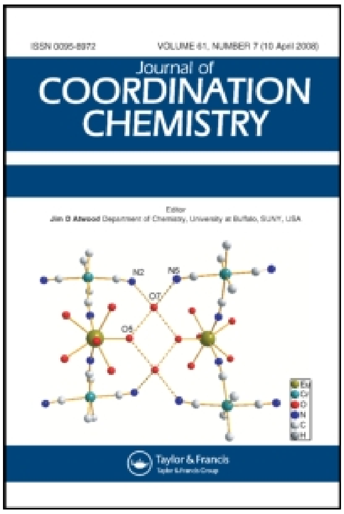

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Synthesis, characterization and anti-microbial activity of poly(ethylene oxamide-<i>N,N</i>'-disuccinate) and its polymer metal complexes

T. Ahamad[a]; V. Kumar[a]; S. Parveen[a]; N. Nishat[a]
[a] Department of Chemistry, Materials Research Lab, New Delhi, India

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Synthesis, characterization and anti-microbial activity of poly(ethylene oxamide-*N*,*N*′-disuccinate) and its polymer metal complexes

T. AHAMAD, V. KUMAR, S. PARVEEN and N. NISHAT*

Department of Chemistry, Materials Research Lab,
Jamia Millia Islamia, New Delhi, 110025, India

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Poly(ethylene oxamide-*N*,*N*′-disuccinate), abbreviated as (PEODS), has been synthesized by condensation of oxamide-*N*,*N*′-disuccinic acid and 1,2-ethylene glycol. Coordination polymers were synthesized by the reaction of (PEODS) with hydrated acetates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The resulting polyester-metal complexes were characterized by elemental analysis, UV-Visible, FT-IR, ^{1}H-NMR, ESR spectroscopy and magnetic susceptibilities. Thermal behavior of all the synthesized compounds revealed that polymer metal complexes are more stable than the polymeric ligand. In addition all the synthesized polymers were screened for anti-bacterial activity against *B. subtelillisr*, *B. megaterium*, *S. aureus*, *E. coli*, *S. typhi*, *P. aeruginosa*, *S. boydii* and for antifungal activity against *C. albicans*, *T. species*, *A. flavus*, *A. niger*, *F. species*, *M. species*, and *P. species* by agar well diffusion methods. All the polymers showed good anti-bacterial and anti-fungal activity, which increased on coordination with the metal ions.

Keywords: Polyester; Elemental analysis; Condensation; Agar well diffusion methods

1. Introduction

The first polyester resin was synthesized by Berzelius in 1847 and by Gay-Lussac and Pelouze in 1888 [1]. Initially polyesters were used for surface coating where they were known as alkyd resin, the word alkyd being derived from alcohol and acid. It is found that polyester can be applied for surface coating, composite, in the manufacture of fibers (Terylene, Decron) and film (eg. Melinex, mylar) [2]. The incorporation of transition metals into the polymer chain offers potential for the preparation of processable materials with properties, which differ significantly from those of conventional organic polymers. The diverse range of coordination and geometries of transition elements offers the possibility of accessing polymers with unusual conformational, mechanical, and morphological character [3, 4]. Such polymers are of

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*Corresponding author. Tel.: +91-112-682-3254. Fax: +91-112-684-0229. Email: nishat_nchem03@yahoo.co.in

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considerable interest in materials science because the metal atoms can also impart unique redox, electronic, optical and magnetic properties [5].

Polyester with pendant amino groups and carbonyl oxygen of ester group as donor sites may yield metal coordinated polymers with interesting properties. However, few polyesters having amino acid moieties in the main chain were found to be thermally more stable than the polyester itself [6–8]. Further, the nature of metal ions influences thermal degradation and biological degradation of the polyester-metal complexes.

In this study we have synthesized polyester based polymeric ligands derived from amino acids (aspartic acid) with ethylene glycol because compounds with the N and O donor system might inhibit enzyme production of microbes because enzymes that require a free hydroxyl group for their activity are especially susceptible to deactivation by the ions of complexes. The polymer metal complexes of poly(ethylene oxamide-*N,N′*-disuccinate) were synthesized by reaction of polymeric ligands with metal ions. The results reveal that antimicrobial activity of the compounds increase after metal chelation, presumably because chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups.

2. Experimental

2.1. *Materials*

Aspartic acid, diethyl oxalate, ethylene glycol and manganese(II) acetate tetrahydrate, $Mn(CH_3COO)_2 \cdot 4H_2O$, copper(II) acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$, nickel(II) acetate tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$, cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2 \cdot 4H_2O$, zinc(II) acetate dihydrate, and $Zn(CH_3COO)_2 \cdot 2H_2O$ (s. d. fine) were commercially available and used without further purification. All solvents were of reagent grade and distilled before use.

