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In vitro antibacterial and antifungal assay of poly-(ethylene oxamide-*N*,*N*′-diacetate) and its polymer–metal complexes

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A new polyester, poly-(ethylene oxamide-*N*,*N*′-diacetate) (PEODA), containing glycine moiety was synthesized by the reaction of oxamide-*N*,*N*′-diacetic acid and ethylene glycol and its polymer–metal complexes were synthesized with transition metal ions. The monomer oxamide-*N*,*N*′-diacetic acid was prepared by the reaction of glycine and diethyl oxalate. The polymer and its metal complexes were characterized by elemental analysis and other spectroscopic techniques. The *in vitro* antibacterial activities of all the synthesized polymers were investigated against some bacteria and fungi. The analytical data revealed that the coordination polymers of Mn(II), Co(II) and Ni(II) are coordinated with two water molecules, which are further supported by FTIR spectra and TGA data. The polymer–metal complexes showed excellent antibacterial activities against both types of microorganisms; the polymeric ligand was also found to be effective but less so than the polymer–metal complexes. On the basis of the antimicrobial behavior, these polymers may be used as antifungal and antifouling coating materials in fields like life-saving medical devices and the bottoms of ships. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: polyester; polymer–metal complexes; elemental analysis; condensation; agar well diffusion methods

INTRODUCTION

Owing to the rapid growth in pathogenic bacteria, much research effort has been devoted to the synthesis of new antimicrobial agents. In the last two decades, several antibacterial polymers have been synthesized by immobilization of low-molecular-weight antibacterial agents to polymers.[1–3] Compared with conventional low-molecular-weight biocides, polymeric agents have the advantages that they show enhanced antibacterial activity, efficiency and selectivity, reduced residual toxicity, and prolonged stability.[4–6] Antibacterial polymers have been used as coatings in various areas viz. food processing, filters and biomedical devices. They have also been used in the textile as well as in pharmaceutical industries to form antibacterial fibers, disinfectants and preservatives.[7] Some of the commonly used low-molecular-weight antibacterial agents are fluoroquinolones, quaternary ammonium salts, phosphonium salts and transition metal complexes.[8–13] Among antibacterial agents, transition metal complexes have been the most widely used[14] owing to some advantages over other antibacterial agents, including excellent cell membrane penetration properties. On the other hand, the synthetic polymers are steadily increased to fulfill the need for safety and hygiene.[15] Two approaches are generally employed for the synthesis of these antimicrobial polymers.[16] The first approach involves the introduction of the antibacterial agents to monomers, followed by their polymerization. This method has the advantage that the monomers can be polymerized with several other co-monomers and the composition can be varied easily. The second approach involves the linking of the antibacterial agents directly onto preformed functional polymers. In an effort to discover new class of antibacterial agents that inhibit the pathogenic growth, we

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have previously reported some polymer–metal complexes which exhibit moderate antimicrobial activity and are differentiated from standard antimicrobial drugs like ampiciline, miconazole and kanamycin.[17–19]

In this paper, we report a new antimicrobial agent of poly (ethylene oxamide-*N*,*N*′-diacetate), which was prepared by the condensation of oxamide-*N*,*N*′-diacetic acid with ethylene glycol and its polymer–metal complexes were synthesized with transition metal ions. The obtained polymers were tested for antimicrobial activity against *Bacillus subtelillis, Bacillus megaterium, Staphylococcus aureus, Escheria coli, Staphylococcus typhi, P. aeruginosa* and *Shigella boydii* and for antifungal activity against *Candida albicans, Tubercularia* species, *Aspergillus flavus, Aspergillus niger, Fusarium* species, *Mucer* species and *P.* species. The minimum inhibitory concentration (MIC) values were determined for the synthesized polymers by the agar well diffusion method in DMSO solution.

