

Synthesis, Characterization, and Catalytic Study of Polymeric Metal Complexes Derived from Divalent Transition Metal Ions with 2,4-Dihydroxy Benzophenone and 2,4-Dihydroxy Acetophenone

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ABSTRACT: The polymeric metal complexes of poly (3-hydroxy-4-((Z)-1-(phenylimino)ethyl)phenyl-3-methylbut-2-enoate) designated as [poly(3H4-1PEPMB)] and poly (3-hydroxy-4-((Z)-phenyl(phenylimino)methyl)phenyl-3-methylbut-2-enoate) designated as [poly(3H4-PPMPMB)] containing Cu(II), Ni(II), Co(II), Cd(II), Mn(II), Ca(II), and Zn(II) ions were synthesized. The polymer ligands and metal complexes were characterized by Fourier transform infrared, nuclear magnetic resonance (NMR), thermogravimetric analysis, differential scanning calorimeter (DSC), and X-ray diffraction (XRD) techniques. The XRD study of the complexes revealed highly crystalline nature of polychelates. The polymeric complexes were active for the oxidation of aldehyde group. The oxidation activity of Cu (II) complex of poly (3H4-1PEPMB) was studied for the oxidation of benzaldehyde and its derivatives to corresponding carboxylic acids. The oxidation products were confirmed by GC-MS analysis. The oxidation of aldehydes was quantitative with 100% selectivity for benzoic acid. Thermal analysis of complexes indicated reasonably good thermal stability. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: metal-polymer complexes; polymer characterization; thermal properties; polymerization; catalysis

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INTRODUCTION

The wide importance of polymeric metal complexes based on polymeric Schiff base ligands in inorganic chemistry have been highlighted by the numerous studies.^{1–4} Some of the polymers containing metal ions linked by organic linker showed exceptional thermal stability.⁵ The polymeric Schiff base with multi-dentate coordination sites are known to form complexes with transition-metal ions. The basic properties of Schiff base polymers are due to the C=N linkage in the backbone.⁶ Schiff base polymers are the topic of interest as a consequence of their high thermal stability,⁷ complex forming ability,^{8,9} and semiconducting properties.^{10,11} Polymer-metal complexes have been of interest to many researchers during the past 3 decades in the light of their potential applications in diversified fields like organic synthesis,¹² waste water treatment,¹³ hydrometallurgy,¹⁴ polymer drug grafting,¹⁵ recovery of trace metal ions,¹⁶ and nuclear chemistry.¹⁷ Metal uptake efficiency and reusability of the resin have been studied by Thammisetty et al.¹⁸ In addition, they are also used as models for enzymes.^{19,20} The metal polymer chelates obtained from nickel(II), cobalt(II), and titanium(IV), used as homogeneous catalysts, have been heterogenized by che-

late formation with macro ligands and used as efficient catalysts for polymerization of ethylene as well as butadiene.²¹

The polymer-supported catalysts preserve their homogenous character when examined on molecular basis, but are heterogeneous when considered on functional basis.^{22–25} The simple work-up procedure, facile access to the active site by soluble reagents and the reusability of the catalyst are some of the significant advantages that these systems can offer.²⁶ Polymer-supported materials are extensively used as oxidising agents, reducing agents, photosensitizers, and agriculturally and pharmacologically active reagents.²⁷ Recent studies have shown that transition metals in combination with various oxidizing agents convert a wide range of hydrocarbons to the corresponding oxidized products.²⁸ These oxidations are moulded on certain enzymes that perform the oxidation of hydrocarbons in natural systems.²⁹

The applications of polymer-metal complexes in the field of catalysis have been widely investigated. Polymer-metal complexes are used as immobilized reagents useful for industrial purposes. Oxidation with molecular oxygen catalysed by transition metal complexes provides an attractive route for the preparation of

Table I. Elemental Analysis of 3H4-1PEPMB, 3H4-PPMPMB, Poly(3H4-1PEPMB), Poly(3H4-PPMPMB), and Metal Complexes

Abbreviation	Empirical formula	Carbon Found (Calcd)*	Hydrogen Found (Calcd)*	Nitrogen Found (Calcd)*
(3H4-1PEPMB)	C ₁₉ H ₁₉ NO ₃	73.2 (73.8)	6.1 (6.2)	4.7 (4.5)
(3H4-PPMPMB)	C ₂₄ H ₂₁ NO ₃	77.3 (77.6)	5.61 (5.7)	3.8 (3.8)
Poly(3H4-1PEPMB)	(C ₁₉ H ₁₉ NO ₃) _n	73.2 (73.8)	6.1 (6.2)	4.7 (4.5)
Poly(3H4PPMPMB)	(C ₂₄ H ₂₁ NO ₃) _n	77.3 (77.6)	5.6 (5.77)	3.8 (3.8)
Poly(3H4-1PEPMB)-Cu(II)	C ₁₉ H ₁₉ NO ₃ _a -Cu(II)	67.1 (66.9)	5.4 (5.6)	4.0 (4.1)
Poly(3H4-1PEPMB)-Ni(II)	C ₁₉ H ₁₈ NO ₃ _a -Ni(II)(H ₂ O) _b	64.0 (64.2)	5.9 (5.7)	4.1 (3.9)
Poly(3H4-1PEPMB)-Co(II)	C ₁₉ H ₁₈ NO ₃ _a -Co(II)(H ₂ O) _b	64.0 (64.1)	5.6 (5.7)	3.9 (3.9)
Poly(3H4-1PEPMB)-Mn(II)	C ₁₉ H ₁₈ NO ₃ _a -Mn(II)(H ₂ O) _b	64.8 (64.5)	5.6 (5.7)	3.9 (4.0)
Poly(3H4-1PEPMB)-Zn(II)	C ₁₉ H ₁₈ NO ₃ _a -Zn(II)(H ₂ O) _b	64.1 (63.6)	5.6 (5.6)	3.6 (3.9)
Poly(3H4-1PEPMB)-Cd(II)	C ₁₉ H ₁₈ NO ₃ _a -Cd(II)(H ₂ O) _b	59.3 (59.6)	5.2 (5.3)	3.8 (3.7)
Poly(3H4-1PEPMB)-Ca(II)	C ₁₉ H ₁₈ NO ₃ _a -Ca(II)(H ₂ O) _b	65.8 (65.9)	6.0 (5.8)	4.3 (4.1)
Poly(3H4-PPMPMB)-Ni(II)	C ₂₄ H ₂₀ NO ₃ _a -Ni(II)(H ₂ O) _b	68.8 (69.0)	5.4 (5.3)	3.2 (3.3)
Poly(3H4-PPMPMB)-Zn(II)	C ₂₄ H ₂₀ NO ₃ _a -Zn(II)(H ₂ O) _b	68.2 (68.4)	5.3 (5.3)	3.3 (3.3)