2.2. *Measurements*

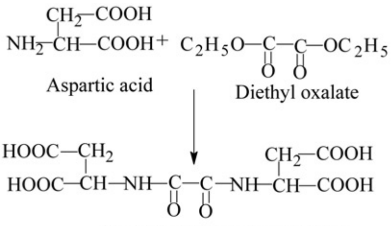
The elemental analysis of metal coordinated polymers were carried out on a Perkin Elmer Model-2400 elemental analyzer (CDRI, Lucknow). The metal content of the polyester was determined by complexometric titration against EDTA after decomposing with concentrated nitric acid (HNO_3). The FT-IR spectra were recorded over the 4000–500 cm^{-1} range on a Perkin Elmer infrared spectrophotometer Model 621 by using KBr pellets. UV-Vis spectra were obtained on a Perkin Elmer Lambda EZ-201 spectrophotometer by using DMSO as solvent. Proton & Carbon-13 nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a JEOL–GSX 300-MHz FX–1000 FT-NMR spectrometer using DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. Thermal behavior of the polyester (thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC)) was carried out on a TA analyzer 2000 in nitrogen atmosphere at a heating rate of 20 or 10 $^{\circ}C\,min^{-1}$ The solubility of the polymers was tested in various solvents at room temperature.

2.3. *Synthesis*

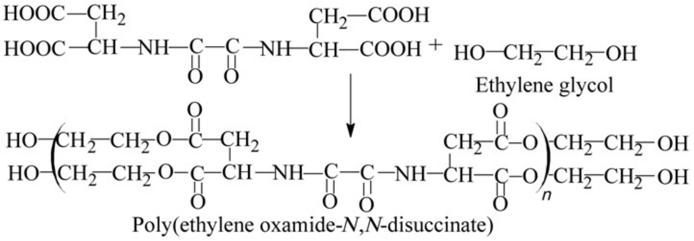
2.3.1. Preparation of oxamide-*N*,*N*′-disuccinic acid. L-aspartic acid 2.66 g (0.02 mol) was dissolved in 35 mL of water and neutralized with NaOH 1.60 g (0.04 mol). Diethyl oxalate 1.34 mL (0.01 mol) in 35 mL ethanol was added to this solution. The homogeneous solution thus obtained was refluxed for 5 h at 60°C with constant stirring. The reaction was monitored by TLC (Thin Layer Chromatography). The resulting mixture was cooled in ice and then excess HCl (pH-1) was added for precipitation of white crystals of free ligand. These crystals were filtered off, washed several times with ethanol and ether and dried over fused calcium chloride. The overall route of the reaction is given in scheme 1. Yield: 75%.

2.3.2. Synthesis of poly(ethylene oxamide-*N*,*N*′-disuccinate) (PEODS). A mixture of 5.32 g (0.02 mol) of oxamide-*N*,*N*′-succinic acid and 1.55 mL (0.025 mol) of ethylene glycol in a 100 mL flask was refluxed with stirring at 175°C for 2 h. The temperature was then increased to 200°C and maintained for 4 h. Excess solvent and unreacted ethylene glycol were removed in vacuum by using a rotatory evaporator; unreacted oxamide-*N,N*′-succinic acid was removed by washing thoroughly with water and methanol. The overall route of the reaction is given in scheme 2. The yield of the product was about 80%.

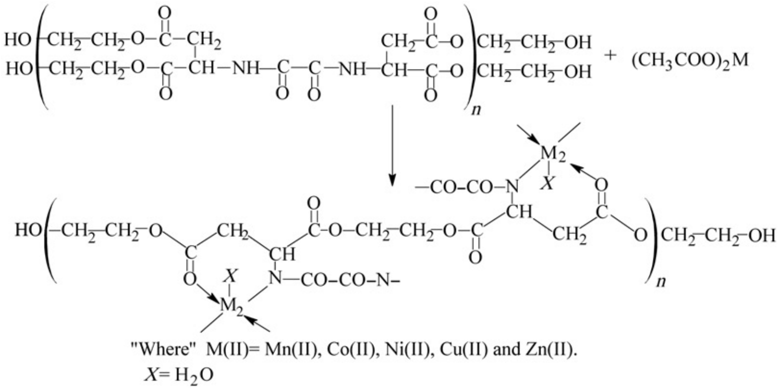
2.3.3. Synthesis of polyester-metal complexes. Coordination polymers were synthesized by mixing a hot solution of metal acetate (0.01 mol) in 50 mL ethanol with solution of the ligand (0.01 mol) in 50 mL of ethanol. The resulting mixture was heated on a boiling water bath for 4 h. The colored precipitates of polyester metal complexes were filtered off, washed several times with hot water and finally with ethanol, and



Scheme 1. Synthesis of oxamide-*N*,*N*′-disuccinic acid.



Scheme 2. Synthesis of poly(ethylene oxamide-*N*,*N*′-disuccinate).



