Polymer Vol. 37 No. 13, pp. 2865-2869, 1996
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0032-3861/96/$15.00+0.00

Synthesis and characterization of a new metal chelating polymer and derived Ni(II) and Cu(II) polymer complexes

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(Received 26 October 1995)

2-Hydroxy-4-acryloyloxybenzaldehyde (2H4ABA) prepared from acryloyl chloride and 2,4-dihydroxybenzaldehyde, was polymerized in 2-butanone at 65°C using benzoyl peroxide as initiator. Polychelates were obtained in *N,N*-dimethylformamide solution of poly(2H4ABA) with aqueous solution of Cu(II)/Ni(II) ions. The polymers and polychelates were characterized by elemental analysis and spectral studies. The infra-red spectral data of polychelates suggest that the metals are coordinated through the oxygen of the aldehyde group and oxygen of the phenolic-OH group. The electronic spectra, e.p.r and magnetic moments of polychelates show an octahedral and square planar structure for poly(2H4ABA)–Ni(II) and poly(2H4ABA)–Cu(II) complexes respectively. X-ray diffraction studies revealed the highly crystalline nature of polychelates. The thermal properties of polymer–metal complexes and their catalytic activity are discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(2-hydroxy-4-acryloyloxybenzaldehyde); chelating resin; catalytic activity)

INTRODUCTION

Polymer–metal complexes are currently attracting considerable attention for a variety of applications[1–6], like development in nuclear chemistry, organic synthesis, waste water treatment, pollution control, hydrometallurgy, polymer drug grafts, preconcentration and recovery of trace metal ions. In addition, they are also used as mechanochemical systems and as models of bio-inorganic systems. A number of polymer-bound chelating ligands, including polydentate amines, crown ethers and porphyrins, have been reported[7–9]. The free radical polymerization of Cu complex with Schiff's base ligand containing the vinyl group and radical polymerization of methacrylate monomers coordinated to Co(III) have been studied[10]. The preparation of pendant type polymer–metal complexes having a uniform structure by the substitution reaction between a polymer ligand and a metal ion such as Co(III) or Cr(III) has also been studied[11]. Selective chelation of specific metal ions from a metal ion mixture by using a number of tetradentate ligands attached to polystyrenedivinylbenzene have been reported[12]. Polymer containing hydroxamic acid has been studied as a polymeric chelating agent for iron. The successful studies on polymer metal complexes from this laboratory has led us to undertake a renewed look into this class of polymers[13–16]. The present study deals with the synthesis, characterization and thermal property, evaluation of a new poly(2-hydroxy-4-acryloyloxybenzaldehyde) and its Cu(II) and Ni(II) complexes.

EXPERIMENTAL

Materials

Benzoyl peroxide (BDH) was recrystallized from chloroform/methanol mixture, 2,4-dihydroxybenzaldehyde (Aldrich) was recrystallized from ethanol. Acryloyl chloride was prepared by the procedure reported elsewhere[17]. Copper acetate and nickel acetate (Fluka) were used as received.

Synthesis of 2-hydroxy-4-acryloyloxybenzaldehyde (2H4ABA)

2,4-Dihydroxybenzaldehyde (1 mmol), triethylamine (1 mmol), 2-butanone (200 ml) and hydroquinone (0.5 g) were taken in a three necked flask equipped with stirrer, thermometer and stoppered funnel and the contents were cooled to ≃ ± 5°C. Acryloyl chloride (1 mmol in 25 ml of 2-butanone) was added dropwise with constant stirring at that temperature. The reaction mixture was gradually allowed to attain room temperature and stirring continued for 2 h. The byproduct, quaternary ammonium salt, formed was filtered off. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo*. The crude 2-hydroxy-4-acryloyloxybenzaldehyde was recrystallized from ethanol (m.p. 50–52°C). The i.r. and ^1H n.m.r. spectra are consistent with the assigned structure.