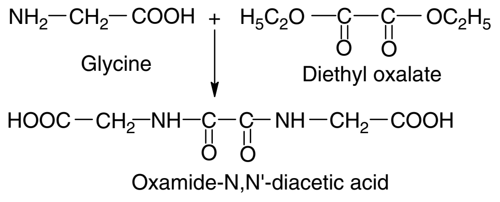
EXPERIMENTAL SECTION

Materials and bacterial strains

Glycine, diethyl oxalate, ethylene glycol (Sigma-Aldrich) and manganese (II) acetate tetrahydrate $[Mn(CH_3COO)_2^{\bullet}4H_2O]$, copper (II) acetate monohydrate $[Cu(CH_3COO)_2^{\bullet}H_2O]$, nickel-(II) acetate tetrahydrate $[Ni(CH_3COO)_2^{\bullet}4H_2O]$, cobalt (II) acetate tetrahydrate $[Co(CH_3COO)_2^{\bullet}4H_2O]$, zinc(II) acetate dihydrate $[Zn(CH_3COO)_2^{\bullet}2H_2O]$ (S. D. Fine) were commercially available and used as received. Solvents such as acetone, methanol, ethanol, diethyl ether, dimethylformamide (DMF) and dimethylsulphoxide (DMSO) were purified by standard procedures before their use. The entire microorganisms were provided by Microbiology Laboratory, School of Life Science, JNU, New Delhi.

Measurements

The elemental analyses of metal coordinated polymers were carried out on a Perkin Elmer Model-2400 elemental analyzer (CDRI, Lucknow). The metal contents of the polyester were determined by complexometric titration against EDTA after decomposing with concentrated nitric acid. The FT-IR spectra were recorded over the (4000–400 cm^{-1}) range on a Perkin Elmer infrared spectrophotometer model 621 using KBr pellets. The UV–vis spectra were carried on a Perkin Elmer Lembda EZ-201 spectrophotometer using DMSO as a solvent. Proton and carbon-13 nuclear magnetic resonance spectra 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 [thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC)] of the polyester was determined on a TA analyzer 2000 in nitrogen atmosphere. TGA and DSC were carried out at a heating rate of 20 and 10 °C min^{-1}, respectively. The solubility of the polymers was tested in various solvents at room temperature.



Scheme 1.

Synthesis

Preparation of oxamide-N,N′-diacetic acid

Oxamide-*N*,*N*′-diacetic acid was prepared by the procedure reported in Rogozhin.[20] A 1.50 g (0.02 mol) aliquot of glycine was dissolved in 25 ml of water and neutralized by an equivalent amount of NaOH, and 1.34 ml (0.01 mol) diethyl oxalate in 15 ml of ethanol was added to the aqueous solution. After that the mixture was heated at 60 °C with stirring for 3 h. Then the mixture was kept into ice-cooled water, excess HCl was added to obtain white crystals, which were filtered and washed with cooled ethanol and diethylether.

The overall route of the synthesis of oxamide-*N*,*N*′-diacetic acid is given in Scheme 1. Yield 80%. ^1H-NMR-(300 MHz, DMSO, δ) 11.10 (s, 2H, COOH), 3.90 (s, 2H, C$\underline{H}$-NH); 8.06 (s, 2H, CH-N$\underline{H}$); FT-IR (KBr pellets $\nu_{(max)}$ cm^{-1}) 3324–3235, 2962–2850, 2760–2540, 1402, 1265. Anal. calcd for $[C_6H_8N_2O_6]$ C-42.35, H-3.52, N-16.47, found C-42.38, H-3.50, N-16.45.

Synthesis of poly-(ethylene oxamide-N,N′-diacetate) (PEODA)

A mixture of 3.40 g (0.02 mol) of oxamide-*N*,*N*′-diacetic acid and 1.55 ml (0.025 mol) of ethylene glycol was refluxed and stirred at 175 °C for 2 h. The temperature was then increased up to 200 °C and the mixture was further heated for 4 h. Excess ethylene glycol was removed under vacuum using a rotatory evaporator; unreacted oxamide-*N*,*N*′-diacetic acid was removed by extracting the product thoroughly with water. The resulting polyester free from the reactant was dried over silica gel under vacuum. The yield of the product was about 80%.

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 the 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 corresponding colored precipitates of polyester metal complexes were filtered off, washed several times with hot water and finally with ethanol and dried in a vacuum desicator over calcium chloride at room temperature.

