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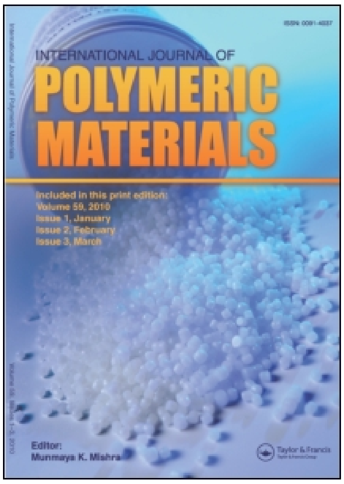

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Polymeric chelates of epoxy based polyesters containing oxine as pendent groups

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POLYMERIC CHELATES OF EPOXY BASED POLYESTERS CONTAINING OXINE AS PENDENT GROUPS

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Polymer chelates of epoxy based polyester ligands containing oxine as pendent group, have been prepared with different metal ions like Zn^{+2}, Cu^{+2}, Ni^{+2} and Co^{+2}. These novel polymer ligands have been synthesized by condensation of 5-chloromethyl-8-quinolinol hydrochloride respectively with epoxy based prepolyhydroxy ester of succinic acid (EPPE-Su) and of sebacic acid (EPPE-Se) in presence of base catalyst. All these polymer ligands and polymer chelates are characterized by elemental analyses, IR and diffuse reflectance spectral studies for their structure determination. The thermal stability of all polymer chelates have been estimated by thermogravimetric analyses (TGA). Besides this, all the polychelates have also been characterized for their magnetic susceptibility and metal to ligand stoichiometry estimation.

Keywords: polychelates, EPPE-Su, EPPE-Se, oxine

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INTRODUCTION

In last few decades polymer chelates derived from polymer ligands attracted the attention of many investigators [1, 2]. An efficient method for synthesizing such chelates is to introduce a metal ion in preformed polymer ligand. Literature survey reveals that polymers bearing 8-quinolinol moiety have many potential applications in areas such as waste water treatment to recover metals, protective coatings, water disinfectants, antifouling paints, antimicrobial, surgical materials, gels and ointment for medical uses [3–9].

Manolova *et al.* [3] published a series of papers on polymers and copolymers of 8-quinolinol either present as end group or as pendent group with a view to study their complexing ability and biological activity [4–10]. On the basis of this, the present authors have made an attempt to synthesize novel

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polymer ligands of polyhydroxyester containing 8-quinolinol as a pendent group, namely [5-methyleneoxy-8-quinolinoyl] polyesters (MQP) which have not been yet reported. In this ligand, the 5-position of 8-quinolinol has been blocked by the condensation reaction of 5-chloromethyl-8-quinolinol hydrochloride respectively with polyhydroxyester of EPPE-Su and EPPE-Se with a view to obtain only the chelating site of 8-quinolinol to be free. The metal chelates of two such (MQP-Su and MQP-Se) ligands have been prepared by using Cu^{+2}, Co^{+2}, Ni^{+2} and Zn^{+2} transition metal ions. Both preformed ligands and their metal chelates have been characterized further as discussed in the following experimental section.

EXPERIMENTAL

Materials

All the chemicals were of LR grade. Commercial epoxy resin, (DGEBA *i.e.*, diglycidyl ether of bisphenol-A) was purchased from Merigold Paints, Vallabh Vidyanagar, India. The epoxy equivalent of this DGEBA was found to be ≈ 200.

Procedures

The two parent polyhydroxyester ligands [MQP-Su and MQP-Se] were synthesized by polycondensation of two polyester resins EPPE-Su and EPPE-Se of DGEBA respectively with two aliphatic acids, *viz*.- succinic acid and sebacic acid; followed by the reaction with 5-chloromethyl-8-quinolinol hydrochloride. The experimental details are as follows:

Synthesis of Polymeric Ligands

The parent ligands [(MQP-Su) and (MQP-Se)] were prepared in three steps as:

(1) Synthesis of polyhydroxy esters (EPPE-Su; EPPE-Se): Polyhydroxy esters (EPPE-Su; EPPE-Se) were prepared by following the method reported in literature [11]. For this purpose, in a stirred glass round bottom flask with condenser, DGEBA (0.1 mole) and succinic acid (0.12 mole) in 50 ml acetone were mixed, followed by the addition of 10% pyridine (based on weight of DGEBA) as catalyst. The reaction mixture was refluxed until the reaction mixture gave the negative test for epoxy group [12]. After completion of the reaction, the reaction mixture was washed several times with large amount of acetone to remove unreacted succinic acid. The resin thus obtained was viscous liquid of polyhydroxy esters of succinic acid (EPPE-Su). Similarly polyhydroxy ester of sebacic

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acid (EPPE-Se) was prepared. Both were found to be soluble in alcohol and their yield was about 70%.