Scheme 3. Synthesis of polymer-metal complexes.

dried in a vacuum desiccator over calcium chloride at room temperature. The overall route to the synthesized metal complexes is given in scheme 3.

2.4. *Preparation of microbial cultures*

The anti-microbial activities of synthesized polyesters were screened *in vitro* for their antibacterial activity against *B. subtelillis, B. megaterium, S. aureus, E. coli*, *S. typhi, P. aeruginosa, S. boydii* and for antifungal activity against *C. albicans, T. species, A. flavus, A. niger, F. species, M. species, P. species* by agar well diffusion methods. Bacteria strains were nourished in nutrient broth (Difco) and yeasts in malt extract broth (Difco) and incubated for 24 and 48 h, respectively. According to the agar diffusion method, bacteria were incubated on Mucller Hinton agar and yeast on Sabouraud dextrose agar. A circular well was made at the center of each peripelet with a sterilized steel borer. The polyester samples were prepared using DMSO as the solvent at a concentration of 50 and 100 $\mu g\,mL^{-1}$ for antibacterial and antifungal activity, respectively. Then 0.1 mL of each test solution was added to the well and the bacteria samples were incubated at 36°C for 24 h and the yeast sample incubated at 25°C for 72 h, and DMSO was used for negative control only; Kanamycin and Miconazol (standard drugs) for positive control for antibacterial and antifungal activity, respectively. The resulting inhibition zones on the palates were measured in mm.

3. Results and discussion

3.1. *Composition*

(PEODS), prepared as in the experimental section, was a viscous liquid, soluble in common organic solvents. All the coordination polymers are colored solid materials; polymer complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are light pink, dark brown, red, green and white, respectively, and insoluble in common organic solvents. The molecular weight of the coordination polymers could not be determined by GPC due to their insoluble nature in tetrahydrofuran (THF). The analytical data of the polymeric ligand (PEODS) and its polymer metal complexes are given in table 1.

Table 1. Elemental analysis of the polymeric ligand and its polymer metal complexes.

Compound abbreviation	Empirical formula	Elemental analysis Carbon	Hydrogen	Nitrogen	Metal
PEODS	$(C_{14}H_{16}O_{10}N_2)_x$	45.78 (45.79)	4.33 (4.34)	7.52 (7.51)	– –
PEODS–Mn(II)	$(C_{14}H_{14}O_{10}N_2)_x$-$x$ Mn(II) · 2xH_2O	36.42 (36.45)	3.49 (3.45)	6.07 (6.09)	11.91 (11.94)
PEODS–Co(II)	$(C_{14}H_{14}O_{10}N_2)_x$-$x$ Co(II) · 2xH_2O	36.23 (36.25)	3.47 (3.46)	6.03 (6.05)	12.48 (12.46)
PEODS–Ni(II)	$(C_{14}H_{14}O_{10}N_2)_x$-$x$ Ni(II) · 2xH_2O	36.24 (36.25)	3.47 (3.48)	6.03 (6.04)	12.43 (12.44)
PEODS–Cu(II)	$(C_{14}H_{14}O_{10}N_2)_x$-$x$ Cu(II)	38.79 (38.75)	3.72 (3.74)	6.45 (6.46)	14.66 (14.67)
PEODS–Zn(II)	$(C_{14}H_{14}O_{10}N_2)_x$-$x$ Zn(II)	38.60 (38.61)	3.70 (3.71)	6.42 (6.43)	15.01 (15.00)

x-Number of repeating units of polymeric chain. Calculated, (Observed) value metal to ligand stoichiometry.

The analytical data agreed with 1:1 metal to ligand ratio. The coordination polymers of Mn(II), Co(II), and Ni(II) coordinate two molecules of water with each metal ion, indicated by the FT-IR and TGA data.

3.2. *FT-IR spectra*

Important IR bands and their assignments for PEODS and its polymer metal complexes are summarized in table 2. The spectrum of the polymeric ligand shows a very broad and strong band in the region 3500–3200 cm^{-1} due to *Asym* and *Sym* νNH [11], and for νOH (terminal) group of polymer as ethylene glycol is taken in excess during synthesis of PEODS. The presence of methylene is confirmed by the appearance of two strong bands at 2940–2840 cm^{-1} of νCH_2 (*Sym* & *Asym* stretching) and a band between 1485–1455 cm^{-1} due to CH_2 bending [12]. The C=O bands from the ester and amide occur in the region 1735–1715 cm^{-1} and 1680–1650 cm^{-1}, respectively [13]. The C=O frequency is slightly lowered due to hydrogen bonding. The bands observed at 1050 and 880 cm^{-1} in the spectrum of the ligand have a contribution of C-N and NH in [poly(ethylene oxamide-N,N′-disuccinate)]. A weak band at 750 cm^{-1} is assigned to –$(CH_2)_2$-of the polymeric chain [14]. The spectra of metal coordination polymers are compared with the parental ligand to elucidate the bonding in formation of complexes. The strong absorption band due to νNH becomes very broad after coordination with metal ions. The coordination of water with central metal ions is conformed by the appearance of a strong band in the region 1660–1650 cm^{-1} and in the region 660–650 cm^{-1} for δHOH deformation and rocking modes of coordinated water [15]. These bands disappear in the spectrum of Cu(II) and Zn(II) metal complexes due to the absence of coordinated water molecules. The band of C=O (oxamide) is shifted to lower frequency in the spectra of coordination polymers, indicating that coordination of metal at oxamide occurs rather than C=O of ester because the C=O of ester is not shifted. The appearance of new bands in the region 650–640 cm^{-1} are attributed to νM–O and stretching frequency bands in the 535–520 cm^{-1} region are attributed to νM–N, which further confirms the coordination through nitrogen and oxygen.