Antibacterial assessment

The antibacterial activity of the polymeric ligand and its polymer–metal complexes were tested against different microorganisms in DMSO as a solvent. The sample concentration was 50 and 100 μg ml^{-1} for antibacterial

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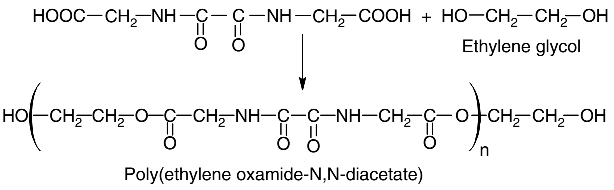
and antifungal studies, respectively. Bacterial strains were nourished in nutrient broth (Difco) and yeasts in malt extract broth (Difco) and incubated for 24 and 48 h, respectively. According to the agar diffusion method bacteria were incubated on Mueller-Hinton Agar and yeast on Sabouraud dextrose agar. The wells were dug in the media with the help of a sterile steel borer. Then 0.1 ml of each sample was introduced in corresponding well. Other wells were supplemented with solvent (DMSO) for positive control and standard drug viz. Kanamycin (antibacterial) and Miconazole (antifungal) for negative control. The resulting zones of inhibition on the plates were measured in millimeters.

RESULTS AND DISCUSSION

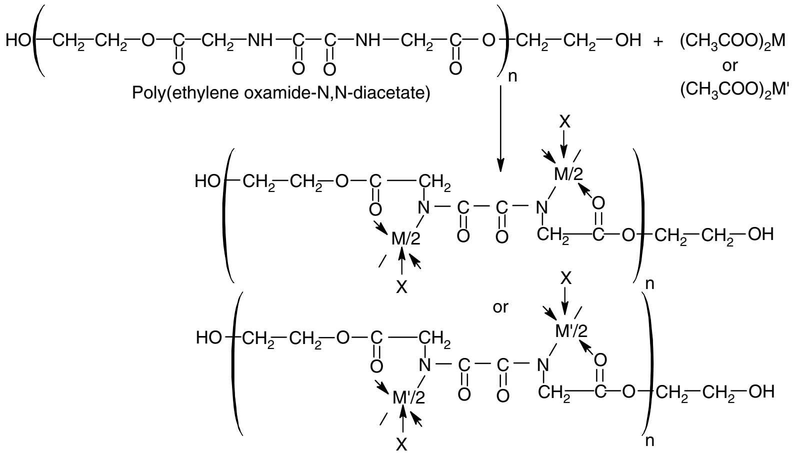
PEODA was prepared by the procedure in the Experimental section and shown in Scheme 2. The polymeric ligand is a viscous liquid, soluble in common organic solvents, while the coordination polymers are colored solid materials, soluble in DMSO and DMF but insoluble in common organic solvents. The overall route of the synthesis of metal complexes is given in Scheme 3. 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 (PEODA) with its polymer–metal complexes are given in Table 1, and agreed with 1 : 1 molar metal to polymeric ligand ratio. The analytical data revealed that the coordination polymers of Mn(II), Co(II) and Ni(II) coordinate with two molecules of water with each metal ion, which is also supported by the FT-IR and TGA data.



Scheme 2.

FT-IR spectra

The important IR bands and their assignments of ligand PEODA and its polymer–metal complexes are summarized in Table 2. A very broad and strong band is observed in the region 3500–3200 cm^{-1} due to *asym* and *sym* νNH,[21] and for the ν OH (terminal) group of the polymer as ethylene glycol is taken in excess during synthesis of the polymeric ligand. The presence of the methylene group is confirmed by the appearance of two strong bands at 2940–2840 cm^{-1} of νCH_2 *sym* and *asym* stretching and a band between 1485–1455 cm^{-1} due to CH_2 bending mode.[22] The C═O band, which has the main contribution in ester and amide, occurs in the regions 1735–1715 and 1680–1650 cm^{-1}, respectively.[23] The C═O frequency is slightly lowered due to hydrogen boding. The band observed at 1050 cm^{-1} in the spectrum of the ligand has a mixed contribution of C–N and NH in poly-(ethylene oxamide-*N*,*N*′-diacetate). Another weak band is observed at 750 cm^{-1}, which is assigned to $-(CH_2)_2-$ of the polymeric chain.[24] The spectra of metal coordination polymers are compared with their corresponding ligands to elucidate the participation of a specific group or moieties in the formation of complexes. The strong absorption band due to ν NH 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 δ HOH deformation and rocking modes of the coordinated



"Where" M = Mn(II), Co(II), and Ni(II).
M' = Cu(II) and Zn(II)
X = H_2O

Scheme 3.

