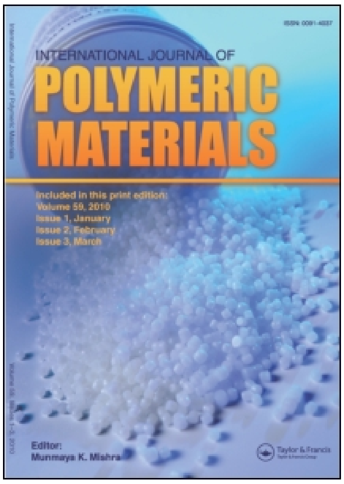

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Arun Singh[a]; Jayesh Bhanderi[a]
[a] Department of Chemistry, Government Geetanjali P.G. Girls College, Bhopal, India

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Poly(Ester Amide) with Pendent 8-Quinolinol Moiety as a Novel Oligomeric Ligand

Arun Singh and Jayesh Bhanderi
Department of Chemistry, Government Geetanjali P.G. Girls College,
Bhopal, India

The poly(ester amide) (PEA) was prepared by polycondensation of 1,4-phenylene-bisphthalamic acid and the epoxy resin diglycidyl ether of bisphenol-A. The PEA was then treated with 5-chloromethyl-8-quinolinol hydrochloride. The resultant oligomer, designated as PEA-8-quinolinol (PEAQ), was characterized by elemental analysis, IR spectral studies and thermogravimetry. The metal chelates of PEAQ with Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, *and* Co^{2+} *metal ions were prepared and characterized by metal:ligand ratio, IR and reflectance studies, magnetic properties, thermogravimetry and microbicidal activity.*

Keywords: epoxy resin, magnetic properties, microbicidal activity, oligomeric, polyester amide, metal chelates, spectral studies, thermogravimetry

INTRODUCTION

A survey of the literature reveals that polymers bearing 8-quinolinol moiety have many potential applications in areas such as wastewater treatment to recover metals, protective coatings, water disinfectants, antifouling paints, antimicrobial, surgical materials, and gels and ointment for medical uses [1–7]. Several scientists [8–11] published a series of papers on polymers and copolymers of 8-quinolinol either present as an end group or as a pendent group with a view to study their complexing ability and biological activity. A study of 8-quinolinol containing polyester has also been reported [12]. On the basis of this,

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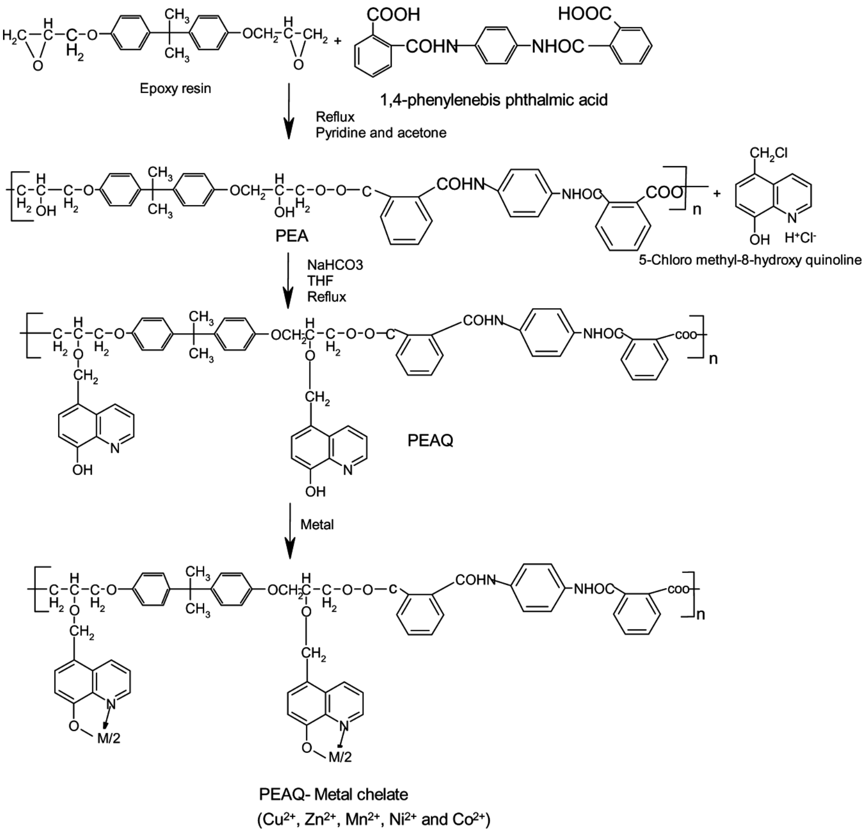
Address correspondence to Arun Singh, Department of Chemistry, Government Geetanjali P.G. Girls College, Bhopal, India. E-mail: dr.arunsingh@rediffmail.com