Table 2. Important IR spectral bands and their assignment.

Assignment	PEODS	PEODS–Mn(II)	PEODS–Co(II)	PEODS–Ni(II)	PEODS–Cu(II)	PEODS–Zn(II)
NH (*asym* and *sym* and OH	3500–3250(s, b)	3480–3240(s, b)	3480–3230(s, b)	3480–3210(s, b)	3500–3220(s, b)	3480–3200(s, b)
CH_2 (*Asym*, (*Sym*)	2940–2865(s)	2940–2840(s)	2940–2850(s)	2940–2850(s)	2940–2855(s)	2940–2860(s)
C=O	1730–1718(s)	1730–1720(s)	1730–1725(s)	1730–1718(s)	1730–1720(s)	1730–1715(s)
Ester δHOH (water) oxamide	–	1665(s)	1650(s)	1665(w)	–	–
νC=O	1680(s)	1665(s)	1650(w, b)	1665(s)	1660(v, s)	1658(m)
δ(CH) bending due to	1465(s)	1455(m)	1460(s)	1465(w)	1475(s)	1465(s)
–N–CH_2–N δ(C–N) (oxamide)	1430(s)	1430(m)	1430(s)	1430(s)	1425(m)	1425(s)
νM–O	–	650(s)	640(s)	640(s)	645(s)	643(b)
νM–N	–	535(w)	525(s)	520(s)	520(m)	535(s)

s, strong; *vs*, very strong; m, medium; b, broad; w, weak.

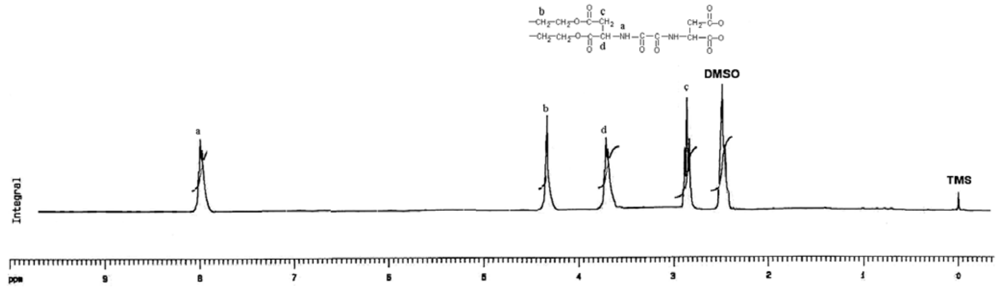


Figure 1. ^{1}H-NMR spectrum of PEODS.

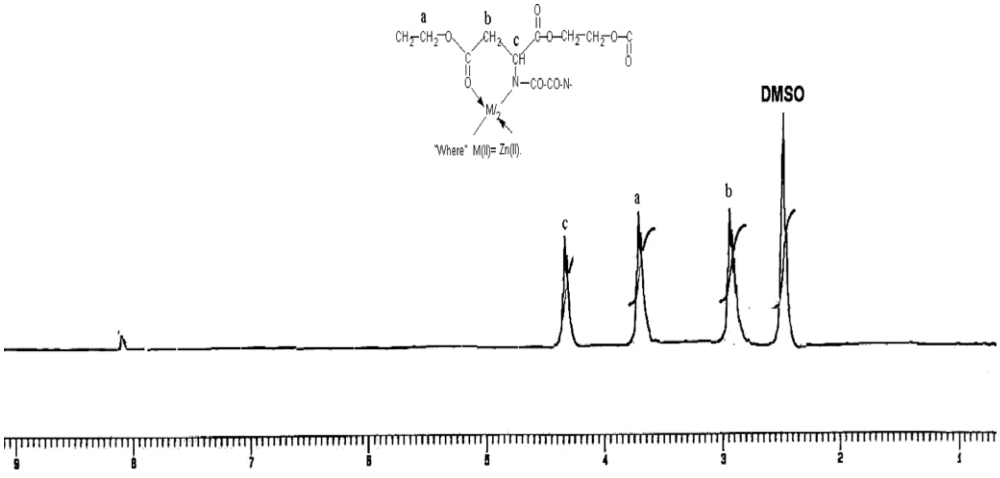


Figure 2. ^{1}H-NMR spectrum of [PEODS–Zn(II)].