Polymerization

2-Hydroxy-4-acryloyloxybenzaldehyde (2H4ABA) (3.5 mmol), 2-butanone (50 ml) and benzoyl peroxide (0.5 g) were taken in a standard reaction tube (100 ml) and purged with nitrogen gas for half an hour, closed and kept in a

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thermostat at 65°C for 6 h. A large excess of methanol was added to the content and the precipitated poly (2H4ABA) was filtered, washed with methanol and purified by *N,N*-dimethylformamide/methanol mixture. The purified polymer was dried *in vacuo* at 50°C for constant weight.

Synthesis of poly(2H4ABA)-metal chelates

Polymer-metal complexes were prepared at room temperature by solution technique. A typical procedure for the preparation of polymer-Cu(II) chelate is as follows: poly(2H4ABA) (2 mmol of repeat unit) was dissolved in 100 ml of DMF and the pH of the solution was adjusted to 7 with dilute NH_4OH. An aqueous solution of Cu(II) acetate (5 mmol) was added dropwise to the polymer solution with constant stirring. The mixture was then digested on a water bath for 2 h and kept overnight at room temperature. The precipitated poly(2H4ABA)-metal complex was filtered, washed with hot distilled water, followed by ethanol and dried at 60°C *in vacuo*. A similar procedure was adopted for the preparation of Ni(II) chelate.

Measurements

The elemental analysis of 2H4ABA, poly(2H4ABA) and the polychelates were carried out using Heareus carbon-hydrogen analyser. The amount of copper and nickel present in the polymer metal complexes were estimated using a titrimetric procedure after decomposing the polymers. The viscosity measurements of poly(2H4ABA) were made in an Ubbelohde suspended level viscometer using DMF at room temperature. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of poly(2H4ABA) were determined by gel permeation chromatography (Water 501) using THF and calibrated with polystyrene standards. The i.r. spectra of poly(2H4ABA) and metal complexes were recorded on a Perkin-Elmer 782 spectrophotometer using KBr pellet. The ^{1}H n.m.r spectrum of poly(2H4ABA) was recorded on a Hitachi 90 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard.

The magnetic moments were measured using Gouy method and corrected for the diamagnetism of the component, using Pascal's constant. The diffuse reflectance spectra (8000-26 000 cm^{-1}) were measured on a Karl-Zeiss VSU-28 spectrophotometer. The e.p.r. analysis was carried out at room temperature using a Varian spectrophotometer. X-ray diffraction experiments were performed in a Philips, PW1820 diffractometer and Statton camera, using CuKα radiation of wavelength 1.542 Å. The glass transition temperatures of poly(2H4ABA) and the metal complexes were determined by a differential scanning colorimeter with Du Pont 900 thermal analyser at a heating rate of 15°C min^{-1} in air. Thermogravimetric analysis was carried out in a Mettler TA3000 thermobalance using 0.5 mg of sample at a heating rate of 15°C min^{-1} in air.

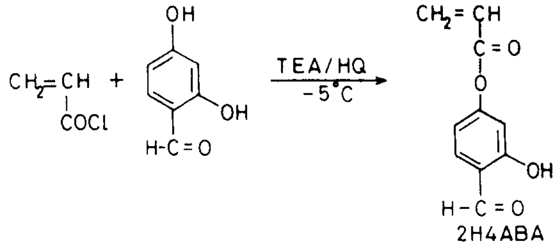
The electrical conductivity of the polychelates was measured on pellets of 10 mm diameter and 2-3 mm thickness using a Keithley electrometer. The equipment was calibrated with standard Gallium sample. Catalytic activity was carried out in Schlenk tube under nitrogen atmosphere. Cyclohexanol (2.5 mmol), 2-butanone (4 ml), polymer Cu(II) complex (0.05 mmol based on metal) and H_2O_2 (0.5 mmol) were taken and stirred magnetically at 75°C for 4 h. Aliquots (1 μl) were withdrawn and analysed by g.c.