(2) Preparation of 5-chloromethyl-8-quinolinol hydrochloride: 5-chloromethyl-8-quinolinol hydrochloride was prepared by chloromethylation of 8-quinolinol reported in literature [13]. Accordingly, a mixture of 8-quinolinol (7.3 gm, 0.05 mole), concd. HCl (8 ml) and 37% formalin solution (8 ml, 0.05 mole) was treated with dry gaseous hydrochloric acid for 1.5 hr. The resulting yellow solid was filtered, washed and dried. The yield was 77% and m.p. 280°C.

(3) Preparation of polymer ligands (MQP-Su; MQP-Se): MQP-Su and MQP-Se were prepared by employing the method reported for 5-alkoxymethyl-8-quinolinol [13]. According to this method sodium bicarbonate (0.1 mole) was added to a suspension of 5-chloromethyl-8-quinolinol hydrochloride (0.1 mole) and EPPE-Su (0.05 mole) in THF. The reaction mixture was refluxed for 2 hr. with frequent shaking. The resulting solution was made alkaline with dilute ammonia solution and the solid separated was filtered off. The solid MQP-Su was collected and dried. The yield was 65%. It was green in color. MQP-Se was prepared in a similar manner.

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Synthesis of Polymer Chelates

The metal chelates of MQP-Su and MQP-Se preformed polymer ligands were synthesized by reaction with corresponding metal acetates. The detail procedure is as follows:

A dried MQP-Su polymer (0.01 mole) was dissolved in 200 ml aqueous solution of 20% formic acid and warmed on a water bath for 10 minutes. To this solution, a warm solution of metal acetate (0.01 mole) in 50% aqueous formic acid solution was added drop wise with constant stirring. The reaction mixture was made alkaline with dilute ammonia solution in order to precipitate out polymer chelates. The resultant contents were further digested on water bath for an hour. Finally, the solid polymer chelates were filtered off, washed with hot water followed by acetone, DMF and dried in air. The polymer chelates of MQP-Su and MQP-Se with Cu^{+2}, Ni^{+2}, Co^{+2} and Zn^{+2} metal ions are prepared in a similar manner.

Measurements

Elemental analyses for C, H and N content were carried out on Carlo Erba elemental analyzer (Italy). IR spectra of polymer ligands and their metal chelates were scanned on a NICOLET-400 DR FTIR spectrophotometer in KBr phase. The metal content analyses of polychelates were performed by decomposing a weighed amount of each polymer chelate followed by EDTA titration as reported in literature [14].

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Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using Mercury tetrathiocynato cobaltate(II) $Hg[Co(NCS)_4]$ as a calibrant. The diffuse reflectance spectra of all the solid polychelates were recorded on a Backman DK-2A spectrophotometer with solid reflectance attachments. MgO was employed as the reference compound. Thermal behavior of these metal chelates were studied by TGA performed on Du Pont 950 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Characterization of Polymer Ligands MQP-Su and MQP-Se

Both MQP-Su and MQP-Se were light green powders, soluble in solvents such as water, acetone, dioxane, DMSO and DMF. Results of elemental analyses of MQP-Su and MQP-Se for C, H and N reported in Tables 1 and 2 are found to be consistent with the predicted structure as shown in Scheme 1.

