

Research Article

Antimicrobial Bioplastics: Synthesis and Characterization of Thermally Stable Starch and Lysine-Based Polymeric Ligand and Its Transition Metals Incorporated Coordination Polymer

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Potato-based starch was dissolved in distilled water until paste form of starch was found. Paste form of starch polymer by the process of polycondensation reacted with an essential amino acid lysine in a basic medium. The viscous product obtained was then filtered and after a short period of drying was then coordinated with a series of transition metals as Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The synthesized polymeric ligand and its polymer metal complexes were spectroscopically characterized, thermally analyzed, and biologically evaluated. In this work, FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, CHN, TGA, SEM, antimicrobial screening, and ASTM- D5338-93, a CO_2 evolution method of biodegradable, studies were carried out. The confirmation of the synthesis was done with these instrumental and spectroscopic techniques. Metals-coordinated polymer complexes were found to be more thermally stable and less biodegradable than the virgin parent ligand. Metal-coordinated polymers of all metals were found to be antibacterial and antifungal, with a range of weak to mild zone of inhibition values in agar well diffusion method for antimicrobial studies. Cu(II) polymer metal complex showed the highest value of antimicrobial activity because of the highest stability constant.

1. Introduction

Starch is one of the finest example of the low-cost abundant material which has got manifold uses in various multidimensional applications. Etherification, esterification, oxidation, cross-linking, and graft copolymerization through hydroxyl groups are the various chemical modifications that are most common, while having a starch molecule as a reactant in different chemical synthesis. Adsorption capacity of the polysaccharide chain is enhanced after the introduction of amino groups. The presence of amino groups in besides hydroxyl groups is highly advantageous for conducting modification reactions [1]. Water insoluble granules of starch have broader application in enhancing the physical properties of many foods [2]. In other cases the presence of amino groups in the polysaccharide chain increases the adsorption capacity [3]. The presence of amino groups in the reaction besides of hydroxyl groups is advantageous for conducting various modification reactions. Several cross linkers such as

glutaraldehyde [4–6], epichlorohydrin [7], ethylene glycol diglycidyl ether [8, 9], and oxidized cyclodextrin [10] have been used to modify the polysaccharide for application in heavy toxic metal ion removal. The classical methods for the removal of metal ions from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion-exchange, and adsorption. Among all the above methods, adsorption is highly effective and economical. Polysaccharides behave as an excellent adsorbent for the removal of metal ions, dyes, and proteins. These biopolymers have recently received a great deal of attention due to their sustainability and environment-friendly attitude. Nontoxicity, hydrophilicity, biodegradability, and biocompatibility are a vast range of applications in biomedical field, which polysaccharides can furnish, as well as their usage in the field of cosmetic, food, and textile industries [11]. Amino groups in the polysaccharide chain increase the adsorption capacity. Cross linked chitosan resin chemically modified with lysine has been used to investigate the adsorption of Pt(IV), Pd(II),

and Au(III) from aqueous solutions [12]. Muzzarelli and Rocchetti [13] reported that through the hydroxyl group and amino group, polysaccharide can form a stable chelate compounds with many transition metal ions. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions form complexes with ligands which have more or less electronegative donor atoms. Chelating agents like N and S groups are highly efficient for the selective sorption of precious metal ions [14–17]. The work carried out here is polymer reaction of lysine grafted on the starch polymer which is further coordinated with few transition metal(II) ions and then spectroscopically characterized and biologically and thermally evaluated.

2. Experimental

2.1. Materials. MERCK (Mumbai) provides the required chemicals. Starch, Lysine, ethanol, and sodium hydroxide were found to be in pure state and so was used without further purification. A standard procedure was used to purify solvents such as acetone, DMF, DMSO, and methanol (S.d fine chemicals). No further purification was involved with manganese (II) acetate tetrahydrate $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ copper (II) acetate tetrahydrate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, nickel (II) acetate tetrahydrate $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, cobalt (II) acetate tetrahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, and zinc (II) acetate tetrahydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ were used as such. A.M.U., Agriculture and Microbiology Department, Aligarh provided the necessary microorganism for biodegradation in composting conditions and for the development of bacterial culture colony in agar well diffusion method for antimicrobial studies.