Table 1. Elemental analysis of the polymeric ligands and their polymer–metal complexes

		Elemental analysis			
Compound abbreviation	Empirical formula	Carbon	Hydrogen	Nitrogen	Metal
PEODA	$(C_8H_{10}O_{16}N_2)_x$	47.76	4.38	12.16	—
		(47.76)	(4.39)	(12.17)	—
PEODA–Mn(II)	$(C_8H_8O_6N_2)_x - x$ Mn(II). $2xH_2O$	30.11	3.79	8.87	17.21
		(30.15)	(3.75)	(8.79)	(17.24)
PEODA–Co(II)	$(C_8H_8O_6N_2)_x - x$ Co(II). $2xH_2O$	29.83	3.75	8.69	17.98
		(29.84)	(3.74)	(8.65)	(18.00)
PEODA–Ni(II)	$(C_8H_8O_6N_2)_x - x$ Ni(II). $2xH_2O$	29.85	3.76	8.70	17.93
		(29.85)	(3.75)	(8.69)	(17.90)
PEODA–Cu(II)	$(C_8H_8O_6N_2)_x - x$ Cu(II)	29.32	3.69	8.54	19.39
		(29.35)	(3.65)	(8.55)	(19.40)
PEODA–Zn(II)	$(C_8H_8O_6N_2)_x - x$ Zn(II)	32.74	3.43	9.50	22.26
		(32.73)	(3.45)	(9.47)	(22.28)

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

Table 2. Important IR spectral bands and their assignments

Assignment	PEODA	PEODA–Mn(II)	PEODA–Co(II)	PEODA–Ni(II)	PEODA–Cu(II)	PEODA–Zn(II)
NH (*asym* and *sym*) and OH	3500–3200(s)	3480–3320(s,b)	3480–3320(s,b)	3480–3240(s,b)	3500–32 100(s,b)	3480–3250(s,b)
CH_2 (*asym*, *sym*)	2940–2855(s)	2940–2840(s)	2940–2850(s)	2940–2845(s)	2940–2850(s)	2940–2850(s)
C=O Ester	1730–1715(s)	1730–1715(s)	1730–1715(s)	1730–1715(s)	1730–1715(s)	1730–1715(s)
δHOH (water) oxamide	—	1660(s)	1655(s)	1660(w)	—	—
νC=O	1680(s)	1655(s)	1650(w,b)	1655(s)	1660(v,s)	1655(m)
δ(CH) bending due to	1460(s)	1470(m)	1465(s)	1465(w)	1485(s)	1475(s)
–N–CH_2–Nδ(C–N) (oxamide)	1435(s)	1435(m)	1430(s)	1430(s)	1425(m)	1430(s)
νM–O	—	640(s)	645(s)	645(s)	640(s)	645(b)
νM–N	—	530(w)	520(s)	525(s)	515(m)	530(s)

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

water.[25] These bands disappear in the spectra of Cu(II) and Zn(II) metal complexes due to the absence of coordinated water molecules. The band of C=O (ester) region is shifted to a lower frequency region in the spectra of coordination polymers. This positively indicates that the coordination of the metal at the ester group takes place rather than the C=O of the oxamide group because the C=O of the oxamide group is not shifted from its position. The appearance of new bands in the region 650–640 cm^{-1} is attributed to ν M–O and the stretching frequency bands in the 535–520 cm^{-1} region are attributed to ν M–N, which further confirms the coordination through nitrogen and oxygen.