RESULTS AND DISCUSSION

2-Hydroxy-4-acryloyloxybenzaldehyde (2H4ABA) was prepared and polymerized in 2-butanone using benzoyl peroxide as initiator according to *Scheme 1*.

The polymer is soluble in chloroform, THF, DMF and DMSO and insoluble in common organic solvents like benzene, toluene, methanol and water. Polymer metal complexes were obtained when the DMF solution of poly(2H4ABA) was treated with the aqueous solution of metal ions (Cu(II)/Ni(II)) in the presence of a few drops of ammonia. The polychelates were insoluble in common organic solvents, but sparingly soluble in DMF. The elemental analysis data for 2H4ABA, poly(2H4ABA) and polychelates were presented in *Table 1*. The elemental analysis has shown that the metal to ligand ratio in all the polychelates is 1 : 2.

The intrinsic viscosity [η] was obtained by extrapolating $\eta_{sp/c}$ to zero concentration. The intrinsic viscosity of poly(2H4ABA) was found to be 0.267 dl g^{-1}. The results reveal that the polymer is of high molecular weight. The number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$) of poly(2H4ABA) obtained by gel permeation chromatography (g.p.c)



Scheme 1

Table 1 Elemental analysis of 2H4ABA, poly(2H4ABA), and polychelates

		Calculated %			Found %		
Compound	Formula	C	H	Cu/Ni wt(%)	C	H	Cu/Ni wt(%)
2H4ABA	$C_{10}H_8O_4$	62.50	4.17		62.48	4.20	
Poly(2H4ABA)	$C_{10}H_8O_4$	62.50	4.17		62.48	4.20	
Poly(2H4ABA)-Cu(II)	$(C_{10}H_7O_4)_xCu$	54.54	3.18	13.18	55.56	3.15	13.21
Poly(2H4ABA)-Ni(II)	$(C_{10}H_7O_4)_y$ Ni $(H_2O)_y$	50.63	3.80	11.82	50.61	3.83	11.80

Calculated percentage of C, H, Cu and Ni for polymer-metal complexes based on $x = y = 2$ found $x = 2.02$; $y = 2.01$

Table 2 I.r spectral data of poly(2H4ABA) and its metal chelates

Sample	OH_{str}	$C{=}O_{str}$ Ester	$C{=}O_{str}$ Aldehyde	Ar_{ring} vibr	$C{-}O_{str}$	$M{-}O_{str}$
Poly(2H4ABA)	$3550\text{–}1760_{(s)}$	$1760_{(s)}$	$1640_{(s)}$	$1510_{(m)}$	$1325_{(m)}$	—
Poly(2H4ABA)-Cu(II)	$3200_{(b)}$	$1360_{(s)}$	$1625_{(s)}$	$1520_{(m)}$	$1350_{(m)}$	$550_{(s)}$
Poly(2H4ABA)-Ni(II)	$3600_{(b)}$	$1760_{(s)}$	$1625_{(s)}$	$1580_{(m)}$	$1350_{(m)}$	$540_{(s)}$