*Calculated percentage of C, H, N, for polymer metal complexes based on the value of $a = b = 2$. Found: $a = 2.01$, and $b = 2.0$.

synthetic intermediates and other oxygen containing organic substrates without the use of environmentally hazardous oxidants.³⁰ In the present work, we are reporting the simple synthetic protocol for the synthesis of polymer metal chelates, characterization and their use as catalyst for the oxidation of some aldehydes to corresponding acids using copper (II) complex (catalyst 1) with molecular oxygen as oxidant.

EXPERIMENTAL

Materials

Locally available 2,4-Dihydroacetophenone and 2,4-dihydroxybenzophenone were recrystallized from ethanol before use. Benzoyl peroxide was recrystallized from methanol/chloroform mixture. Aniline, triethylamine, methyl ethylketone, ethanol, chloroform, methanol, benzaldehyde, and their derivatives were used as received. Metal (II) precursor solutions were prepared from their chloride or acetate salt.

Methods and Characterization Techniques

The LC-MS chromatogram was done by Waters Micromass equipment (model Q-TOF micro); Fourier transform infrared (FTIR) spectra of complexes were recorded on Perkin-Elmer spectrometer (model: GX-FTIR) using KBr pellet; CHN analysis was done on Perkin-Elmer CHNS/O analyzer (model: Series II, 2400); X-ray diffraction (XRD) patterns were recorded on Rigaku Miniflex II X-ray diffractometer at ambient temperature with a scanning speed of 1° per minute in an angular scanning range (2θ) from 10–40°; NMR spectra were recorded on Bruker Avance-II spectrophotometer (¹H on 200 MHz, and ¹³C on 500 MHz) using dimethylsulphoxide (DMSO)-*d*₆ as solvent and TMS as an internal reference; molecular weights (M_w and M_n) of polymer ligands were determined by gel permeation chromatography (Waters, model: Alliance 410) using tetrahydrofuran (THF) as an eluent; thermogravimetric analysis (TGA) was done on Mettler Toledo (model: TGA/SDTA 851e) equipment in flowing air (flow rate of 50 mL/min) at a heating rate of 10°C min⁻¹; DSC was performed on Mettler Toledo system

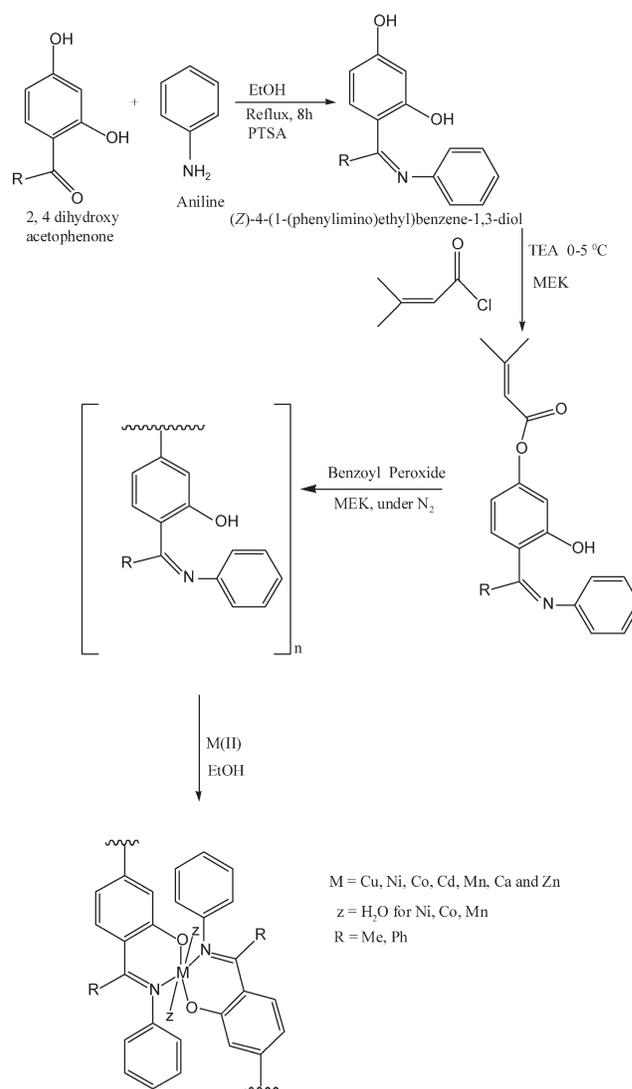


Figure 1. Scheme of synthesis of polymer metal complexes.