^{1}H-NMR spectra and ^{13}C-NMR spectra of polyester and their complexes

The proton magnetic resonance spectra of amino acid-based polyester and their Zn(II) metal complexes were recorded in DMSO-d_6 with tetramethysilane as internal reference. In Fig. 1, ^{1}H NMR spectra of polymeric ligand showed a peak for methylene protons of the glycol moiety at 4.36 ppm, while the methyene proton of glycine moiety in PEODA appeared at 3.82 ppm.[26] The oxamide N–H protons showed a resonance signal at 7.96 ppm in PEODA. In the Zn(II) complexes, the intensity of N–H proton peaks had completely disappeared. This is due to the coordination of nitrogen with the metal ion after deprotonation, which is also confirmed by FTIR spectra of the polymer–metal complexes. It was observed that DMSO had no coordination effect on the spectra of the ligands or on their metal complexes.[27]

The ^{13}C NMR spectrum of the Zn(II) chelated (PEODA) is given in Fig. 2. The ^{13}C-NMR spectra of PEODA showed resonance signals at 162.7 and 192.6 ppm due to the carbonyl carbon of oxamide and carbonyl carbon of ester groups, respectively. The methylene carbons of glycol moiety in all

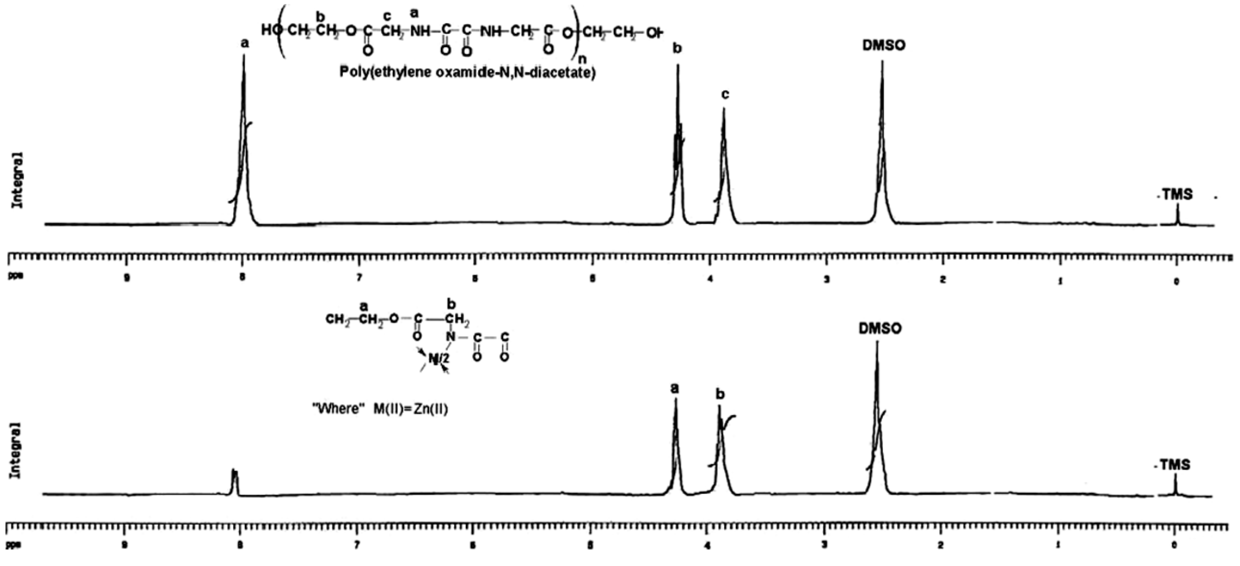


Figure 1. ^{1}H-NMR spectra of (PEODA) and (PEODA)–Zn(II).

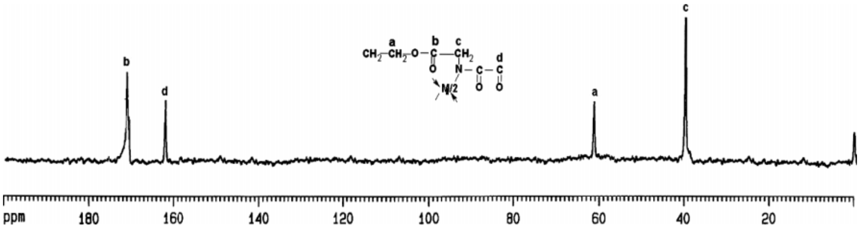


Figure 2. ^{13}C NMR spectra of [PEODA–Zn(II)].