3. Synthesis

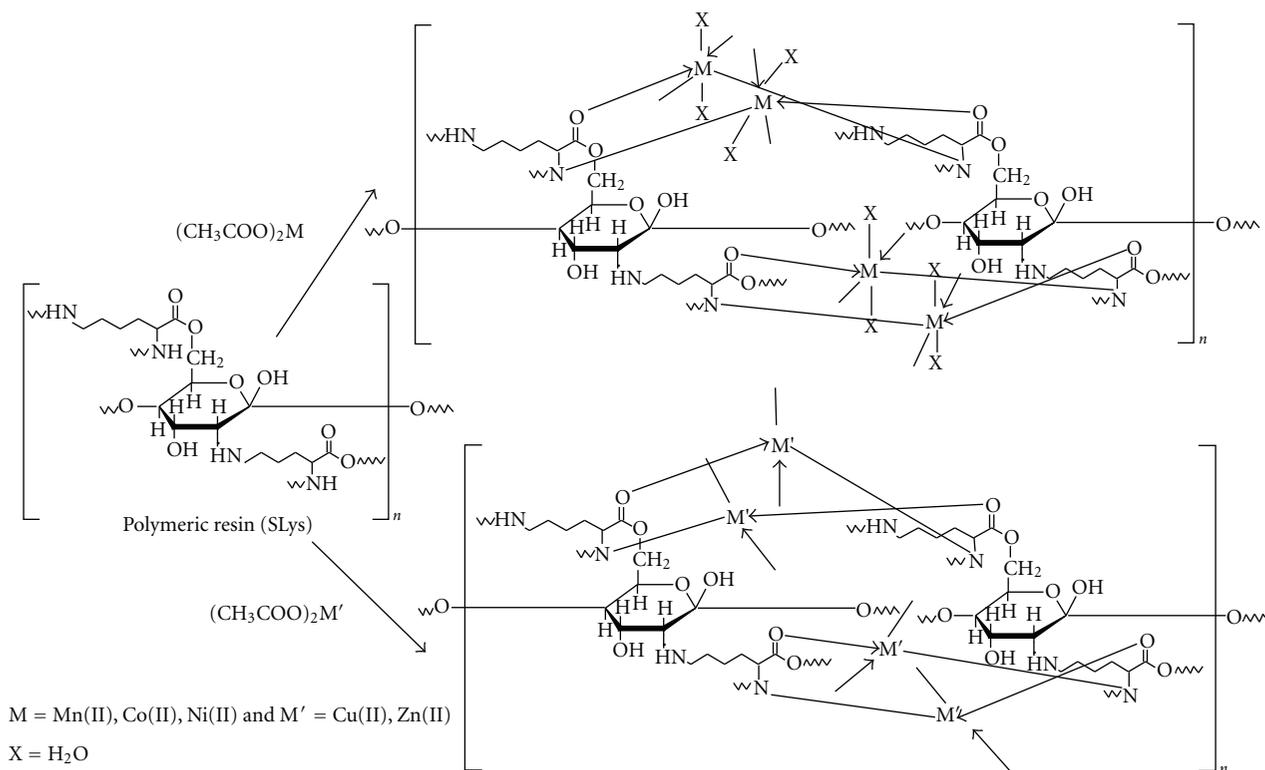
3.1. Synthesis of Polymeric Resin. Polycondensation of paste form of starch with lysine in 2:1 molar ratio was carried out [18] given in Figure 8. (0.02 mol) 1.296 gm of lysine and (0.01 mol) 1.62 gm of starch poured with 110 mL deionized water were placed in a 250 mL three-necked round-bottom flask, equipped with a stirrer and a condenser, at a constant temperature water bath at 100°C for 3 h. High speed stirring was used to carry out the reaction. The medium used was basic and was adjusted to pH of 8 with the dilution of NaOH. Thin layer chromatography (TLC) using ethanol as an eluent was used to monitor the reaction. Mud brown-colored viscous product was obtained. Several washing with ethanol and acetone are done and then the product was left to dry in a vacuum oven under reduced pressure at 65°C for 9 h. The obtained light mud brown powder of starch-lysine-based polymeric ligand (poly-SLys) was obtained in 76% yield. Solubility check showed that the synthesized product was found to be slightly soluble in distilled water at high temperature and completely soluble in DMSO and was found insoluble in common organic solvents like ethanol, methanol, carbon tetrachloride, DMF, THF, CHCl_3 , and so forth.

3.2. Synthesis of Metal Complexes. 1:2 molar ratio of ligand (poly-SLys): metal (metal salts) were used to prepare the metal complexes of different transition metals as given in Scheme 1. (0.01 mol) 3.10 gm of poly-SLys and (0.02 mol) 3.98 gm of Cu(II) salt as a typical procedure for the preparation of the Cu(II) complex is carried out and both were dissolved in a minimum quantity (~30 mL) of hot DMSO separately. Constant stirring was applied while mixing the solutions in hot condition at 70°C for 5 h. A light brown green-colored product was obtained which was reprecipitated in distilled water. This product was filtered and washed with alcohol, acetone and dried in a vacuum desiccator on calcium chloride; yield was found to be 71%. Another series of similar procedure was adopted for the synthesis of the other metal complexes in a same molar ratio but in a varying amount of metal salts such as poly-SLys-Mn (II), poly-SLys-Co(II), poly-SLys-Ni(II), and poly-SLys-Zn(II). Their yields were found to be 62%–69%, and the obtained product solubility was found in dimethyl sulfoxide (DMSO) and its insolubility was found in some common organic solvents such as DMF, THF CCL_4 , CHCl_3 acetone, and distilled water.