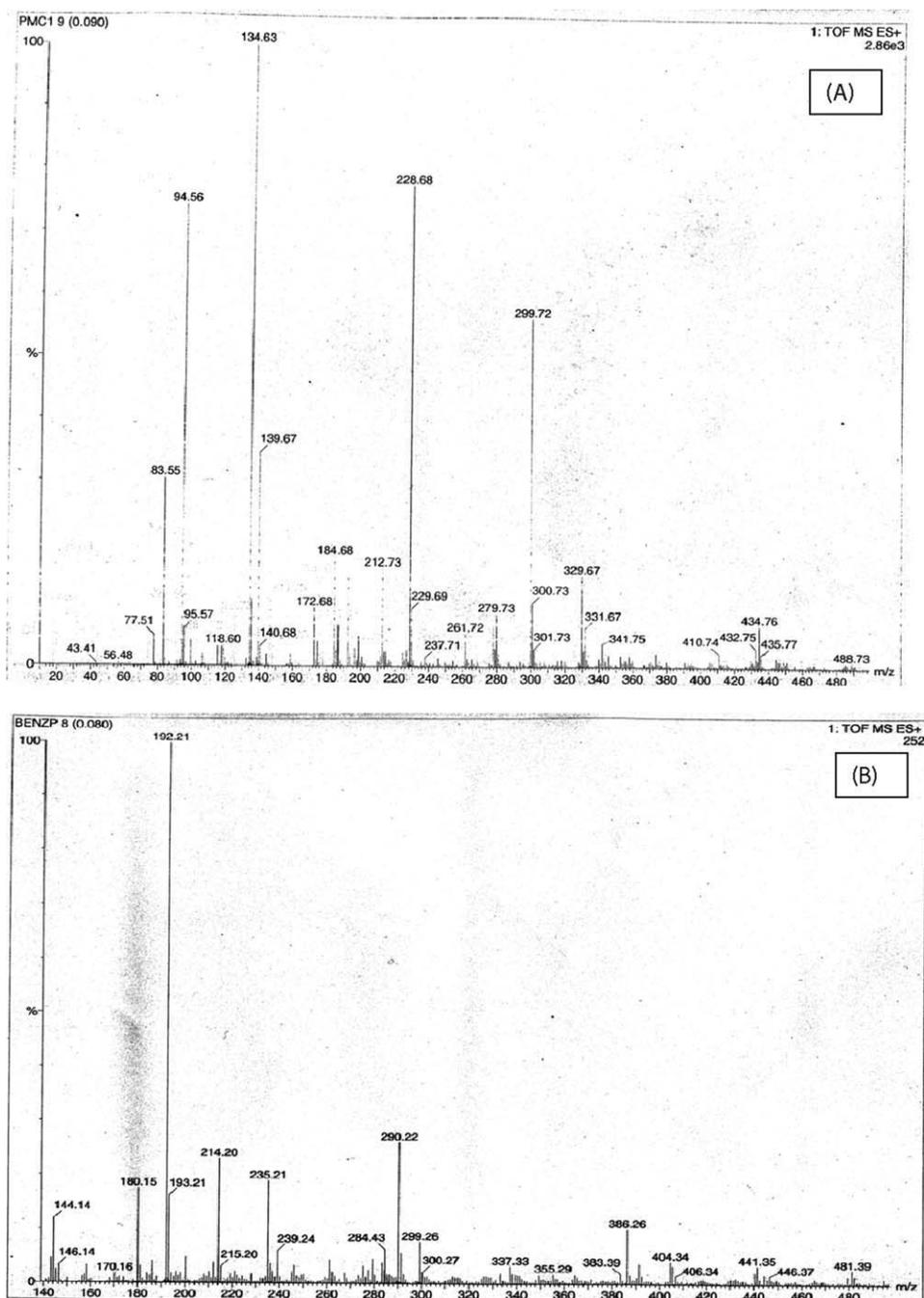


Figure 2. LC-MS chromatograms: (A) (Z)-4-(1-(phenylimino)ethyl)benzene-1,3-diol (4-1PEBD) and (B) 4-((Z)-phenyl(phenylimino)methyl)benzene-1,3-diol (4-PPMBD).

(model: DSC-822) at a heating rate of $15^{\circ}\text{C min}^{-1}$ in air; conductivity of the polychelates was measured from 2–3 mm thick pellets of 10-mm diameter using Keithley electrometer and GC-MS of oxidation products was done on Shimadzu GC-MS equipment (model: QP-2010 spectrometer).

Synthesis of Ligand Units

Synthesis of (Z)-3-hydroxy-4-(1-(phenylimino)ethyl)phenyl 3-methylbut-2-enoate (3H4-1PEPMB). 3H4-1PEPMB was prepared in two steps. In the first step, 4-{1-(phenylimino)ethyl}-

benzene-1,3-diol (4-1PEBD) was synthesized by reacting the ethanolic solution of 2, 4-dihydroxyacetophenone (1 mmol, 152 mg) with aniline (1.2 mmol, 105 mg) in 10 ml ethanol. The reaction mixture was refluxed for 8 h. The solvent was removed under vacuum to isolate 4-1PEBD (yield 80%, 182.4 mg). In second step 3, 3-dimethyl acryloylchloride (1 mmol, 118 mg) was dissolved in 5-mL methylethylketone (MEK) at 5°C and solution was added slowly into solution of 4-1PEBD (0.5 mmol, 114 mg) and triethylamine (0.5 mL) in MEK. The reaction mixture was stirred for 2 h at ambient temperature and washed