TABLE 1 Elemental analyses and magnetic moment of MQP-Su and their metal chelates

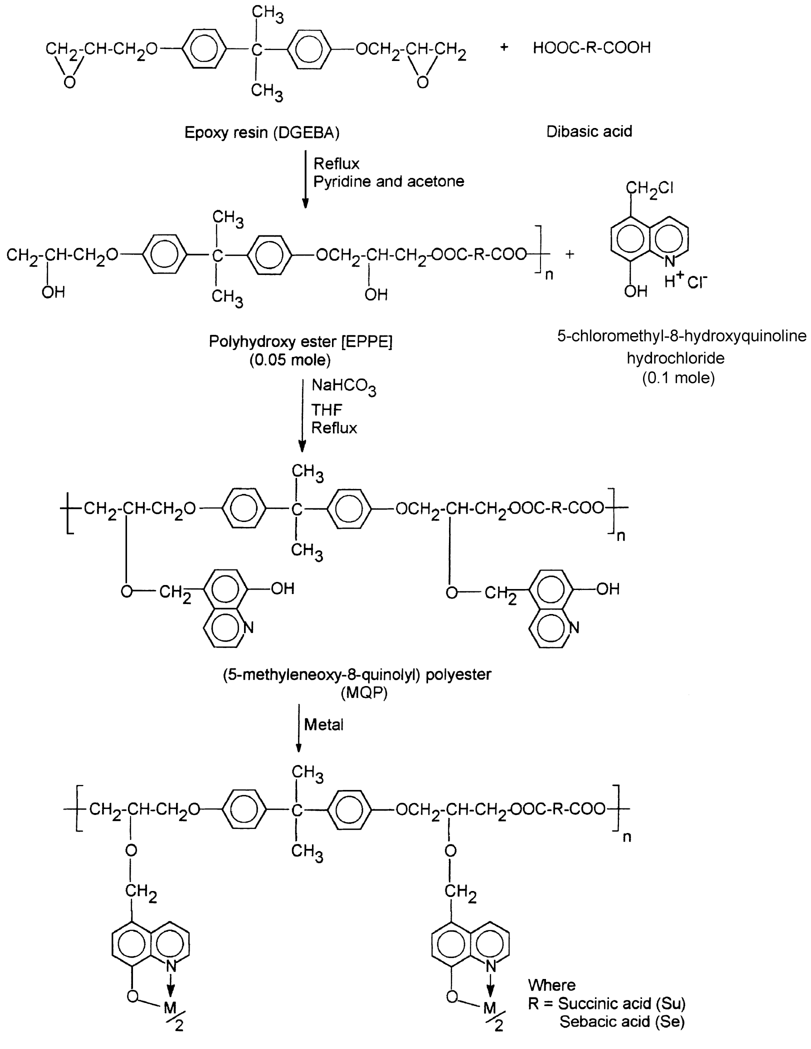
	Elemental analyses								
Sample	*C%*		*H%*		*N%*		*M%*		μ_{eff}
designation	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*B.M.*
MQP-Su	69.94	69.50	5.69	5.12	3.62	3.17	–	–	–
MQP-Su(Cu^{+2})	64.78	64.11	5.03	4.95	3.35	3.02	7.62	7.02	1.79
MQP-Su(Ni^{+2})	65.16	65.01	5.06	4.91	3.37	3.13	7.08	7.01	3.02
MQP-Su(Co^{+2})	65.14	65.07	5.06	4.83	3.37	3.17	7.10	6.83	4.01
MQP-Su(Zn^{+2})	64.64	64.25	5.02	4.89	3.35	3.29	7.82	7.17	D

D = Diamagnetic.

TABLE 2 Elemental analyses and magnetic moment of MQP-Se and their metal chelates

	Elemental analyses								
Sample	*C%*		*H%*		*N%*		*M%*		μ_{eff}
designation	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*B.M.*
MQP-Se	71.49	71.12	6.50	6.32	3.27	2.97	–	–	–
MQP-Se(Cu^{+2})	66.55	66.52	6.09	5.87	3.0	2.80	6.90	6.50	1.72
MQP-Se(Ni^{+2})	66.90	66.50	6.12	5.92	3.06	2.93	6.41	6.14	3.1
MQP-Se(Co^{+2})	66.88	66.44	6.12	5.89	3.06	2.97	6.44	6.20	4.12
MQP-Se(Zn^{+2})	66.42	66.14	6.07	5.91	3.03	2.87	7.09	6.93	D

D = Diamagnetic.