3.3. *^{1}H-NMR spectra of polyester and its zinc complex*

The proton magnetic resonance spectra of amino acid based polyester and its Zn(II) complex in DMSO-δ_6 with tetramethylsilane as internal reference are shown in figures 1 and 2. The aspartic acid based polyester (PEODS) displays signals at 4.34–4.36 and 2.73–2.98 ppm due to the methylene protons of glycol and aspartic acid moiety, respectively [16]. The N–H signals of the polymeric ligand appear at 8.02 ppm due to oxamide protons. In the Zn(II) complex of PEODS, the intensity of N–H protons is reduced [17], due to coordination with the metal after deprotonation, which is also confirmed by FTIR spectra of the polymer metal complexes. The intensity of other peaks also decreased due to coordination of transition metal ions. It was observed that DMSO has no coordination effect on the spectra of the ligand or on its metal complexes.

3.4. *^{13}C-NMR spectra of PEODS and its zinc complex*

The ^{13}C-NMR spectrum of the Zn(II) chelated PEODS is given in figure 3. The ^{13}C-NMR spectrum of PEODS has resonances at 163.6 ppm and 171.4–173 ppm

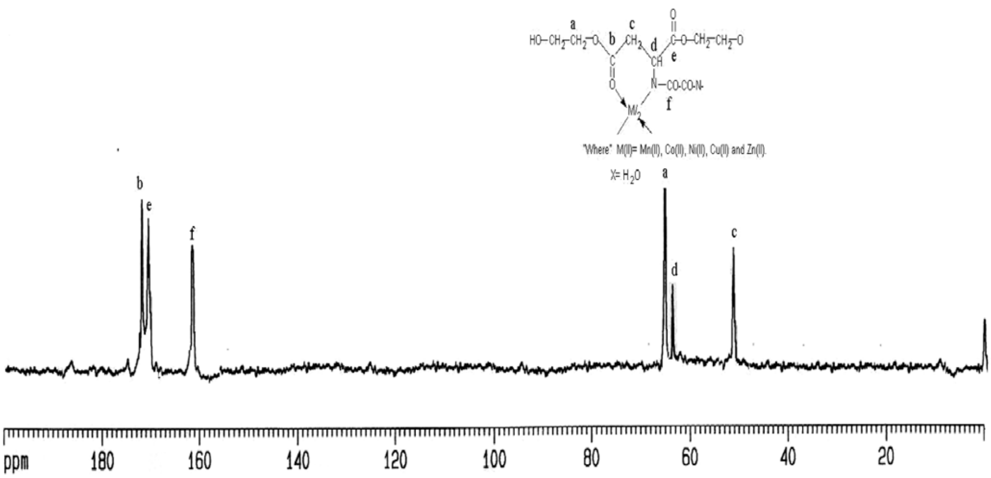


Figure 3. ^{13}C-NMR spectrum of [PEODS–Zn(II)].

for the oxamide and ester, respectively. For PEODS there are two ester carbonyls, NH–CH–C=O and NH–CH–CH_2–C=O, which show resonances at 171.4 and 173.2 ppm, respectively. The methylene carbons of glycol have signals in the region 63.66–64.33 ppm. For PEODS another methine signal is also observed at 39.6 ppm. The methylene carbons of the amino acid have resonances at 48.6 ppm for PEODS. ^{13}C-NMR spectra of the polymer zinc complex display signals at 39–40 ppm, 66.4–66.6 ppm, 169.4–172.3 ppm, etc. [18], shifted downfield in comparison with the corresponding signals of the ligand, indicating coordination to the zinc.

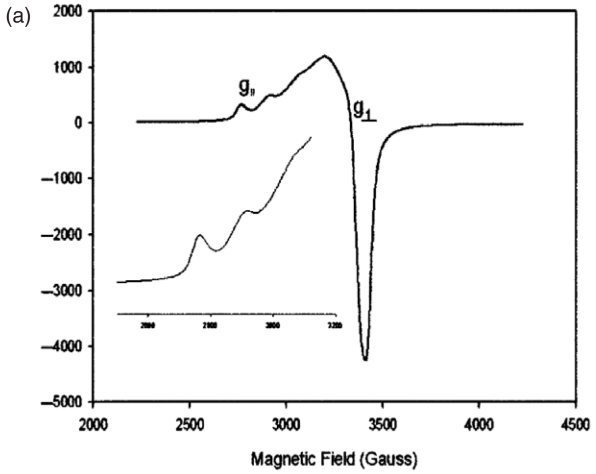
3.5. *Electronic spectra and magnetic moments*