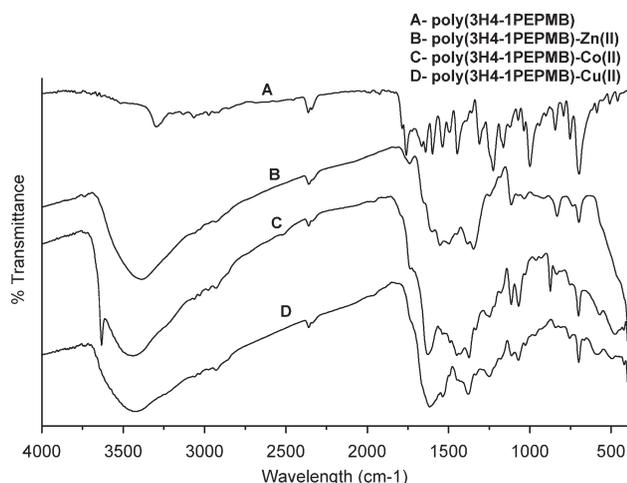


Figure 3. FTIR spectra: (A) poly(3H4-1PEPMB), (B) poly(3H4-1PEPMB)-Zn(II), (C) poly(3H4-1PEPMB)-Co(II) and (D) poly(3H4-1PEPMB)-Cu(II).

with distilled water followed by 5% NaOH solution and dried over anhydrous Na_2SO_4 . The product 3H4-1PEPMB was obtained after removal of solvent under vacuum and recrystallization from ethanol.

Synthesis of 3-hydroxy-4-((Z)-phenyl(phenylimino)methyl)-phenyl-3-methylbut-2-enoate (3H4-PPMPMB). Similar to 3H4-1PEPMB, the 3H4-PPMPMB was prepared by refluxing an ethanolic solution of 2, 4-dihydroxybenzophenone (1 mmol, 214.1 mg) with aniline (1.2 mmol, 105 mg) in 10 ml ethanol for 8 h and by removing solvent under vacuum to isolate 4-(Phenyl-phenylimino-methyl)-benzene-1, 3-diol (4-PPMBD) yield 86% (249.4 mg). So obtained 4-PPMBD (0.5 mmol, 145 mg) and triethylamine (0.5 mL) were dissolved in MEK and added slowly under continuous stirring into the solution of 3, 3-dimethyl acryloylchloride (1 mmol, 118 mg) in 5-mL MEK at 5°C and reaction mixture was stirred for 2 h at ambient temperature. The solvent was removed and the product 3H4-

1PEPMB was recrystallized from ethanol. Elemental Analysis of ligands 4-1PEBD, 3H4-1PEPMB, 4-PPMBD and 3H4-PPMPMB is given in Table I.

Polymerization

The ligands units (3H4-1PEPMB and 3H4-PPMPMB) were homopolymerized in methyl ethyl ketone using free radical initiator (benzoyl peroxide) at 70°C under N_2 for 60 min. Poly(3H4-1PEPMB) and poly(3H4-PPMPMB) were precipitated in methanol, purified by chloroform to obtain desired polymer. The product was dried *in vacuo* (Yield, 78%).

Preparation of Polymeric Metal Complexes

A series of polymer-metal complexes of poly(3H4-1PEPMB) and poly(3H4-PPMPMB) having different metal ions [Cu(II), Ni(II), Co(II), Cd(II), Mn(II), Ca(II), and Zn(II)] were synthesized in alkaline medium. In a typical procedure to poly(3H4-1PEPMB) or poly(3H4-PPMPMB) (0.50 mmol of the repeat unit) dissolved in 10 mL (3 M) NaOH solution was added 0.25 mmol solution of metal salt (chloride or acetate) dropwise under constant stirring. The metal complex of poly(3H4-1PEPMB) ligand was precipitated by adjusting the pH of the reaction mixture to 7 with the help of 1 N NaOH solution. The precipitated poly(3H4-1PEPMB)M(II) or poly(3H4-PPMPMB)M(II) complex was filtered and washed with hot distilled water followed by ethanol and then dried at 65°C *in vacuo*. The synthesis scheme of ligands and metal complexes is given in Figure 1.

Oxidation of Various Aldehyde

The metal complexes were screened for the catalytic oxidation of series of aldehydes. The oxidation reaction was carried out by taking aldehyde (2 mmol) and metal complex (0.2 mol %) in acetonitrile (2 mL) at 50°C using molecular oxygen as oxidant. The product of oxidation was confirmed by GC-MS analysis of the reaction mixture.

Table II. IR Spectral Data of Poly(3H4-1PEPMB), Poly(3H4-PPMPMB), and Metal Complexes

Sample	OH (Stretching)	C=O (Stretching)	C=N (Stretching)	M—N (Stretching)
Poly(3H4-1PEPMB)	3100–3400 _(b)	1760 _(m)	1600–1650 _(b)	-
Poly(3H4-PPMPMB)	3050–3400 _(b)	1775 _(m)	1600–1700 _(b)	-
Poly(3H4-1PEPMB)-Cu(II)	-	1742 _(m)	1580–1650 _(b)	490 _(s)
Poly(3H4-1PEPMB)-Ni(II)	3440 _(b)	1730 _(m)	1570–1660 _(b)	400 _(s)
Poly(3H4-1PEPMB)-Co(II)	3380 _(b)	1728 _(m)	1600–1710 _(b)	420 _(s)
Poly(3H4-1PEPMB)-Mn(II)	3350 _(b)	1731 _(m)	1600–1690 _(b)	425 _(s)
Poly(3H4-1PEPMB)-Zn(II)	-	1699 _(m)	1600–1700 _(b)	400 _(s)
Poly(3H4-1PEPMB)-Cd(II)	-	1716 _(m)	1590–1720 _(b)	420 _(s)
Poly(3H4-1PEPMB)-Ca(II)	-	1710 _(m)	1580–1690 _(b)	440 _(s)
Poly(3H4-PPMPMB)-Ni(II)	3460 _(b)	1640 _(m)	1600–1640 _(b)	410 _(s)
Poly(3H4-PPMPMB)-Zn(II)	-	1694 _(m)	1545–1600 _(b)	415 _(s)

b = broad; m = medium; s = strong.