SCHEME 1 Synthesis of PEAQ-metal chelates.

the present authors have made an attempt to synthesize poly(ester amide) containing 8-quinolinol as a pendent group. The synthesis, characterization and chelating properties of the novel (5-methyleneoxy 8-quinolinolyl) poly(ester amide) PEAQ are being presented in this communication. The whole research work is shown in Scheme 1.

EXPERIMENTAL

Materials

All the chemicals were of LR grade. Commercial epoxy resin (DGEBA, diglycidyl ether of bisphenol-A) was purchased from the local market. The epoxy equivalent of this DGEBA was found to be ≈170. The bisamic acid 1,4-phenylenebisphthalamic acid was prepared by a reported method [13].

Synthesis of Polymeric Ligands

The ligand PEAQ was prepared as follows.

Synthesis of Poly(Ester Amide) (PEA)

The synthesis of PEA was prepared by a method reported for the synthesis of PEA based on unsaturated bisamic acid and diamine [14]. In a stirred glass round-bottom flask with condenser, DGEBA (0.1 mol) and 1,4-phenylenebisphthalamic acid (0.12 mol) in 50 ml acetone were mixed, followed by the addition of 1 ml pyridine as catalyst. The reaction mixture was refluxed until the reaction mixture gave a negative test for epoxy group [15]. After completion of the reaction, attaining a constant acid value i.e., 50 mg KOH/gm, the reaction product was washed several times with large amounts of acetone to remove unreacted reactants. The poly(ester amide) resin thus obtained was in the form of a semisolid mass. Yield was 90%.

Analysis:

$(C_{43}H_{40}N_2O_8)_n$ $(712)_n$

	C %	H %	N %
Calcd	72.47	5.61	3.93
Found	72.3	5.6	3.9

M_n(VPO)(DMF): 4400. The M_n value indicates our product to be an Oligomer in nature and not a truly high molecular weight polymer.

Preparation of 5-Chloromethyl-8-Quinolinol Hydrochloride

According to the reported method [16], a mixture of 8-quinolinol (7.3 gm 0.05 mol) concd HCl (8 ml) and 37% formalin solution (8 ml 0.05 mol) was treated with dry gaseous hydrochloric acid for 1.5 h. The resulting yellow solid was filtered, washed and dried. The yield was 77% and m.p. 280°C [16].

Preparation of Polymeric Ligand PEAQ

It was prepared by employing the method reported for 5-alkoxymethyl 8-quinolinol [16]. According to this method, sodium bicarbonate (0.1 mol) was added to a suspension of 5-chloromethyl 8-quinolinol hydrochloride (0.1 mol) and PEA (0.05 mol) in THF. The reaction mixture was refluxed for 2 h with frequent shaking. The resulting mixture was made alkaline with dilute ammonia solution and the separated solid was filtered off. The solid PEAQ was collected, washed with alcohol and air-dried. The yield was 65%. It was green in color.

Synthesis of Polymeric Chelates

The polymeric metal chelates of PEAQ were synthesized by reaction of PEAQ with the corresponding metal acetates. The detailed procedure is as follows.