The electronic spectra of all the synthesized polymers were recorded in DMSO solution. The various crystal field parameters (Dq, B, β and β^0) were calculated by known equations and values, given in table 3. The magnetic moment of PEODS-Mn(II) is 5.32 B.M., suggesting the presence of five unpaired electrons. The electronic spectrum of this complex exhibits three absorption bands at 18530, 22640, and 24660 cm^{-1}, which may be assigned to $^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$ (ν_1), $^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$ (ν_2) and $^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$ (ν_3) transitions, respectively suggesting octahedral geometry [19]. The magnetic moment of PEODS–Co(II) complex is found to be 4.48 BM which is in the range expected for Co(II) with octahedral geometry [20]. The electronic spectrum in DMSO shows three bands at 7420, 15070 and 18785 cm^{-1} due to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_1), $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_2) and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ (ν_3) transitions, respectively. The ligand field parameters (Dq, B, β and β^0) are calculated by using Tanabe-Sugano diagrams. The above discussion indicates octahedral geometry around Co(II), accounting for the two coordinated H_2O's in making the octahedral environment. The PEODS–Ni(II) complex shows three bands at 9020, 14080 and 24500 cm^{-1} assigned to the spin allowed transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ (ν_1), $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ (ν_2) and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ (ν_3), respectively. The ν_1:ν_2 value is 1.64 and corresponds to usual range (1.6–1.82) for nickel(II) complexes having octahedral structures [21].

Table 3. Magnetic susceptibility, electronic, and ESR spectral parameters of polyester metal complexes.

		ESR		Electronic spectral data					
Abbreviation	Magnetic moment[a] (μ_{eff})	g^H	$g^\perp$	Electronic Transition (cm^{-1})	Assignment	10Dq	B′	β	$\beta(\%)$
PEODS–Mn(II)	5.32			24660	$^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
				22640	$^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$				
				18530	$^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
PEODS–Co(II)	4.48			18785	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	8480	824	0.85	15
				15070	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
				7420	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
PEODS–Ni(II)	2.68			24500	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	8565	874	0.81	19
				14080	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
				9020	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$				
PEODS–Cu(II)	1.86	2.35	2.12	24670	Charge-transfer				
				14585	$^2A_{1g} \leftarrow {}^2B_{1g}$				

[a] Bohr magneton.



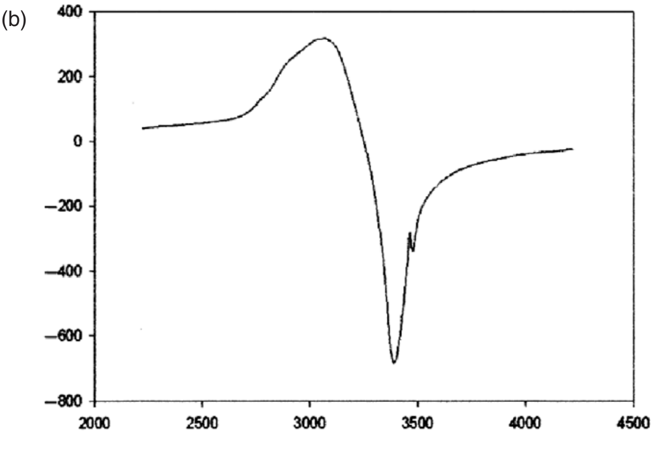


Figure 4. ESR spectra of PEODS–Cu(II).