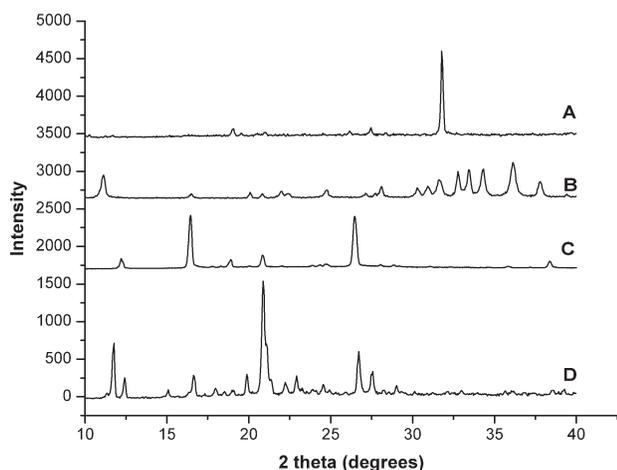


Figure 4. XRD patterns: (A) poly(3H4-1PEPMB), (B) poly(3H4-1PEPMB)-Cu(II), (C) poly(3H4-PPMPMB) and (D) poly(3H4-PPMPMB)Zn(II).

RESULTS AND DISCUSSION

The ligands 4-1PEBD and 4-PPMBD were synthesized as per details given above. The different components of reaction mixtures were identified by LC-MS analysis. The LC-MS chromatogram of reaction mixtures of 4-1PEBD and 4-PPMBD have been given in Figure 2(A,B), respectively. The LC-MS of 4-1PEBD [refer Figure 2(A)] have major mass ion peaks (M/e) of mass number 94.56, 134.63, 228.68, and 299.72. The peak at 94.56 corresponds to aniline (unreacted), 134.63 peak corresponds to fragmented portion of product (4-1PEBD), peak 228.68 represents ligand 4-1PEBD and peak 299.72 dimer of dihydroxy acetophenone. The LC-MS chromatogram of 4-PPMBD [refer Figure 2(B)] have major mass ion peaks (M/e) of mass number 192.21, 214.20 and 290.22. The peak 192.21 represents dimer of aniline, peak 214.20 represents unreacted dihydroxy benzophenone and peak 290.22 represents ligand 4-PPMBD.

The ligands were polymerized in MEK using benzoyl peroxide as an initiator. The polymers were soluble in chloroform, dimethylformamide, DMSO, and THF. The polymer metal chelates were synthesised by reacting the alkaline solution of poly(3H4-1PEPMB) and poly(3H4-PPMPMB) with aqueous solutions of

metal ions of Cu(II), Ni(II), Co(II), Cd(II), Mn(II), Ca(II), and Zn(II). The chemical composition of ligands and chelates as determined through elemental analysis indicated the metal to ligand ratio of $\sim 1 : 2$ (refer Table I). The weight average molecular weight (M_w) and number average molecular weight (M_n) of the polymers, poly(3H4-1PEPMB) and poly(3H4-PPMPMB) as determined by gel permeation chromatography were 2.15×10^4 D and 1.67×10^4 D, respectively. The polydispersity (M_w/M_n) was 1.29.

IR Spectroscopic Study

The IR spectrum of the polymeric ligands and complexes (Figure 3) showed a broad band in the region of $3297\text{--}3630\text{ cm}^{-1}$ due to NH, NH_2 stretchings and intermolecular hydrogen bonding due to phenolic-OH. The strong band in the spectrum of ligand [Figure 3(A)] and spectra of complexes [Figure 3(B–D)] in the region of $1640\text{--}1772\text{ cm}^{-1}$ depict the vibrations of $>\text{C}=\text{O}$ group present in polymeric ligand as well as in metal complexes. The absorption at 1630 cm^{-1} attributed to the stretching vibrations of $>\text{C}=\text{N}$ group and the absorption at 1510 cm^{-1} is due to the aromatic skeleton ring. The IR spectral studies of the polymer metal complexes provided evidence of the complexation of the metal ion with the polymeric ligand. The strong absorption at 1630 cm^{-1} is due to stretching vibrations of $>\text{C}=\text{N}$ present in ligand which shifted to the lower region ($\sim 1545\text{ cm}^{-1}$) in complexes. This confirms the coordination of ligand with metal ions through imine nitrogen (Refer Table II). The medium intensity absorption band at $1310\text{--}1345\text{ cm}^{-1}$ observed in the polymer due to the vibration of C–O bond of phenolic group shifted towards high frequency in the spectra of polymer metal complexes indicating the involvement of phenolic group in bonding with metal ion. The ligand stretching frequencies of the functional groups involved in the coordination shift their absorption frequencies that can be taken as an evidence of coordination.

NMR and XRD Studies

^1H NMR spectrum of 3H4-1PEPMB shows resonance peak at 8.32 ppm due to Ar-OH. The signals at 7.06–7.52 ppm were of aromatic protons. The $-\text{CH}$, $-\text{CH}_3-\text{C}=\text{N}$, and two CH_3 , $\text{C}=\text{C}$ proton signals were observed at 5.69, 2.19, 1.87, and 1.63 ppm respectively. The formation of chelates was confirmed by XRD. The XRD patterns of polyligands poly(3H4-1PEPMB) and