s = strong: m = medium; w = weak; b = broad

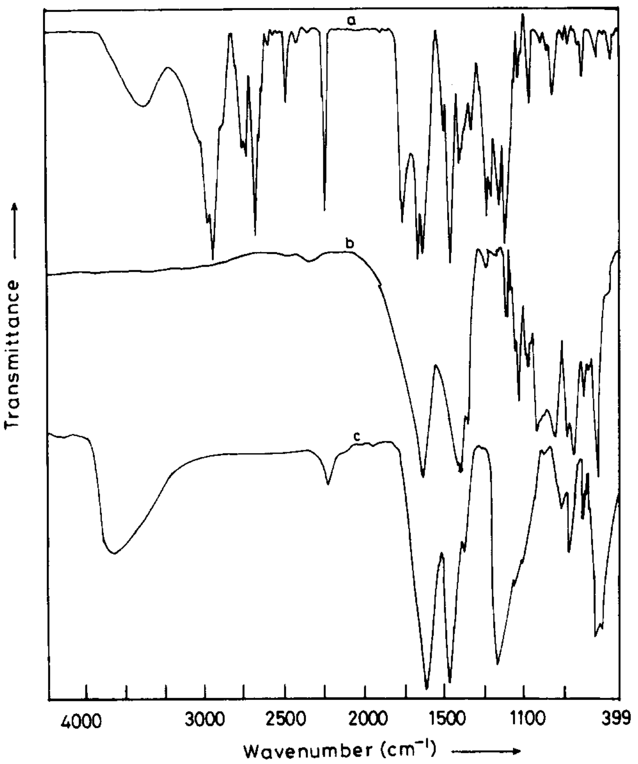


Figure 1 *FT*i.r spectra of poly(2H4ABA) (a), poly(2H4ABA)–Cu(II) (b) and poly(2H4ABA)–Ni(II) (c)

using tetrahydrofuran are: $\bar{M}_n = 1.15 \times 10^4$, $\bar{M}_w = 2.03 \times 10^4$. The polydispersity index $(\bar{M}_w/\bar{M}_n)$ for poly-(2H4ABA) is 1.76.

Figure 1 shows the i.r. spectra of poly(2H4ABA) and its polychelates. A broad band in the region of 3000–3300 cm^{-1} in the spectrum of poly(2H4ABA), which may be assigned to inter- and intra-molecular hydrogen bonded phenolic-OH stretching[18], presumably formed between phenolic-OH and aldehydic oxygen. The phenolic-OH stretching disappears in the spectra of polychelates indicating the coordination participation with metal ions[19]. Ni(II) polychelates show a strong absorption band in the region (3550 cm^{-1}) owing to coordination of H_2O molecules to Ni(II). This band remains even when the polymer–metal complexes were heated up to 150°C. Poly(2H4ABA) exhibits strong bands at 1750 and 1630 cm^{-1}, ascribed to C=O of ester and carbonyl groups respectively. In the spectra of polychelates the band at 1570 cm^{-1} shifts to lower frequency indicating the coordination through the oxygen of the aldehyde group[20–22]. The medium intense band at 1150 cm^{-1} in the C=O vibration of hydrogen bonded ring system shows a small positive shift indicating involvement of phenolic-OH in bonding with metal ion[23,24]. The band around 550 cm^{-1} corresponds to the metal–oxygen vibration[25]. The other absorptions observed are presented in *Table 2*.

The ^{1}H n.m.r spectrum of poly(2H4ABA) shows the singlet at 10.76 ppm due to the aromatic-OH. The resonance signals at 9.57 ppm are due to the aldehydic proton. The signals at 6.46–7.36 ppm are due to aromatic protons. The resonance signals at 1.25 and 2.25 ppm correspond to methylene and methine protons.

Figure 2 shows the diffuse reflectance spectra for poly-(2H4ABA)–Cu(II) and poly(2H4ABA)–Ni(II). The diffuse reflectance spectrum of Cu(II) polymeric chelate contains two bands, one at 14 950 cm^{-1} and another at 22 655 cm^{-1} which may be assigned to the d–d transition corresponding to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and to a symmetry-forbidden ligand metal charge transfer band of a square planar configuration. Similar observations for Cu(II) complexes were reported by several workers[26,27]. The electronic spectrum of Ni(II)–poly-(2H4ABA) shows three bands at 9500, 15 725 and 24 665 cm^{-1}, which may be due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{ig}(P)$ transitions respectively. The results are in accordance with octahedral spin-free nickel complexes exhibiting three bands in their electronic spectra[28,29].