SCHEME 1

IR spectra of both polymer ligands are shown in Figure 1. Examination of these spectra reveals that they are found to be similar in shape. A broad band in the range of 3370 – 3400 cm^{-1} is assigned to stretching vibration of O—H bonded with ring containing nitrogen [15]. The absorption bands at 1465,1430,1512 and 1606 cm^{-1} in the IR spectra of MQP-Su and bands at 1468,1420,1501 and 1600 cm^{-1} in the IR spectra of MQP-Se are characteristics for 8-quinolinol moiety [16]. The weak bands at 2726 and 2820 cm^{-1} attributes to aliphatic stretching vibration of methylene groups

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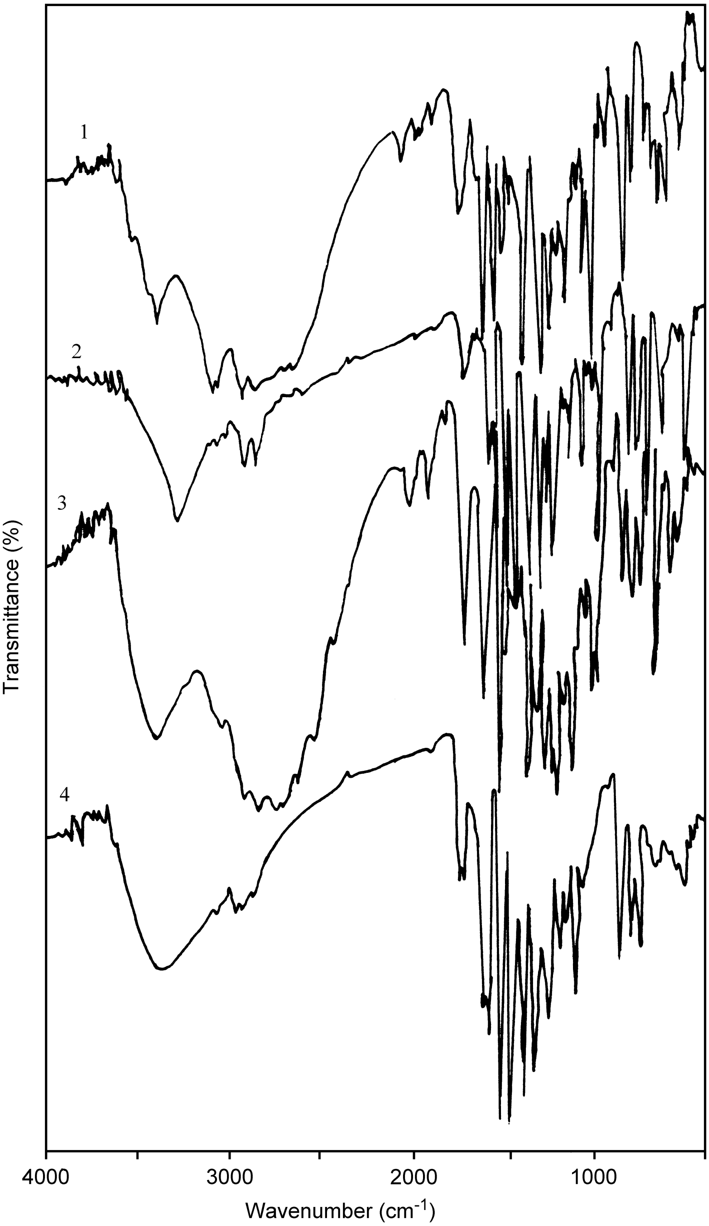

FIGURE 1 FT-IR spectra of: 1, MQP(Se); 2, MQP(Se)-Cu^{+2}; 3, MQP(Su); 4, MQP(Su)-Cu^{+2}.

(—CH_2—) and at 1065 and 1165 cm^{-1} are due to C—O stretching of aliphatic ether group. An intense and clear band of an ester carbonyl ($>C{=}O$) of polyhydroxy ester has been indicated by the strong absorption frequency around 1735 cm^{-1}. In addition to these evidences of MQP-Su and MQP-Se ligands, the IR spectrum of parent ligands has many characteristic bands occurring in 5,5′-methylene bis(8-quinolinol) [17], further conforming the predicted structure as shown in Scheme 1.

The thermal behavior of polymer ligands MQP-Su and MQP-Se were studied by thermogravimetric analyses. The TGA data of polymer ligands are reported in Tables 3 and 4, and their thermograms are shown in Figure 2. Examination of these data reveals that both the ligands degrade in a single step and decompose in the temperature range of 300–450°C. Almost 90% weight loss is reached at 500–600°C temperature.