Table III. Empirical Formulae and Magnetic Moment of Polymer Metal Complexes

Abbreviations	Empirical formula	Magnetic Moment (BM)
Poly(3H4-1PEPMB)-Cu(II)	$\text{C}_{19}\text{H}_{19}\text{NO}_3\text{a}-\text{Cu(II)}$	2.10
Poly(3H4-1PEPMB)-Ni(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Ni(II)(H}_2\text{O)}$	2.99
Poly(3H4-1PEPMB)-Co(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Co(II)(H}_2\text{O)}$	3.37
Poly(3H4-1PEPMB)-Mn(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Mn(II)(H}_2\text{O)}$	5.68
Poly(3H4-1PEPMB)-Zn(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Zn(II)(H}_2\text{O)}$	Dimagnetic
Poly(3H4-1PEPMB)-Cd(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Cd(II)(H}_2\text{O)}$	Dimagnetic
Poly(3H4-1PEPMB)-Ca(II)	$\text{C}_{19}\text{H}_{18}\text{NO}_3\text{a}-\text{Ca(II)(H}_2\text{O)}$	Dimagnetic
Poly(3H4-PPMPMB)-Ni(II)	$\text{C}_{24}\text{H}_{20}\text{NO}_3\text{a}-\text{Ni(II)(H}_2\text{O)}$	3.33
Poly(3H4-PPMPMB)-Zn(II)	$\text{C}_{24}\text{H}_{20}\text{NO}_3\text{a}-\text{Zn(II)(H}_2\text{O)}$	Dimagnetic

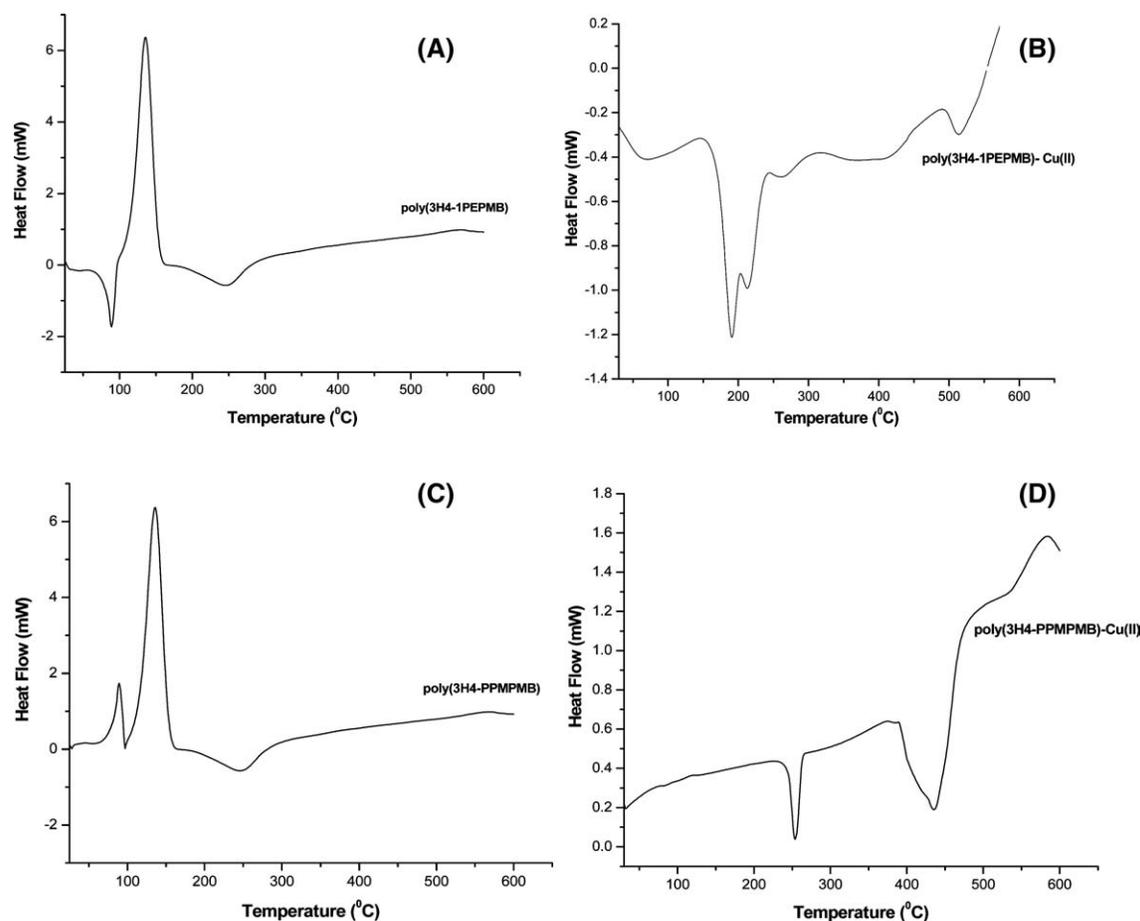


Figure 5. DSC Curves: (A) poly(3H4-1PEPMB), (B) poly(3H4-1PEPMB)-Cu(II), (C) poly(3H4-PPMPMB) and (D) poly(3H4-PPMPMB)-Cu(II).

poly(3H4-PPMPMB) and of metal complexes poly(3H4-1PEPMB)-Cu(II) and poly(3H4-PPMPMB)-Zn(II) have been shown in Figure 4 as A, B, C and D respectively. From the XRD study of polyligands and complexes it is seen that XRD patterns of metal complexes have well-defined peaks indicating their crystalline nature.^{31,32} The crystallinity in the metal complexes is due to the inherent crystalline nature of the metallic compounds. The difference in the reflection for ligand and chelates may be ascribed to the variation in the crystallinity of the ligand polymer-metal complexes. The magnetic moments of polymer metal complexes (Table III) indicate that complex of Zn, Cd, and Ca are diamagnetic while the complex of Cu, Ni, Co, and Mn have magnetic moment in the range of 2.10–5.66 BM.