The e.p.r. spectrum of cupric complex shows a strong signal characteristic to that of bivalent copper which is attributed to the square planar cupric ion in the centre with the oxygen of phenolic-OH and carbonyl oxygen groups on the x and y axis. Low spin Ni(II) in an octahedral field with tetragonal distortion is expected to have spin orbit coupling parameter of $g > 0$, and as a consequence $g^{\parallel} > g^{\perp}$. The e.p.r. parameters calculated for the Ni(II) complex are $g^{\parallel} = 2.525$ and $g^{\perp} = 2.16$. The g values are very consistent with Ni(II) in an octahedral environment.

Cu(II)-polychelates have a magnetic moment of 1.58 BM indicating the square planar configuration. The magnetic moment of 3.21 BM and the paramagnetic behaviour of Ni(II) complexes suggest distorted octahedral geometry for Ni(II) polychelates. The X-ray diffraction studies indicate that poly(2H4ABA) is amorphous whereas its polychelates possess good crystallinity. The crystallinity in polychelates may not be due to any ordering in poly(2H4ABA) induced during metal chelates anchoring, more so, since anchoring of metals to poly(2H4ABA) would imply interchain cross-linking between poly(2H4ABA) interchains, which should further reduce rather than enhance any such ordering. The appearance of crystallinity in poly-(2H4ABA)–metal complexes may be because of the inherent crystallinity nature of the metallic compounds.

Typical d.s.c. heating curves for poly(2H4ABA) and its polychelates are shown in *Figure 3*. The glass