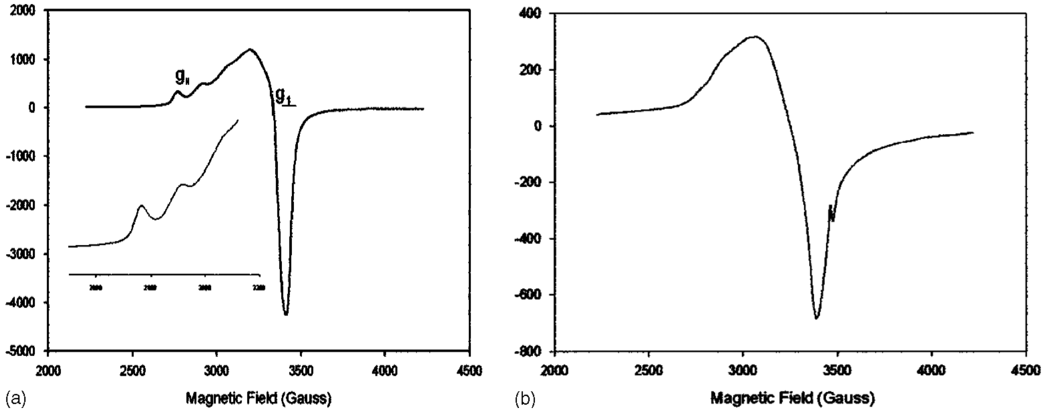


Figure 3. ESR spectrum of PEDOA–Cu(II).

the polymeric ligand showed a signal in the region 63.66–65.4. The methylene carbons of glycol were at 4.33 ppm. The methylene carbons of amino acid moiety showed resonance signals at 40.3 ppm in the case of PEODA. ^{13}C NMR spectra of the polymer–metal complexes displayed signals at 39–40, 66.4–66.6, 169.4–172.3 ppm, etc.[28] These signals show a downfield shift in comparison with the corresponding signals of the ligands, indicating the coordination with the central metal ion.

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 using known

Table 3. Magnetic susceptibility, Electronic, and ESR spectral parameters of polyester and its polymer–metal complexes

		ESR		Electronic spectral data					
Abbreviation	Magnetic[a] moment (μ_{eff})	g^{H}	$g^{\perp}$	Electronic transition (cm^{-1})	Assignment	10*Dq*	*B*′	β	β%
PEODA–Mn(II)	5.68			24 620	$^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
				22 880	$^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$				
				18 645	$^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
PEODA–Co(II)	3.97			19 600	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	9640	813	0.84	16%
				16 280	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
				8560	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
PEODA–Ni(II)	2.96			24 220	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	8526	870	0.83	17%
				13 920	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
				9005	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$				
PEODA–Cu(II)	1.78	2.30	2.07	25 050	Charge-transfer				
				15 365	$^2A_{1g} \leftarrow {}^2B_{1g}$				

[a] Bohr magneton.

equations and the values are given in Table 3. The magnetic moment of PEODA–Mn(II) was 5.68 BM, which suggests the presence of five unpaired electrons. The electronic spectrum of this complex exhibited three absorption bands at 18 645, 22 880 and 24 620 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 the octahedral geometry.[29] The PEODA-Co (II) polychelate had magnetic moment 3.97 BM due to four unpaired electrons and showed three bands at 8560, 16 280 and 19 600 cm^{-1} due to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_2)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ transitions, respectively. The calculated values of *Dq*, *B*, β and β^0 and the magnetic moment value suggest an octahedral environment around Co(II) ion.[30] The Ni(II) PEODA complex showed three bands at 9005, 13 920 and 24 220, 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 $\nu_1 : \nu_2$ value for the present compound was 1.64 and this corresponds to the usual range (1.6–1.82) reported for nickel (II) complexes having an octahedral structure.[31] The spectral parameters were: $Dq = 8526$ cm^{-1}, $B' = 870$ cm^{-1}, $\beta = 0.83$, $\beta^0 = 17\%$. The reduction of racah parameter from the free ion value of 1040 cm^{-1} to 870 cm^{-1} and the β value of 0.83 indicate the covalent nature of the compound. The electronic spectrum of the PEODA-Cu (II) complex exhibited bands at 15 365 and 25 050 cm^{-1}, assigned to $^2A_{1g} \leftarrow {}^2B_{1g}$ and the charge transfer band, indicating a square planar geometry.[32] Thus the electronic spectral study further supports the structure proposed for the polymeric complexes.