Characterization of Polymer Chelates

The polymer chelates of MQP-Su and MQP-Se with different metal ions such as Cu^{+2}, Ni^{+2}, Co^{+2} and Zn^{+2} vary in color from dark green to brown. IR spectrum of some selected polymer chelates are shown in Figure 1. They generally resemble each other. Comparison of IR spectra of the parent ligands with their polymer chelates has revealed certain characteristics differences as mentioned below.

One of the significant differences to be expected between IR spectrum of parent ligand and its metal chelates is the absence of a broad band in the region of 3370–3450 cm^{-1} due to O—H stretching vibration frequencies in IR spectrum of polymer chelates as the oxygen of this O—H of parent ligand has formed a bond with the metal ion. However, this band has become more broad in the IR spectrum of polychelates. This is explicable by the fact that water molecules might have strongly absorbed to the chelates during the formation.

Another noticeable difference is that the bands due to C=N stretching vibration of 8-quinolinol at 1606 cm^{-1} in IR spectrum of MQP-Su and MQP-Se are shifted to lower frequency. The band at 1400 cm^{-1} in the IR spectrum of MQP-Su and MQP-Se has assigned to inplane O—H deformation and this is shifted towards higher frequency in the spectra of polymer chelates indicating the formation of metal-oxygen bonds [15]. This has been further confirmed by a weak band at 1100 cm^{-1}, corresponding to C—O—M stretching frequency [15]. All these characteristic features of IR suggest the general structure of polymer chelates as shown in Scheme 1.

Examination of data about metal content in each polymer chelates (Tabs. 1 and 2) has revealed a 1 : 1 metal : ligand stoichiometry in all the polychelates. Magnetic moment (μ_{eff}) data of polymer chelates given in Tables 1 and 2 reveals that all metal chelates like Cu^{+2}, Ni^{+2} and Co^{+2} are

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TABLE 3 Thermogravimetric analysis of EPPE-Su, MQP-Su, and its metal chelates

	% Weight loss at different temperature(°C)											
Sample	100	200	300	400	450	500	550	600	T_0°C	T_{10}°C	PDT[a]	$IPDT$[b]
EPPE-Su	8	18	59	85	90	94	–	–	50	175	300	471
MQP-Su	3	6	15	33	50	60	65	70	50	200	450	551
MQP-Su(Cu^{+2})	3	5	16	44	54	64	69	72	50	225	400	596
MQP-Su(Ni^{+2})	6	8	23	68	84	92	95	97	50	200	325	592
MQP-Su(Co^{+2})	7	8	22	66	72	77	81	83	50	200	350	594
MQP-Su(Zn^{+2})	4	14	52	74	79	82	85	86	50	180	310	590

[a] PDT(Temperature for maximum rate of polymer degradation).

[b] IPDT(Intigral procedural decomposition temperature).

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TABLE 4 Thermogravimetric analysis of EPPE-Se, MQP-Se, and its metal chelates

	% Weight loss at different temperature(°C)											
Sample	100	200	300	400	450	500	550	600	T_0°C	T_{10}°C	*PDT*[a]	*IPDT*[b]
EPPE-Se	7	24	63	75	77	78	79	80	50	135	250	442
MQP-Se	5	7	18	46	59	66	71	74	50	175	450	564
MQP-Se(Cu^{+2})	1	4	14	32	48	58	64	68	50	225	425	597
MQP-Se(Ni^{+2})	6	12	29	71	77	82	83	86	50	175	325	585
MQP-Se(Co^{+2})	5	15	30	60	70	77	87	90	50	175	350	595
MQP-Se(Zn^{+2})	3	12	50	70	75	80	82	84	50	160	300	590

[a] PDT(Temperature for maximum rate of polymer degradation).
[b] IPDT(Intigral procedural decomposition temperature).