3.3. Measurements. The infrared (IR) spectra were recorded on a Perkin-Elmer infrared spectrometer model 621 by using KBr pellets. The $^1\text{H-NMR}$ spectra were recorded on a JOEL-FX-100 FT NMR instrument in dimethyl sulfoxide (DMSO) solution and tetramethylsilane (TMS) as an internal standard. The elemental analysis of carbon, hydrogen, and nitrogen was carried out on a Perkin-Elmer model-2400 elemental analyzer (CDRI Lucknow). The percentage of metals was determined by complexometric titration against EDTA after decomposing it with concentrated nitric acid (HNO_3). The solubility of polymeric ligand and its metal polychelates were checked at room temperature in different solvents. The thermal stability of polymer and its metal polychelates has been evaluated for recording thermograms by TA analyzer 2000 at a heating rate of 20°C per minute under nitrogen atmosphere. The electronic spectra of the metal complexes were recorded on a Perkin-Elmer Lambda-EZ 201, and magnetic susceptibility measurements were done with vibrating sample magnetometer. The morphological changes have been evaluated by using the instrument JEOL JSM840 SEM. The biodegradable testing was carried out through ASTM-D5338-93 and CO_2 evolution method in the laboratory itself, and the antimicrobial studies were carried out by agar well diffusion method.

4. Results and Discussions

The polymeric resin (poly-SLys) was prepared by the polycondensation process in the molar ratio of 2:1 in alkaline medium, according to Figure 8, and metal complexes were prepared by the reaction of poly-SLys with metal acetate in 1:2 molar ratio according to Scheme 1. All the products were obtained in good yields. The polymeric resin was found to be soluble in water and DMSO, while all the metal complexes were soluble in DMSO only and insoluble in common organic



SCHEME 1

solvents like methanol, ethanol, THF, DMF, CHCl_3 , CCl_4 , and so forth. The elemental and spectral analysis provides good evidence that the compounds are polymeric and these data are also in agreement with the molecular structure given in Scheme 1. The results of elemental analysis and yields of the synthesized compounds are given in Table 1. The SEM analysis provided the morphology or the change occurred in a reaction and the uniformity of the obtained product. Biological studies showed the characteristic application in regard to its futuristic approach.

4.1. FT-IR Spectra. Table 2 provides the lists of all the important IR bands of the polymeric ligands and their polymer metal complexes, with their observed-assignments of frequencies. In the IR spectra of poly-SLys-stretching bands appeared in the region 3382 cm^{-1} which may be attributed to νOH [19]. The stretching frequencies for $\nu\text{C-O}$ and CH_2 scissoring appeared at 1051 cm^{-1} and 1415 cm^{-1} for poly-SLys. The vibrational band for $\nu\text{C=O}$ appeared at 1650 cm^{-1} poly-SLys. In poly-SLys, stretching band at 1514 cm^{-1} and 1157 cm^{-1} was also observed, which is attributed to $\nu\text{N-H}$ bending and $\nu\text{C-N}$. In the case of polymer metal complexes of poly-SLys, the $\nu\text{C=O}$ stretching and $\nu\text{C-N}$ stretching registered a significant shift from 1650 cm^{-1} to $(1621-1625)\text{ cm}^{-1}$ and 1157 cm^{-1} to $(1122-1126)\text{ cm}^{-1}$ frequencies indicating the participation of metal through the oxygen of ester group and the involvement of proton from $-\text{NH}-$ group by its disappearance, and another $-\text{NH}-$ group was found

left as such without any chemical reaction. These stretchings were also supported by the appearance ($\nu\text{M-O}$) and ($\nu\text{M-N}$) stretching vibrational bands at $619-613\text{ cm}^{-1}$ [20] and $580-589\text{ cm}^{-1}$ [21]. Another stretching vibrational band at 895 cm^{-1} in complexes of Mn(II) , Co(II) , and Ni(II) also appeared, which may be assigned to $\text{M-H}_2\text{O}$. This band was also supported by UV visible spectra by the occurrence of octahedral geometry.

4.2. $^1\text{H-NMR}$ Spectra. The vibrational band ranges in the ^1H NMR spectra of polymeric resin (poly-SLys) and its metal complexes with Zn(II) are given in text below and also provided in Figures 1 and 2. The poly-SLys resin observed a vibrational frequency band at 4.37 ppm for protons of CH_2-O group. The band appeared at 4.44 ppm due to proton of CH-NH group in poly-SLys. The vibrational bands of the protons of pyranose ring of starch appeared at 5.109 , 5.022 , 4.351 , 4.315 , and 3.998 ppm . In the spectrum of poly-SLys- Zn(II) complex, the appearance of M-N bond in FTIR spectrum, due to loss of a proton from $-\text{NH}-$ group and the singlet peak of $-\text{CH-N}-$ confirm the coordination with observation of band at 4.212 ppm [22, 23].