A dried PEAQ polymer (0.01 mol) was dissolved in 200 ml aqueous solution of 20% formic acid and warmed on a water bath for 10 min. To this solution a warm solution of metal acetate (0.01 mol) in 50% aqueous formic acid solution was added dropwise with constant stirring. The reaction mixture as made alkaline with dilute ammonia solution in order to precipitate out polymeric chelates. The resultant contents were further digested on a water bath for an hour. Finally, the solid polymer chelates were filtered off, washed with hot water followed by acetone and DMF, and dried in air. Thus the polymer chelates of PEAQ with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} transition metal ions have been prepared.

MEASUREMENTS

Elemental analyses for C, H, and N content were carried out on a TF 1101 elemental analyzer (Italy). IR spectra of polymers and their metal chelates were scanned on a NICOLET 760 DR FTIR spectrophotometer in KBr phase. The metal content of polychelates were determined by decomposing a weighed amount of each polymer chelate followed by EDTA titration as reported in the literature [17]. Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using Mercury-tetrathiocyanatocobaltate (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 a thermogravimetric analyzer.

RESULTS AND DISCUSSION

Characterization of PEAQ

The PEA sample was in the form of a pasty mass. The C, H, N contents are consistent with the predicted structure. The number average molecular weight by end group COOH analysis and by VPO method is 4400 indicating an oligometric size of the product. It was directly used for further reaction product, i.e., PEAQ.

PEAQ was light green powder insoluble in solvents such as water, acetone, dioxane, DMSO and DMF. Results of elemental analyses of PEAQ for C, H, and N, reported in Table 1, are found to be consistent with the predicted structure as shown in Scheme 1. Examination of IR spectrum of PEAQ reveals a broad band in the range of 3370–3400 cm^{-1}, assigned to stretching vibration of O−H bonded with ring-containing nitrogen [18]. The absorption bands at 1465, 1430, 1512 and 1606 cm^{-1} are characteristics for 8-quinolinol moiety [17]. The weak bands at 2726 and 2820 cm^{-1} are attributed to aliphatic chain. The band at 1165 cm^{-1} is due to C–O stretching of the aliphatic ether group. An intense and clear band of an ester and amide carbonyl of polyester amide has been indicated by the strong absorption frequency around 1735 cm^{-1}. In addition to these, the IR spectrum of the parent oligomer has many characteristic bands occurring in 5,5′methylene bis(8-quinolinol)-[18], further confirming the predicted structure as shown in Scheme 1.

The thermal behavior of PEAQ was studied by thermogravimetric analysis. The TGA data are presented in Table 2 and its thermogram is shown in Figure 1. Examination of these data reveals that the oligomer degrades in a single step and decomposes in the temperature range of 300–450°C. Almost 90% weight loss is reached at 500–600°C temperature.

TABLE 1 Elemental Analyses of PEAQ and Metal Chelates

	Elemental analysis								
	C %		H %		N %		M %		
Sample designation	Cald	Found	Cald	Found	Cald	Found	Cald	Found	Magnetic moment μ_{eff}
PEAQ	71.45	71.4	5.10	4.9	5.29	5.2	–	–	–
PEAQ (Cu^{2+})	67.52	67.5	4.64	4.6	5.00	4.9	5.67	5.6	1.78
PEAQ (Ni^{2+})	67.82	67.8	4.66	4.6	5.02	5.0	5.26	5.24	3.00
PEAQ (Co^{2+})	67.80	67.7	4.66	4.5	5.02	4.9	5.28	5.27	4.03
PEAQ (Mn^{2+})	68.05	68.0	4.68	4.6	5.04	4.8	4.94	4.90	5.39
PEAQ(Zn^{2+})	67.41	67.3	4.63	4.6	4.99	4.8	5.83	5.82	D

D = Diamagnetic.

