_2O$	517.37	90	light brown	64.29 (64.94)	4.53 (4.63)	5.07 (5.41)	12.26 (12.63)	4136.18

Table 2 IR bands electronic spectra and magnetic moments of the ligand (H_2L) and its polymeric metal chelates (ML)

Compounds	IR bands/cm^{-1} ν_{-OH}	ν_{C-N}	$\nu_{C=C-(aromatic)}$	ν_{C-O-M}	ν_{M-O}	$\nu_{C=O}$	ν_{-CH_2-}	electronic spectra and magnetic moments Absorption bands/cm^{-1}	Transition	μ_{eff}/B.M.
H_2L	3400 1420	1580	1556	—	—	1720	2920 2850	–	–	–
$[CuL(H_2O)_2]_n$	3440 1408	1560	1546	1110	504	1700	2940 2850	26.115 15.970	charge transfer $^2Eg\rightarrow{}^2T_{2g}$	1.73
$[CoL(H_2O)_2]_n$	3442 1410	1569	1538	1106	502	1710	2942 2852	23.200 15.565 8.938	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$	3.88
$[NiL(H_2O)_2]_n$	3432 1400	1570	1542	1108	502	1702	2945 2858	26.315 16.666 9.302	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ $^3A_{2g}(P)\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{2g}(P)$	3.30
$[MnL(H_2O)_2]_n$	3426 1402	1572	1540	1110	500	1708	2942 2860	22.435 18.650 15.550	$^6A_{1g}\rightarrow{}^4A_{1g}.\ {}^4Eg$ $^6A_{1g}\rightarrow{}^4T_{2g}(4G)$ $^6A_{1g}\rightarrow{}^4T_{1g}(4G)$	5.92
$[ZnL(H_2O)_2]_n^*$	3431 1408	1562	1544	1111	503	1706	2938 2848	–	–	D

*Zn-AFO is diamagnetic (D) in nature

Table 3 TG data and thermal decomposition parameters of ligand (H_2L) and its polymeric metal chelates (ML)

Compounds	Percentage mass loss at different temperature/°C												T_0/ °C	T_{10}/ °C	PDT	IPDT	Activation energy E_a/kJ mol^{-1}
	100	150	200	250	300	350	400	450	500	550	600	650					
H_2L	1.37	2.73	4.10	8.18	8.80	11.50	24.70	26.54	38.79	68.72	87.76	97.50	25	350	550	553.87	48.41
$[CuL(H_2O)_2]_n$	12.07	12.66	13.26	27.50	84.00	84.50	–	–	–	–	–	–	25	195	250	350.00	30.96
$[CoL(H_2O)_2]_n$	7.50	8.16	8.94	10.21	13.61	38.46	76.20	83.00	–	–	–	–	25	265	350	375.00	36.40
$[NiL(H_2O)_2]_n$	7.38	12.51	15.98	19.45	25.70	33.34	80.98	81.67	–	–	–	–	25	200	350	433.00	35.56
$[MnL(H_2O)_2]_n$	3.82	7.40	10.98	14.28	16.51	25.25	30.25	45.23	68.37	86.38	–	–	25	300	500	513.75	38.91
$[ZnL(H_2O)_2]_n$	4.15	7.40	9.10	12.34	16.45	21.38	25.47	40.23	65.64	83.63	–	–	25	300	450	467.00	37.66

PDT=temperature for maximum rate of thermal decomposition
IPDT=integral procedural decomposition temperature

The two weak bands at 2940 and 2860 cm^{-1} are attributed to aliphatic stretching vibrations of methylene groups (–CH_2–) [24] and a sharp band at 1700–1710 cm^{-1} attributed to the carbonyl group (=C=O), of dimethylolacetone group present in both copolymeric ligand and of polymeric metal chelates. In conclusion, all of these inferences of IR data support our proposed structure of HQDMA (H_2L) copolymeric ligand and its polymeric metal chelates (ML) as shown in Scheme 1.

Magnetic moments and electronic spectra

Magnetic moments (μ_{eff}) of the polymeric metal chelates are given in Table 2. Examination of these data reveals that all the polymeric metal chelates other than that of Zn(II) are paramagnetic, while that of Zn(II) is diamagnetic in nature. The results of electronic spectra (Table 2) and that of magnetic moment indicate the octahedral geometry for Cu-HQDMA, Ni-HQDMA, Co-HQDMA and Mn-HQDMA polymeric metal chelates [25–27].