Thermal Analysis Studies

DSC analysis curves of polyligands, poly(3H4-1PEPMB) and poly(3H4-PPMPMB) and their Cu(II) complexes given in Figure 5(A–D) revealed that polychelates incorporated polymers were more stable than their respective polymer counterparts. This may be due to the increase in the intermolecular friction and restricted the movement of macromolecular chains of polymer on the insertion of the metal ions into the polymer chain as a result of chelation. Another factor that may be responsible for the enhancement of the thermal stability of polymer-metal complexes matrix is the increase in the degree of crosslinked net-

works structures of polymer metal complex. The small thermal effects observed in poly(3H4-1PEPMB)-Cu(II) may be due to the slow decomposition of organic moiety (Figure 5(B) poly(3H4-1PEPMB)-Cu(II)). The phase change and decomposition of free ligand begins at $\sim 100^\circ\text{C}$, whereas the metal complex of same ligand is stable up to 150°C . Thermo gravimetric analysis curves of poly(3H4-1PEPMB) and its Cu(II) and Ni(II) complexes have been given in Figure 6 and of poly(3H4-PPMPMB) and its Zn(II) and Ni(II) complexes have been shown in Figure 7. The thermal decomposition temperatures and corresponding weight losses of ligands and complexes have been incorporated in Table IV. It is seen that initial decomposition temperatures (IDT) and weight losses are more for ligands in comparison of their metal complexes. This indicates relatively high thermal stability of complexes. The TGA data support the DSC analysis. The decomposition of polymeric ligands indicated two transitions while their metal complexes indicated three transitions (Figures 5–7). The initial decomposition temperature of poly(3H4-1PEPMB) and its Cu(II) complex is in close proximity but latter decomposed at slightly lower temperature which is rather unusual attributed to the unfavorable geometry around the central metal ion. The decomposition of ligands and complexes occurred in the temperature range of $50\text{--}750^\circ\text{C}$. The decomposition at lower temperatures attributed to the volatilization of low molecular weight species

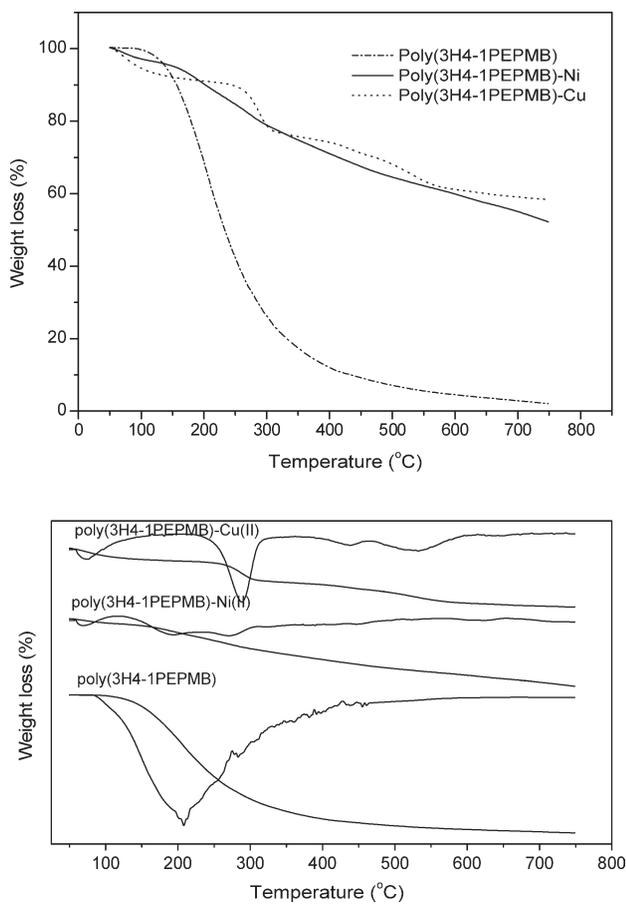


Figure 6. TGA and dW/dT curves of poly(3H4-1PEPMB), poly(3H4-1PEPMB)-Ni(II) and poly(3H4-1PEPMB)-Cu(II).

while those at higher temperatures is due to the cleavage of the polymeric chain followed by the volatilization of the cleavage products. It is evident from the decomposition temperatures that the Ni (II) complexes are more stable than Cu (II) and Zn (II) chelates. The polymer chelate essentially takes up a coiled form in solution. Because of the steric constraints forced by the geometry around the metal ion, it may not possible for metal ions to occupy all available sites for coordination.

Catalytic Study

Cu (II) complex of poly(3H4-1PEPMB) was screened as catalyst for the oxidation of benzaldehyde and its derivatives; and oxidation products was analyzed by GC-MS. A small fraction of the reaction mixture was removed from the reaction vessel and was analyzed. The polymeric metal complex being a heterogeneous catalyst was removed from reaction mixture by filtration and product was obtained via extraction and recrystallized from ethanol. The oxidation product of aldehyde was confirmed as corresponding carboxylic acid. The result of catalytic oxidation of benzaldehyde and its derivatives have been shown in Table V. It is seen that oxidation of benzaldehyde occurs to maximum extent (99%) whereas the conversion in the case of oxidation of benzaldehyde derivatives to corresponding acids is low; and oxidation of derivatives decreases as molecular size of substituent increases. For example oxidation of substituted benzaldehydes is as follow-