TABLE 2 Thermogravimetric Analysis of PEAQ and its Metal Chelates

	% Weight loss at different temperature (°C)					
Sample	100	200	300	400	500	600
PEAQ	4	9	30	48	63	70
PEAQ (Cu^{2+})	2	4	20	50	70	90
PEAQ (Ni^{2+})	1.5	3	18	48	73	90
PEAQ (Co^{2+})	1.5	3	18	50	75	94
PEAQ (Zn^{2+})	2	4	19	51	74	93
PEAQ (Mn^{2+})	2	4	45	70	90	95

Characterization of Polymeric Chelates

The polymeric chelates of PEAQ with different metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Zn^{2+} vary in color from dark green to brown. The IR spectra of all of the polymeric chelate of PEAQ are similar to each other in their general shape, but the comparison of the IR spectrum of the parent PEAQ with those of its chelates has revealed certain characteristic differences.

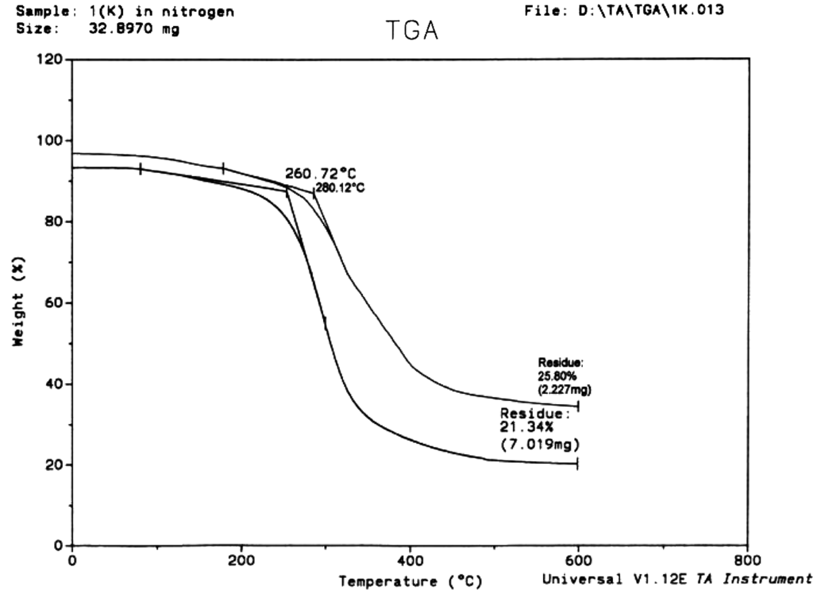


FIGURE 1 TGA thermogram of (1) PEAQ (upper) and (2) PEAQ-Mn^{+2} polychelate (lower).

One of the significant differences between the IR spectrum of the parent and that of its metal coordinated oligomers is the presence of much broader bands in the region of 3000–3600 cm^{-1} for the oligomeic chelates 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 may have been strongly absorbed to the polymer sample during its formation. Another noticeable difference is that the band, due to C=N stretching vibration of 8-hydroxyquinoline at 1600 cm^{-1} in the IR spectrum of PEAQ, is shifted to lower frequency, whereas the band at 1420 cm^{-1} in the IR spectrum of PEAQ assigned to in-plane –OH deformation [19] is shifted towards higher frequency in the spectra of the coordination oligomers. This may be due to chelation of metal with 8-hydroxyquinoline. These features have been further confirmed by a weak band at 1100 cm^{-1} corresponding to C-O-M stretching [19] and a band around 780 and 640 cm^{-1} corresponding to the M-N vibration in coordination polymers. Thus, all these characteristic features of the IR spectra suggest the structure of the polymeric chelate shown in Scheme 1.