Thermogravimetric studies

For the preliminary comparison of diverse polymeric materials, the methods, which has so far proved most versatile is the thermogravimetric analysis (TG) in the dry nitrogen atmosphere because it gives the true value of residual mass as function of temperature and time. However, in TG, the analytical results are not only dependent upon the types of thermal decomposition reaction, but they are also affected by the procedural details such as sample size, particle size, atmosphere employed, heating rate etc. and therefore TG results are highly empirical and trivial. In order to furnish such results in a more definite order, the two methods ‘differential procedural decomposition temperature (PDT)’ and ‘integral procedural decomposition temperature (IPDT)’ are used. In the first method, PDT is estimated from the peak maxima of DTG, where as IPDT can be obtained from the normalized data of curve, a method reported in literature [28] and the other parameters T_0, T_{10} and IPDT are estimated for studying the thermal stability. Accordingly, in the present study, the thermal stability was estimated in terms IPDT and PDT by using the equation:

$$\text{IPDT}=$$

$$T_0+\frac{\text{area under the peak of normalized curve}}{\text{total area of the curve}}(T_\mathrm{f}-T_0)$$

where, T_0=initial temperature, T_f=final temperature. These data of T_0, T_{10}, PDT and IPDT of thermal decomposition of parent ligand and its chelates are given in Table 3.

Scrutinization of the results of thermogravimetric analyses (TG) of copolymeric ligand reveals the two steps degradation process (Fig. 1). A very slight decrease in mass loss (2–3%) depicted from the curve in the temperature range 50–150°C for the copolymeric ligand may be attributed to loosely hold moisture present [29] in the polymeric ligand. The temperature range for the first and the second step of thermal degradation are observed at 150–350 and 350–650°C, respectively. These two steps of thermal degradation in ligand can be explained as; the first step of decomposition may be due to minor degradation that has occurred in aliphatic bridge attached to oxine moiety. The mass loss occurred in this step is equal to 11.58% (cal. 12.43%) based on the assumption of dimethylolacetone of copolymeric ligand. While the second fast decomposition step of degradation is due to complete degradation of the ligand with 97.5% mass loss. Hence, these results suggest the following probable stages of thermal degradation;

$$(i)\qquad [H_2L]{\cdot}nH_2O\xrightarrow[50\text{–}150°\text{C}]{\text{loss of moisture}}[H_2L]+nH_2O$$

$$(ii)\quad [H_2L]\xrightarrow[150\text{–}350°\text{C}]{}\begin{array}{l}\text{8HQ+loss of aliphatic chain}\\ –CH_2–CH_2–CO–CH_2–CH_2–\end{array}$$

$$(iii)\qquad \text{8HQ}\xrightarrow[350\text{–}650°\text{C}]{}\text{97.5\% loss}$$

Similarly, scrutinization of the results of thermogravimetric analyses (TG) of polymeric metal chelates reveals the single step degradation process (Fig. 1). Initially mass loss occurred below 150°C in thermal degradation of all of the polymeric chelates may be due to mass loss of hydrated water, where as that obtained in the temperature range 150–200°C might be due to presence of metal coordinated two water molecules [29]. This water loss is remarkably high about 7% and it is in agreement with the calculated mass loss (7.5%) assuming the presence of two coordinated water molecules and also satisfies the six coordinated sites of metal atom. All the polymeric chelates undergo thermal degradation in a single step in the temperature range of 200–550°C in contrast to two steps thermal degradation of parent polymeric ligand. The temperature at which the thermal degra-

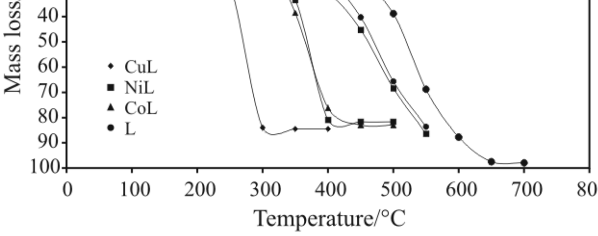


Fig. 1 Curves of HQDMA and its polymeric chelates

dation initiated in a series of five metal chelates is almost same as in the polymer ligand, however it occurred very fast in chelates as compared to that in parent ligand. This evidence may suggest that the parent ligand is thermally more stable than its polymeric metal chelates and can be explicable on the basis of either the thermal decomposition of metal chelates may catalytically be induced by the metal ions [30] or the metal atom in chelates might have developed a considerable strain in the ring of chelates. Further, the mode of thermal degradation in each of the polymer chelates is found to be similar with difference in rate of thermal decomposition, which may be due to different catalytical activity of central metal atom present in each of the polymeric chelates. In conclusion, different stages on the mode of thermal decomposition and the order of thermal stability of metal chelates may be assigned as;