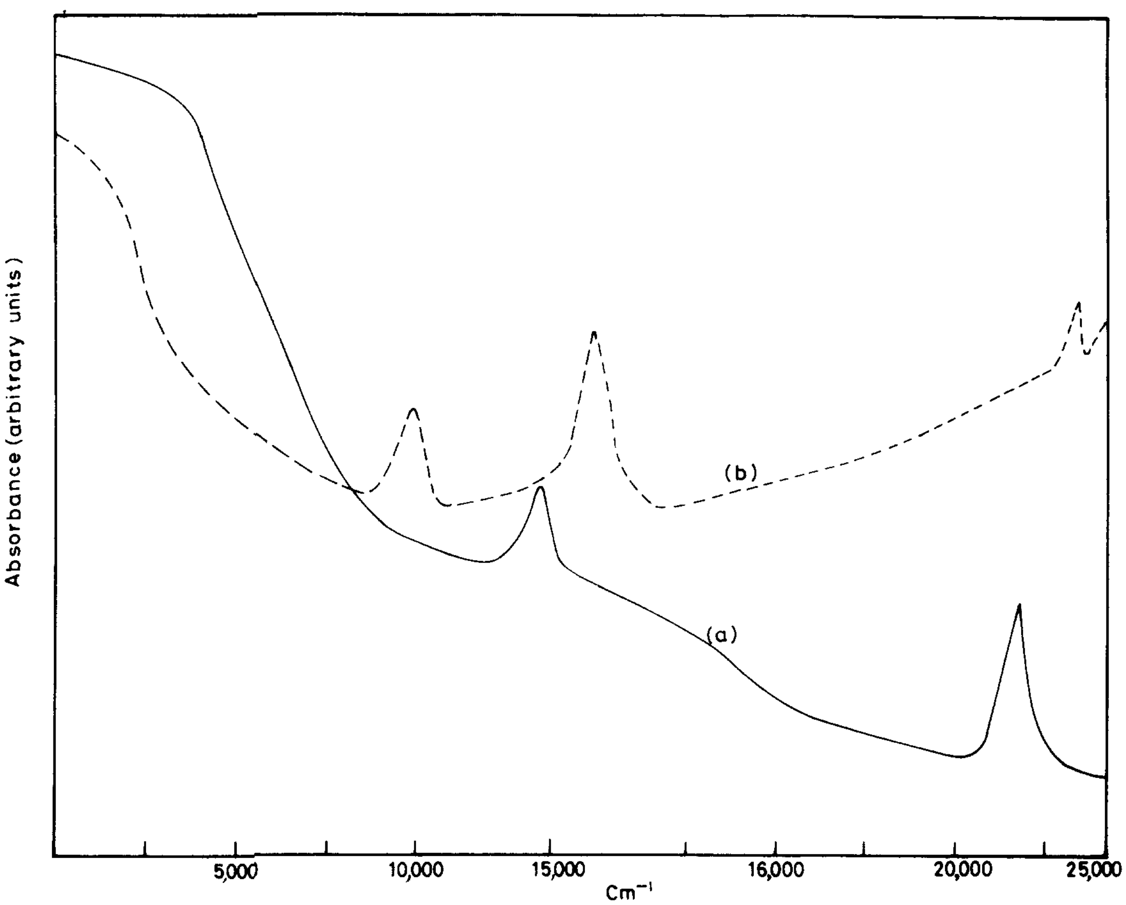


Figure 2 Diffuse reflectance spectra of poly(2H4ABA)–Cu(II) (a) and poly(2H4ABA)–Ni(II) (b)

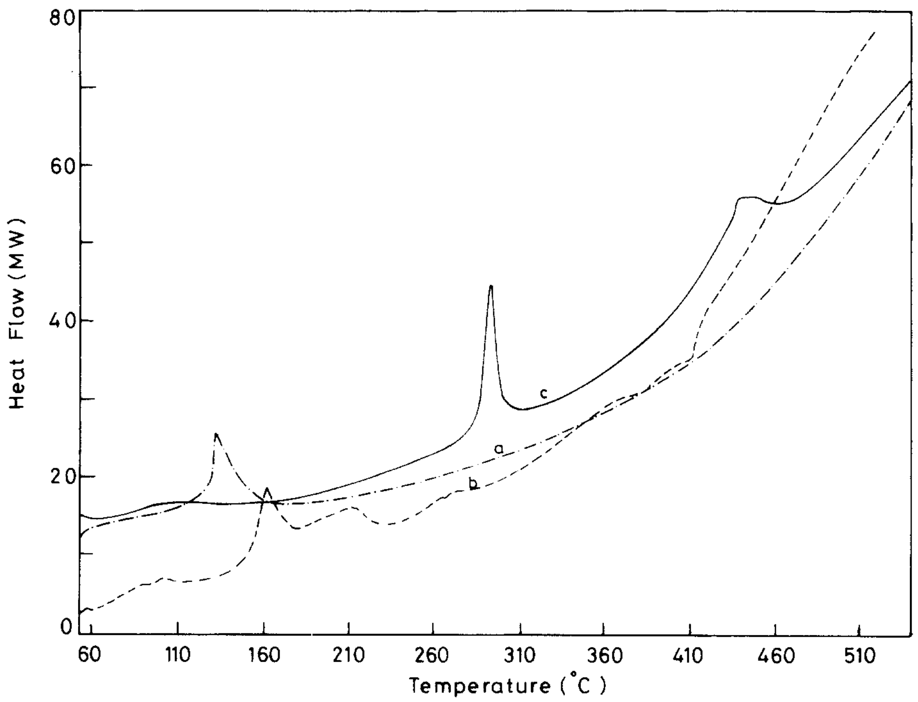


Figure 3 D.s.c. heating curves of poly(2H4ABA) (a), poly(2H4ABA)–Cu(II) (b) and poly(2H4ABA)–Ni(II) (c)

transition temperature (T_g) for poly (2H4ABA), poly-(2H4ABA)–Cu(II) and poly(2H4ABA)–Ni(II) chelates are found to be 130, 166 and 308°C respectively. The difference in transition may be ascribed to the crystallinity of the polymer–metal complexes and is in accordance with the X-ray diffraction studies. The t.g.a traces of poly(2H4ABA) and its Cu(II) and Ni(II) chelates are shown in *Figure 4*. The differential thermal analytical data are presented in *Table 3*. All the polychelates start to decompose at 200°C. At about