ESR spectra

The ESR spectra of PEODA-Cu(II) recorded in DMSO at 300 and 77 °C are shown in Fig. 3(a, b). The ESR spectrum shows the importance of studying the metal ion environment. The ESR spectrum of PEODA-Cu(II) is anisotropic with resolved hyperfine structure. This anisotropic spectrum shows a $g_{II} > g_{\perp}$ with the following values: $g_{II} = 2.308$, $g_{\perp} = 2.0721$, in which $g_{II} > g_{\perp}$. These values indicate that the ground state of Cu(II) is predominately $dx^2 - y^2$, which supports a square planar structure.[33] From the above results, it was found that the bonds between the polymer ligand and metal ion had an ionic character more than a covalent character. The covalent character of a bond became more pronounced when the parameters g_{II} and $g_{\perp}$ were decreased. The most sensitive parameter was the g_{II}, the variation in the g_{II} value being the best indication of the covalent character. According to Kivelson and Neimen, for an ionic environment the g_{II} value is normally >2.3 and for the covalent character the value is less than 2.3. The *g*-values can be used to calculate the *G*-value, with this factor indicating that the ligand is a weak field or strong field ligand. The equation used is as follows:

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

Where *G* is less than 4.0, the ligand forming the Cu^{2+} complex is regarded as a strong field ligand.[34] In these resins, the *G*-value is 5.397, indicating that the resin forms a weak field ligand.[35]

Thermogravimetric analysis

The thermal data of polymeric ligand and its metal complexes are given in Table 4. The polymeric ligand (PEODA) showed a 2.35% weight loss up to 100 °C, which may be due to the loss of absorbed water and different solvents. The observed percentage weight loss in the range 100–200 °C was 14% in PEODA corresponding to the weight of -O-CO-CH_2-NH-CO-CO-NH-CH_2-COOH units.[36] The decomposition of the polyester was suggested on the basis of the decomposition of the simple ester. Above 200 °C, a rapid weight loss was

Table 4. Thermal behaviors of chelated polyester their metal complexes

Weight materials	T_g (°C)	Temperature (°C) corresponding to weight loss of 10%	20%	30%	40%	50%	Char (%) at 700 °C
PEODA	140	160	185	205	210	220	0%
PEODA–Mn(II)	146	396	410	419	422	432	11%
PEODA–Co(II)	159	324	341	360	432	450	28%
PEODA–Ni(II)	164	395	421	452	518	565	20%
PEODA–Cu (II)	187	422	440	464	501	572	36%
PEODA–Zn(II)	165	352	372	396	388	526	32%

T_g (°C), glass transition temperature.

observed in the polymeric ligand and 75% of the weight was lost up to 270–280 °C. The ligand decomposed completely into volatile products up to 550 °C, but the complexes were not completely decomposed up to 800 °C. For Mn(II) and Co(II) complexes of PEDOA, initial weight loss occurred up to 150–160 °C corresponding to the theoretical value for two water molecules.[37] Therefore, it is suggested that the coordinated water molecules are lost up to this temperature range. In the case of PEODA-Ni(II), the weight corresponding to two water molecules was gradually lost up to 250 °C. It is suggested that Ni(II) complexes did not suddenly loss all the coordinated water molecules present in the polymer–metal complexes. The Cu(II) and Zn(II) complexes did not show any weight loss up to 350 °C and this suggests the absence of any coordinated water molecules. After the loss of coordinated water molecules the polymer–metal complexes showed two-step degradation, where the first step was faster than the second. This may be due to the fact that the non-coordinated part of the complexes decomposes first, while the actually coordinated part of all the polymer–metal complexes decomposes later.[38] The results of thermogravimetric analysis revealed that the PEODA-Cu(II) is comparatively more thermally stable than that of Mn(II), Co(II), Ni(II), and Zn(II) complexes. The thermal stability of Cu(II) in both case is higher than that of the other complexes due to the higher stability constant of Cu(II) ions. The order of stability on the basis of thermal residual weight at 700 °C appears to be PEODA-Cu(II) > PEODA-Zn(II) > PEODA-Ni(II) > PEODA-Co(II) > PEODA-Mn(II). This order matches the Irving–Williams order of stability for the complexes of divalent metal ions.[39]