Examination of data about metal content in each polymeric chelate (Tables 1 and 2) has revealed a 1:1 metal:ligand stoichiometry in all the polymeric chelates. Magnetic moment (μ_{eff}) data of polymer chelates given in Table 1 reveal that the metal chelates of Cu^{2+}, Ni^{2+} and

TABLE 3 Spectral Features and Magnetic Moment of PEAQ Metal Chelates

Metal chelates	Electronic spectral data (cm^{-1})	Transition	IR spectral features common for all (cm^{-1})	
PEAQ-Cu^{2+}	23529	Charge transfer	1650	Quinoline moiety
	14950	$^2B_{1g}\rightarrow^2A_{1g}$	1565	
			1500	
			1460	
PEAQ-Ni^{2+}	24096	$^3A_{2g}\rightarrow^3T_{2g}(F)$	2920	CH_2
	14925	$^3A_{1g}\rightarrow^3T_{1g}(F)$	2850	
	9025	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$	1450	
PEAQ-Co^{2+}	22471	$^4T_{1g}(F)\rightarrow^4T_{2g}(F)$	1100	C-O-M & O-M Bands
	14925	$^4T_{1g}(F)\rightarrow^4A_{2g}$	500	
	9550	$^4T_{1g}(F)\rightarrow^4T_{2g}(F)$		
PEAQ-Mn^{2+}	23869	$^6A_{1g}\rightarrow^6A_{2g}(G)$	710	Ar-Cl
	18349	$^6A_{1g}\rightarrow^4T_{2g}(G)$	750	
	16826	$^6A_{1g}\rightarrow^4T_{1g}(G)$		
PEAQ-Zn^{2+}		–	–	–

Co^{2+}, Mn^{2+} are paramagnetic, while that of Zn^{2+} is diamagnetic in nature. The electronic spectral data assignment are shown in Table 3. The diffuse electronic spectrum of PEAQ with $Cu^{+\ 2}$ ions shows two broad bands at 14950 and 23529 cm^{-1} due to $^2B_{1g}\rightarrow{}^2A_1g$ transition and charge transfer spectra, respectively, suggesting a distorted octahedral structure for PEAQ chelates. The PEAQ with Ni^{2+} and Co^{+2} ion polychelates gives two absorption groups, respectively, at 14925, 24096 and 9025 cm^{-1} corresponding to $^3A_{1g}\rightarrow 3T_1g(F)$,$^3A_{2g}\rightarrow{}^3T_2g(F)$, and $^3A_{2g}\rightarrow{}^3T_1g(P)$ and 14925, 22471, and 9550 cm^{-1} corresponding to $^4T_{1g}(F)\rightarrow{}^4A_{2g}$, $^4T_{1g}\rightarrow$ $^4T_{1g}(P)$ and $^4T_{1g}(F)\rightarrow{}^4T_2$ respectively [20–22]. 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 three weak bands at 18349 cm^{-1}, 23869 cm^{-1} and 16828 cm^{-1} assigned to the transition $^6A_{1g}\rightarrow{}^4T_{2g}(G)$, $^6A_{1g}\rightarrow{}^4T_{1g}(G)$ and $^6A_{1g}\rightarrow{}^4T_1g(G)$, respectively, and Indicating an octahedral structure for PEAQ 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 TGA data (typical in Figure 1) of all polymeric chelates are shown in Table 2. Inspection of TGA data and thermograms reveals that the rate of decomposition of all polymeric chelates is initially low, up to 200°C temperature, and rapidly increases to maximum in the range 400–500°C. This might be due to accelerated in situ formation of metal oxide. The thermal stability of all these polymeric chelates is quite similar.

CONCLUSIONS

The investigation described in the present paper reveals the following:

(i) The reaction of epoxy-based poly(ester amide) with 5-chloromethyl-8-quinolino hydrochloride affords a 5-methyleneoxy-8-quinolinoyl poly(ester amide) (PEAQ) oligomers containing 8-quinolinol as a pendent groups.

(ii) The applicability of PEAQ was explored by preparing oligomer chelates using different divalent metal ions. It indicates that the prepared ligands have good chelating property and high thermal stability.

(iii) The metal chelates are thermally less stable than the corresponding polymeric ligand. Further, the oligomeric chelates of Cu^{2+}, Ni^{2+}, and Co^{2+} are paramagnetic, while that of Zn^{+2} is diamagnetic in nature.

Further work in the connection with other polymeric ligands and ion-exchanging properties is under progress.

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