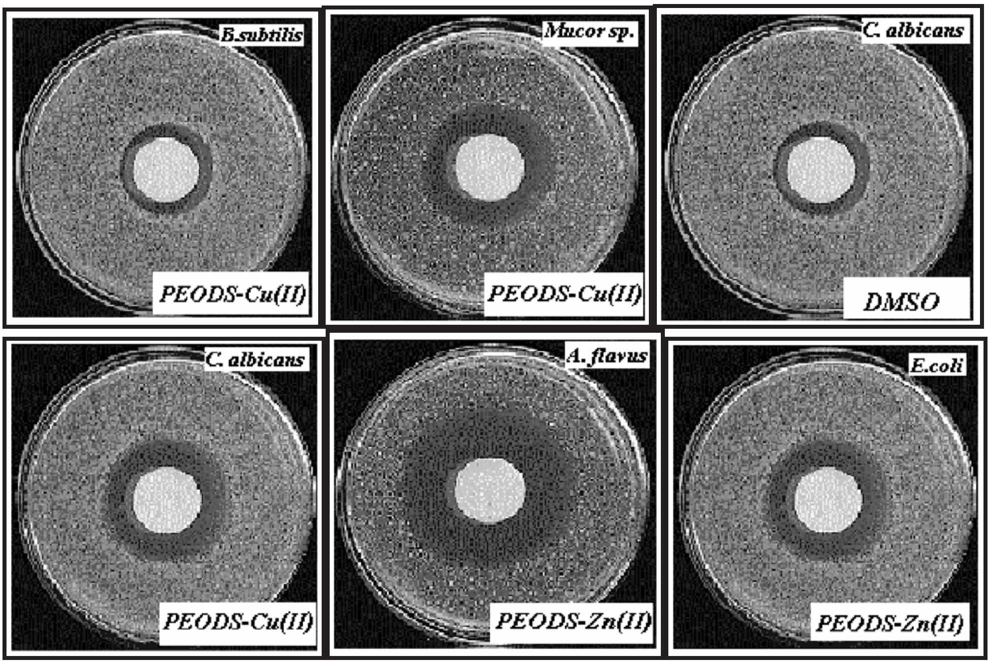


Figure 5. Anti-microbial activity of PEODS and its metal complexes.

The spectral parameters are: $Dq = 8526\,cm^{-1}$, $B' = 870\,cm^{-1}$, $\beta = 0.83$, β^0 value is 17%. The decrease in Racah parameter from the free ion value of $1040\,cm^{-1}$ to $870\,cm^{-1}$ and β value of 0.83 indicate the covalent nature of the compound. The magnetic moment is 2.68 corresponding to octahedral geometry [22]. The Cu(II) complex of PEODS also show two bands at 14585 and $24670\,cm^{-1}$ corresponding to $^2A_{1g} \leftarrow {}^2B_{1g}$ and charge transfer; the magnetic moment of this polymer metal complex is 1.86 consistent with one unpaired electron in square planar geometry [23]. Thus the electronic spectral study supports the structures proposed for the polymeric complexes.

3.6. *ESR spectra*

The ESR spectra of PEODS–Cu(II) recorded in DMSO at 300 and 77°C are shown in figure 4(a) and (b). The ESR spectrum of PEODS–Cu(II) is anisotropic with resolved hyperfine structure. This anisotropic spectrum shows a $g_{II} > g^{\perp}$ with the following values: $g_{II} = 2.3809$, $g^{\perp} = 2.0725$. These values indicate that the ground state of Cu(II) is predominately $dx^2 - y^2$, supporting a square planar structure [24]. The covalent character of a bond becomes more pronounced when the parameters g_{II} and $g^{\perp}$ are decreased, thus the copper-PEODS complex has more ionic character than covalent. The most sensitive parameter is g_{II}, which is the best indication of the covalent character. According to Kivelson and Neimen, for ionic environment, the g_{II} value is normally >2.3 and for the covalent is less than 2.3. The g-values can also be used

Table 4. Thermal behaviors of chelated polyester and its metal complexes.

Materials	Temperature Tg (°C)	Char. (%) weight °C corresponding to weight loss of 10%	20%	30%	40%	50%	at 700°C
PEODS	149	352	372	396	388	526	32%
PEODS–Mn(II)	154	390	415	425	437	445	22%
PEODS–Co(II)	157	325	348	378	450	470	26%
PEODS–Ni(II)	168	374	430	482	510	550	25%
PEODS–Cu (II)	169	400	435	476	520	560	30%
PEODS–Zn(II)	165	329	400	412	415	556	30%

Tg (°C) - glass transition temperature.

to calculate the G value, indicating whether the ligand is a weak field or strong field ligand.

The equation used is:

$$G = \frac{(g_{II} - 2.002)}{(g^{\perp} - 2.002)}$$

where G is less than 4.0 and the ligand forming Cu^{2+} complex is regarded as a strong field ligand [25]. In these resins, the G value is 5.375, indicating that the resin forms a weak field ligand [26].

3.7. *Thermogravimetric analysis*

The thermal data of the polymeric ligand and its metal complexes are tabulated in table 4. PEODS shows a 2.5% weight loss up to 100°C, due to loss of absorbed water and different solvents. The weight loss in the range 100–200°C is 15% in PEODS, corresponding to the weight of $–O–CO–CH_2–CH–NH–CO–CO–NH–CH_2–COOH$ units [27]. The decomposition of polyester has been suggested on the basis of the decomposition of simple ester. Above 200°C rapid weight loss is observed in the polymeric ligand and 75% of weight is lost up to 270–280°C and decomposed completely into volatile products at 550°C; the complexes are not completely decomposed up to 800°C. For Mn(II) and Co(II), complexes of PEODS initial weight loss to 150–160°C corresponds to two water molecules [28]. For PEODS–Ni(II), the two water molecules were gradually lost up to 250°C, suggesting that Ni(II) complex did not suddenly lose the coordinated water molecules present in the polymer metal complex. The Cu(II) and Zn(II) complexes do not show any weight loss up to 350°C, indicating the absence of coordinated water. After the loss of coordinated water molecules, the polymer metal complexes show two-step degradation, possibly due to the non-coordinated part of the complexes decomposing first, while the coordinated part decompose later [29]. The thermogravimetric analysis revealed that the PEODS metal complexes show better thermal stability than PEODS. PEODS–Cu(II) is more thermally stable than Mn(II), Co(II), Ni(II), and Zn(II) complexes. The order of stability on the basis of thermal residual weight at 700°C appears to be PEODS–Cu(II) > PEODS–Zn(II) > PEODS–Ni(II) > PEODS–Co(II) > PEODS–Mn(II), matching the Irving-Williams order of stability for the complexes of divalent metal ions [30].