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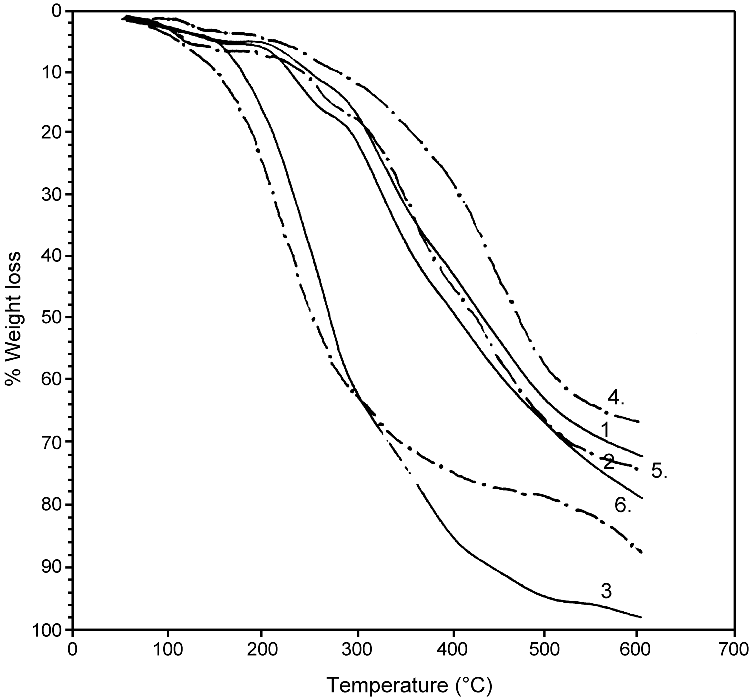

FIGURE 2 TG thermogram of: 1, MQP(Su)-Cu^{+2}; 2, MQP(Su); 3, EPPE-(Su); 4, MQP(Se)-Cu^{+2}; 5, MQP(Se); 6, EPPE-(Se).

paramagnetic, while that of Zn^{+2} is diamagnetic in nature. The electronic spectra of both MQP-Su and MQP-Se with Cu^{+2} ion show two broad bands at 14950 and 23529 cm^{-1} due to $^2T_{1g} \rightarrow {}^2E_g$ transition and charge transfer spectra respectively suggesting a distorted octahedral structure for both MQP-Cu^{+2} polymer chelates. The MQP-Su and MQP-Se with Ni^{+2} and Co^{+2} ion polychelates give two absorption bands respectively at 14925, 24096 cm^{-1} and 14925, 22471 cm^{-1} corresponding to $^4T_{1g} \rightarrow {}^2T_{1g}$, $^4T_{1g} \rightarrow {}^4T_{1g}$(P) transition [17]. Thus, absorption band of diffuse reflectance spectra and the values of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the Ni^{+2} and Co^{+2} polychelates. The spectra of polychelates of Mn^{+2} ion show two weak bands at 17241 cm^{-1} and 25031 cm^{-1} assigned to the transition $^6A_{1g} \rightarrow {}^4T_{2g}$(4G) and $^6T_{1g} \rightarrow {}^4T_{1g}$ (4G) respectively and assigned an octahedral structure for MQP-Mn^{+2} chelates. As the spectrum of the Zn^{+2} chelates is not well resolved it is not interpreted but its μ_{eff} value reveals its diamagnetic nature as expected.

The thermograms of the polyhydroxy esters, polymer ligands and their metal chelates are shown in Figure 2. TGA data were analyzed to obtain

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information about percentage weight loss at different temperatures. In addition to this, each of the thermogram was normalized with a view to obtain the value of PDT (Temperature for maximum rate of polymer degradation) and IPDT (Integral procedural decomposition temperature) according to a method reported in literature [18–20]. The thermal stability of above mentioned polymer samples was obtained on the basis of evaluating stability trend, the TGA parameters *viz.*, T_0 (Initial decomposition temperature), T_{10} (Temperature corresponds to 10% weight loss), PDT and IPDT values shown in Tables 3 and 4. The thermal parameters indicate the order of thermal stability as: metal chelates > polymer ligands > polyhydroxy esters. The rate of decomposition of all polymer chelates, is initially low up to 200°C temperature and gradually increases to maximum in the range 400–500°C. The order of thermal stability of all these polychelates is: MQP-Cu > MQP-Co > MQP-Ni > MQP-Zn.

CONCLUSION

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

Polycondensation of epoxy based polyhydroxy esters with 5-chloromethyl-8-quinolinol hydrochloride yielded a 5-methyleneoxy-8-quinolinoyl polyester (MQP) polymer ligands containing oxine as a pendent groups. The applicability of these polymer ligands was explored by preparing polymer chelates using different divalent metal ions. It indicates that the prepared polymer ligands have good chelating property and high thermal stability. The metal chelates are thermally more stable than the corresponding polymer ligands. Further the polymer chelates of Cu^{+2}, Ni^{+2} and Co^{+2} are paramagnetic, while that of Zn^{+2} is diamagnetic in nature.

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