Anti-microbial activity

The antimicrobial activity of all the synthesized polymers was screened against some bacteria and some fungi. All the synthesized polymers show promising antibacterial activity against all the bacteria and the zones of inhibition are given in Table 5. The PEODA-Cu(II) complex showed zones of inhibition of 22, 22, 20 and 18 mm against *S. aureus, S. typhi, P. aeruginosa* and *S. boydii.*

The maximum zone of inhibition was 21 mm in PEODA-Zn(II) complex, when it was used against *P. aeruginosa.* PEODA-Mn(II) showed the lowest antibacterial activity as compared with the other coordination polymers; on the other hand polymer Cu(II) complexes showed a higher zone of inhibition than its parental ligand and other metal coordinated polymers. The result of antimicrobial activity revealed that all the polymer–metal complexes showed better antibacterial activity than their corresponding ligands. The PEODA showed a higest zone of inhibition of 18 mm against *P. aeruginosa.* The antifungal activity of the synthesized polymers are tested against seven fungi—*C. albicans*, *T.* species, *A flavus, A. niger*, *F.* species, *M.* species and *P.* species—by the agar well diffusion method and the results are given in Table 6. The highest inhibitory zones, i.e. 21 and 22 mm, were measured in PEODA-Cu(II) against *F.* species and *M.* species, respectively. When PEODA was screened against *A. flavus* and *A. niger* the zone of inhibition was found to be 19 mm. In the case of *C. albicans*, *F.* species and *P.* species inhibition zones of 21,

Table 5. Antibacterial 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*
PEODA	14	13	15	17	18	18	18
PEODA–Mn(II)	17	18	16	18	19	21	18
PEODA–Co(II)	14	16	18	19	21	21	18
PEODA–Ni(II)	16	19	17	19	21	22	18
PEODA–Cu(II)	17	18	19	20	22	22	18
PEODA–Zn(II)	16	17	17	19	21	21	18
Kanamycin[a]	15	16	18	17	20	20	18
DMSO[b]	—	—	—	—	—	—	

[a] Standard drug (positive control).

[b] Solvent (negative control) antifungal activity.

Table 6. Antifungal activity of polyesters and their metal complexes

	Zone of inhibition[a] (mm) 50 μg/disk						
Abbreviation	*C.albicans*	*T.species*	*A. flavus*	*A. niger*	*F. species*	*M. species*	*P. species*
PEODA	16	17	18	17	16	17	16
PEODA–Mn(II)	17	19	19	27	20	19	18
PEODA–Co(II)	20	19	19	20	21	21	19
PEODA–Ni(II)	18	20	22	19	21	20	21
PEODA–Cu(II)	21	21	19	19	21	22	22
PEODA–Zn(II)	18	18	17	19	18	19	20
Miconazole[a]	15	16	18	17	20	20	18
DMSO[b]	—	—	—	—	—	—	—

[a] Standard drug (positive control).
[b] Solvent (negative control).

21 and 22 mm were found in PEODA-Zn(II) polychelates respectively.

The results of the investigation revealed that all the synthesized polymers showed significant antimicrobial activity. It has commonly been accepted that polymers of amino acid cause membrane linkage, perhaps by interfering with the change of the phosphate on phospholipids of the membranes. It has been observed that the antimicrobial activity of the ligand increased after chelation. This is because chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups.[40] This process increases the 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 antimicrobial activity of the complexes.[41]

CONCLUSION

The polyester and its metal complexes were prepared in good yield and characterized by various techniques. It has been observed that the attachment of the metal ion in the polymeric backbone enhances thermal as well as antimicrobial activity. The antimicrobial activity of Cu(II) coordinated polymer was found to be greater than that of other metal-coordinated polymers due to the higher stability constant of the Cu(II) ion. Owing to its effective antimicrobial activity, PEODA-Cu(II) may be used as antifungal and antifouling coating materials for various projects such as medical instruments and the bottoms of ships.

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