Table 5. Anti-bacterial activity of polyester and its metal complexes.

Abbreviation	Zone of inhibition[a] (mm) 50 μg/disk						
	E. coli	*B. subtelillis*	*B. megaterium*	*S. aureus*	*S. typhi*	*P. aeruginosa*	*S. boydii*
PEODS	14	15	14	16	18	19	18
PEODS–Mn(II)	16	18	17	16	21	19	18
PEODS–Co(II)	18	17	19	18	20	20	18
PEODS–Ni(II)	16	18	19	18	21	21	18
PEODS–Cu(II)	18	17	19	19	22	22	18
PEODS–Zn(II)	17	19	17	18	21	22	18
Kanamycin[b]	15	16	18	17	20	20	18
DMSO[c]	–	–	–	–	–	–	–

[a] 18–30 mm significant active, 10–17 mm moderate active, <10 mm weak active. [b] Standard drug (positive control). [c] Solvent (negative control) antifungal activity.

Table 6. Anti-fungal activity of polyesters and their metal complexes.

Abbreviation	Zone of inhibition[a] (mm) 50 μg/disk						
	C. albicans	*T. species*	*A. flavus*	*A. niger*	*F. species*	*M. species*	*P. species*
PEODS	16	17	18	17	16	17	18
PEODS–Mn(II)	19	18	19	19	18	19	20
PEODS–Co(II)	19	19	19	18	21	20	18
PEODS–Ni(II)	18	19	19	21	22	21	18
PEODS–Cu(II)	20	21	19	19	22	22	18
PEODS–Zn(II)	18	17	18	19	20	18	18
Miconazole[b]	15	16	18	17	20	20	18
DMSO[c]	–	–	–	–	–	–	–

[a] 18–30 mm significant active, 10–17 mm moderate active, <10 mm weak active. [b] Standard drug (positive control). [c] Solvent (negative control).

4. Anti-microbial activity

The anti-microbial activity of all the synthesized polymers was screened against some bacteria and some fungi as shown in figure 5. All the synthesized polymers show promising anti-bacterial activity against all the bacteria. PEODS shows highest zone of inhibition 19 mm against *P. aeruginosa*. The PEODS–Cu(II) complex shows zone of inhibition 19, 22, 22 and 18 mm against *S. aureus, S. typhi, P. aeruginosa* and *S. boydii*, while the PEODS–Ni complex shows zone of inhibition 18, 21, 21 and 18 mm against these bacteria. The maximum zone of inhibition was 21 and 22 mm in PEODS–Zn(II) when it was treated against *S. typhi* and *P. aeruginosa*. PEODS–Mn(II) shows the lowest antibacterial activity as compared with other metal coordinated polymer metal complexes and polymer Cu(II) complexes show the highest zone of inhibition. The result of antimicrobial activity revealed that all the polymer metal complexes show better antibacterial activity than their corresponding ligands.

The anti-fungal activity of all the synthesized polymers are screened against seven fungi (*C. albicans*, *T. species*, *A flavus*, *A. niger*, *F. species, M. species*, *P. species*) and the results are given in table 6. The highest inhibitory zones, 22 mm, were measured in PEODS–Cu(II) against *F. species* and *M. species*. When PEODS was screened against *A. flavus* and *A. niger* the zone of inhibition was 18 and 17 mm, respectively. In case of

C. albicans, F. species. and *P. species* the inhibition zone, i.e., 18, 20 and 18 mm, were found in PEODS–Zn(II) polychelate.

The antimicrobial activities of the compounds increase after metal chelation. Chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups [31], increasing lipophilic nature of the central metal ion, which in turn favors its permeation to the lipid layer of the membrane. Other factors, viz., stability constant, molar conductivity, solubility and magnetic moment, are also responsible for increasing the anti-microbial activity of the complexes [32].

5. Conclusion

The polyester and its metal complexes were prepared in good yield and characterized by various techniques. Attachment of metal ion in the polymeric backbone enhances thermal as well as anti-microbial activity. Due to the more toxic behavior of Cu(II) its polyester metal complexes PEODS–Cu(II) may be used as anti-fungal and anti-fouling coating materials for various projects.

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