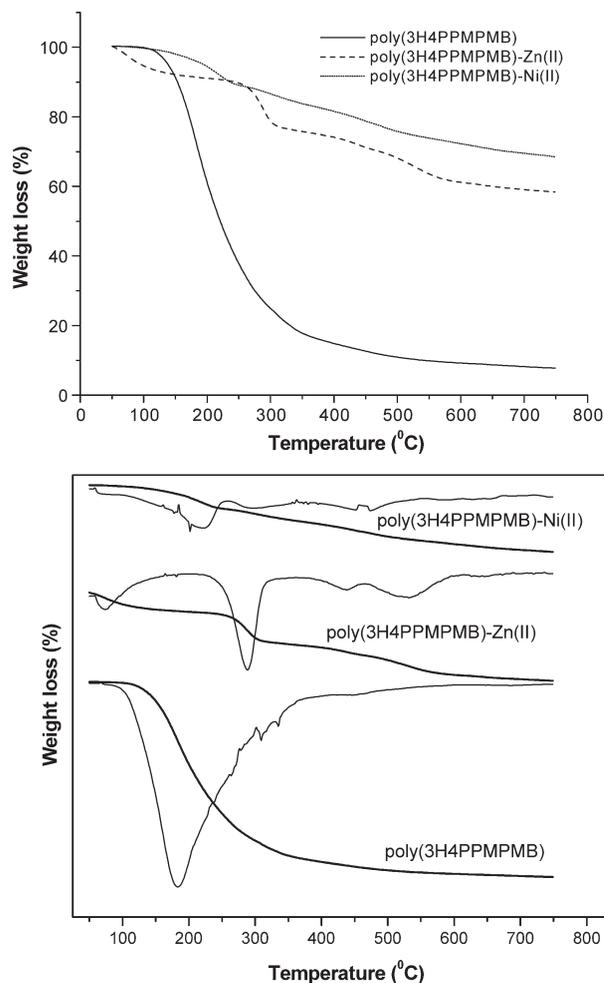


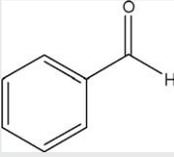
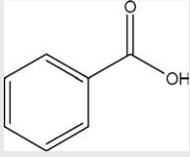
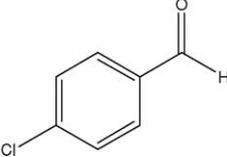
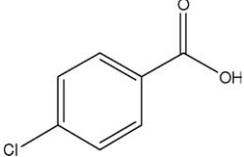
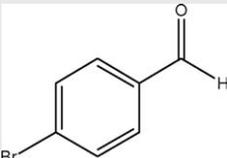
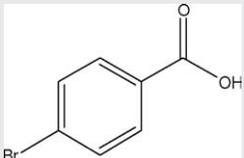
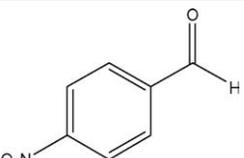
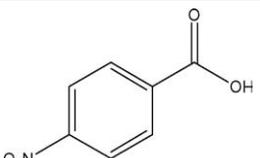
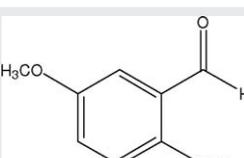
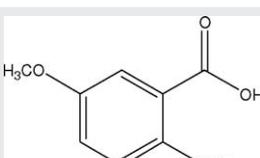
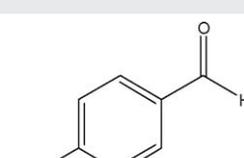
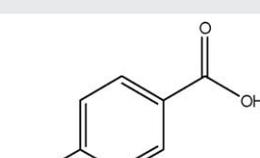
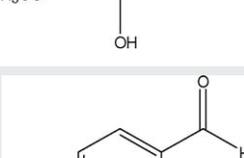
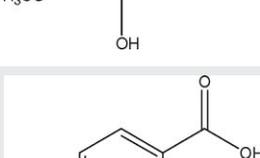
Figure 7. TGA and dW/dT curves of poly(3H4-PPMPMB), poly(3H4-PPMPMB)-Zn(II) and poly (3H4-PPMPMB)- Ni(II).

ing: unsubstituted > monosubstituted (halogen > nitro) > disubstituted (> di methoxy > methoxy hydroxy). The observation of oxidation reaction indicated that Cu(II) complex of poly(3H4-

Table IV. Thermogravimetric Data of Poly(3H4-1PEPMB), Poly(3H4-PPMPMB), and Metal Complexes

Polymer and complexes	Temperature range	% Weight loss
Poly(3H4-1PEPMB)	105-420	96.60
Poly(3H4-1PEPMB)-Cu(II)	100-345	24.70
	345-750	22.83
Poly(3H4-1PEPMB)-Ni(II)	100-375	24.20
	375-750	16.43
Poly(3H4-PPMPMB)	100-335	69.43
	335-740	23.16
Poly(3H4-PPMPMB)-Zn(II)	100-450	22.23
	450-700	10.11
Poly(3H4-PPMPMB)-Ni(II)	100-380	30.71
	380-750	13.21

Table V. Oxidation of Benzaldehyde and Its Derivatives to the Corresponding Acids by Poly(3H4-1PEPMB) Cu (II) Complex

Entry	Substrate ^a	Product	(Yield,%) ^b	Selectivity	Time (h)
1			99	100	3
2			98	96	4
3			98	96	4
4			78	92	5
5			82	94	5
6			86	95	5
7			88	96	5

^aA solution of aldehyde (2 mmol) and Cu(II) complex (0.2 mol%) taken in acetonitrile (2 mL) at 50 °C and molecular oxygen was purged in the reaction mixture under continuous stirring.

^bAll the compounds were characterized by GC-MS analysis.

1PEPMB) is suitable for the oxidation of unsubstituted and mono substituted aldehydes with quantitative yield.

CONCLUSIONS

The water insoluble polymer metal complexes of poly(3H4-1PEPMB) and poly(3H4-PPMPMB) with Cu(II), Ni(II), Co(II),

Cd(II), Mn(II), Ca(II), and Zn(II) were synthesized successfully. Thorough investigations of polymer metals complexes by thermal analysis, XRD, LC-MS, molecular weights, and oxidation activity indicated that functional groups of ligands from different polymer chains involved in the coordination with the metal ions. However metal ions do not occupy all the available sites in the polymer chelate due to steric restrictions. The thermal

stability of the Ni(II) chelate was more than that of the Cu(II) chelate. Spectral data of the complexes in association with magnetic moment suggest a distorted geometry for the complexes. The polymeric complexes were active for the oxidation of aldehyde group. Thermal analysis of the complexes indicated reasonably good thermal stability. Thus this study has described a simple, clean and efficient catalytic oxidation procedure that allows the transformation of aldehydes into the corresponding acids in moderate to high yields using Cu (II) chelate as a catalyst.

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