(A) Mode of thermal decomposition of metal chelates:

(*i*)

$$[ML(H_2O)_2]_n \cdot nH_2O \xrightarrow[50\text{–}110°\text{C}]{\text{loss of moisture}} [ML(H_2O)_2]_n + nH_2O$$

(*ii*)

$$[ML(H_2O)_2]_n \xrightarrow[110\text{–}200°\text{C}]{\substack{\text{loss of coordinated}\\ \text{water molecules}}} [ML]_n + 2H_2O$$

(*iii*)

$$[ML]_n \xrightarrow[200\text{–}550°\text{C}]{} \text{metal oxide}$$

(B) The order of thermal stability of metal chelates:

Zn-HQDMA>Mn-HQDMA>Co-HQDMA≅
Ni-HQDMA>Cu-HQDMA

A comparative study of thermal stability of polymeric chelates has also been carried out with a view to examine structure property relationship [28, 31]. For this purpose the thermal parameters such as T_0, T_{10}, PDT, IPDT are estimated and are furnished in Table 3. The significant difference is observed in the temperatures corresponding to T_{10}, PDT and IPDT. The values of these temperatures are higher in the case of polymeric ligand as compared to those of its metal polymeric chelates indicating that parent polymeric ligand is thermally more stable than its polymeric chelates. The selected normalized curve of HQDMA and Zn-HQDMA polymeric chelates are shown in Fig. 2. Scrutinization of PDT and IPDT values of polymeric chelates have indicated that the Cu-HQDMA polymeric chelates have the least thermal stability, whereas Zn-HQDMA polymeric chelate is the most stable of the five metal polymeric chelates having thermal stability comparable to that of parent copolymeric ligand (HQDMA). Thus, the results of thermogravimetric analyses of polymeric ligand and its polymeric chelates reveal that the polymeric ligand is thermally more stable than its polymeric metal chelates.

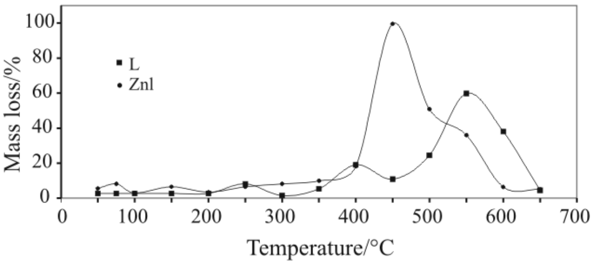


Fig. 2 Normalized curves of ■ – L and ● – ZnL

Further, it is reported in literature that polymers may decompose back to either the monomer or may produce unsaturated hydrocarbons from chain fragments of varying length like alkanes, alkenes and dienes. The kinetics of this rapid process is approximately first order [32]. On the basis of this assumption several methods are reported in literature for the study of kinetics of thermogravimetry. Sharp [33] has made a critical comparison of three methods namely Freeman and Caroll [34], Coat and Redferm [35] and Achar and Brindley [36], and reported that the later two methods can lead to satisfactory kinetic parameters of thermal degradation. Later on, Broido [37] has proposed a very simple and sensitive graphical methods for estimation of kinetic parameters. He proposed the following equation;

$$\ln[\ln(1/y)]=(E_a/R)(1/T)+\text{constant}$$

where the energy of activation 'E_a' is computed from the slope of the plot of ln[(ln(1/*y*)] *vs.* (1/*T*) and reported in Table 3.

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

where R is a gas constant (1.987 kcal mol^{-1}), T=temperature and Y=fraction of numbers of initial molecules.

The energy of activation of parent ligand is 11.57 kcal mol^{-1} for polymeric ligand and those of metal chelates are in the range of 7.4–9.3 kcal mol^{-1}, further supporting the higher thermal stability of copolymeric ligand than polymeric metal chelates.

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