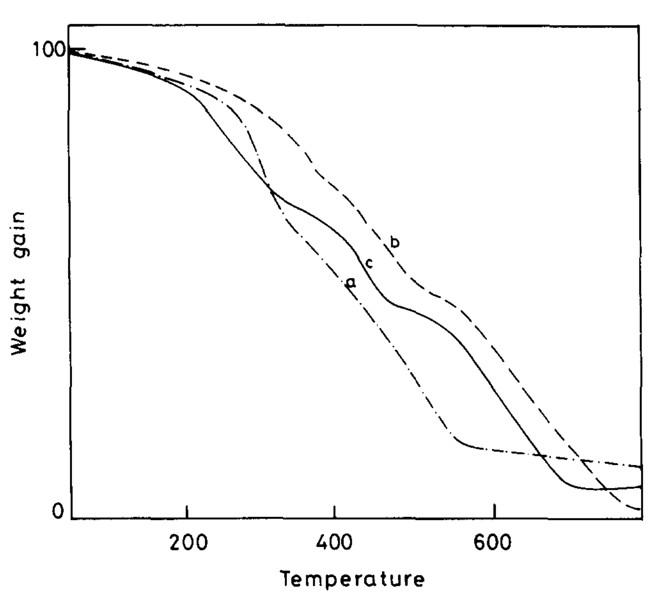
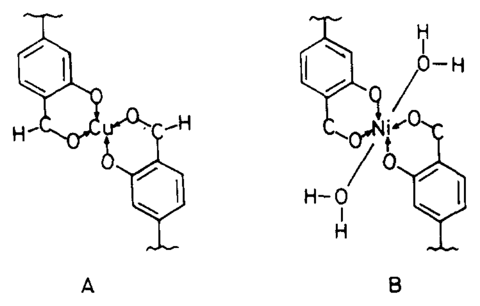


Figure 4 T.g.a traces of poly(2H4ABA) (a), poly(2H4ABA)-Cu(II) (b) and poly(2H4ABA)-Ni(II) (c)

Table 3 Thermogravimetric analysis data of poly(2H4ABA) and its metal chelates

	Weight loss (%) at temperature (°C)				
Sample	200	300	400	500	600
Poly(2H4ABA)	2.75	15.90	42.13	81.71	96.13
Poly(2H4ABA)-Cu(II)	2.97	26.87	37.13	70.91	92.17
Poly(2H4ABA)-Ni(II)	5.17	59.12	73.70	86.17	97.75



Scheme 2

600°C all the polychelates lose about 90% weight. The Cu(II)-polychelates are found to be more stable than Ni(II)-polychelates. The i.r., ^{1}H n.m.r., e.p.r., electronic spectra and the magnetic moments studies confirmed that the chelation of metal ions may possibly be occurring between two groups from different polymeric chains as shown in *Scheme 2*.

The electrical conductivity of Cu(II) and Ni(II) polychelates are 2.05×10^{-9} and $0.38 \times 10^{-9}\,\Omega\,\mathrm{cm}^{-1}$ respectively. The data reveal that the polychelates are poor electrical conductors. On reduction of aldehyde group by $NaBH_4$, the polymer failed to form complexes which confirms the coordination through the oxygen of the aldehyde group and oxygen of the phenolic-OH group and also initiates the polymerization of *N*-vinyl pyrrolidone. Poly(2H4ABA)–Cu(II) complex is found to catalyse the oxidation of cyclohexanol to cyclohexone (10.5% yield) in the presence of H_2O_2 whereas the Ni(II) complex showed negative results. This indicates that catalyst and oxidant are both essential for the oxidation of cyclohexanol. The catalytic activity of the polychelates may be due to the formation of substrate–polychelate complex intermediate leading to products.

ACKNOWLEDGEMENT

T.K. is grateful to the Council of Scientific and Industrial Research, Government of India, New Delhi for the award of Senior Research Fellow.

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