4.3. $^{13}\text{C-NMR}$ Spectra. The $^{13}\text{C-NMR}$ vibrational band ranges of polymeric resin (poly-SLys) and their polymer complex with Zn(II) are discussed and also shown in Figures 3 and 4. The $^{13}\text{C-NMR}$ bands of poly-SLys observed a vibrational bands at 183.78 ppm due to the carbon of ester

TABLE 1: Elemental analysis and yields of the synthesized polymeric compounds.

Compounds	Yield (%)	D.T. (°C)	Elemental analysis			
			% C	% H	% N	% M
(C ₁₈ H ₃₀ N ₄ O ₈)	76	210	50.22	7.02	13.01	—
			48.100	6.640	12.850	—
C ₃₆ H ₆₈ N ₈ O ₂₄ Mn(II) ₄	67	272	35.53	5.633	9.209	18.060
			33.190	5.020	8.450	16.220
C ₃₆ H ₆₈ N ₈ O ₂₄ Co(II) ₄	62	278	35.077	5.560	9.090	19.123
			35.570	5.110	7.370	18.650
C ₃₆ H ₆₈ N ₈ O ₂₄ Ni(II) ₄	69	279	35.104	5.564	9.097	19.060
			33.100	5.360	8.970	17.100
C ₃₆ H ₅₂ N ₈ O ₁₆ Cu(II) ₄	71	275	39.058	4.734	10.122	22.960
			33.100	4.317	10.973	21.123
C ₃₆ H ₅₂ N ₈ O ₁₆ Zn(II) ₄	68	271	38.800	4.703	10.055	23.470
			36.701	4.208	10.880	21.330

TABLE 2: IR bands of polymeric ligand (SLys) and its polymer metal complexes.

Compounds	O–H	C–Ostr	C–Nstr	CH _{sci}	N–H	C=O	M–O	M–N
SLys	3382	1051	1157	1415	1513	1650	—	—
SLys–Mn(II)	3381	1049	1123	1413	1510	1620	615	580
SLys–Co(II)	3380	1047	1124	1412	1511	1625	619	581
SLys–Ni(II)	3378	1048	1122	1411	1512	1621	617	582
SLys–Cu(II)	3379	1049	1126	1411	1509	1623	615	588
SLys–Zn(II)	3380	1046	1123	1410	1508	1622	613	589

group. The vibrational band at 63.21 ppm was due to $-\text{CH}_2-\text{O}$ in poly-SLys [24]. The pyranose carbons of starch molecules in the polymeric resin observed stretching bands in the region 100.80, 97.889, 79.02, 71.620, and 61.20 ppm, respectively, for poly-SLys. For poly-SLys–Zn(II), the ester group was shifted at (158.95 ppm) lower chemical shift values. This was also supported with the formation of M–O band by free electron of oxygen. Carbon of pyranose ring also observed a little lowering in chemical shift values.

4.4. Electronic Spectroscopy. The electronic spectra of all the polymer metal complexes were recorded for their maximum wavelength in DMSO. The tabulated forms of the electronic spectral bands and their respective magnetic moment values are depicted in Table 3. Three bands at 20492 cm^{-1} , 15949 cm^{-1} , and 11299 cm^{-1} with transition of ${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}$, ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$, and ${}^4\text{T}_{1g} \leftarrow {}^6\text{A}_{1g}$ were observed in the electronic spectrum of polymer metal complex SLys–Mn(II). From these band values, mathematical and graphical calculation of crystal field parameter 10Dq , B , β° , and $\beta\%$ are found to be 16317, 777, 0.81, and 19%. The observed magnetic moment of the polymer metal complex was 5.93 BM for SLys–Mn(II). On the basis of electronic spectral bands, an octahedral geometry is proposed for polymer metal complexes. The value of the β° and the value of $\beta\%$ indicate the presence of covalency in the polymer metal complex. SLys–Co(II) has a magnetic moment value of 4.21 BM and a presence of four unpaired electrons and shared three bands at 26316, 19608, 15016 with

assigned transition at ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{1g}(\text{F})$, ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{A}_{1g}(\text{F})$. The Co(II) complex with these parameters is found to be octahedral around the Co(II) ion. In the complex of SLys–Co(II), the calculated values of 10Dq , B , β° , and $\beta\%$ are 18467.2, 923.36, 0.95, and 5%. The reduction of the Racah parameter from the free ion values of 970 to 923.36 and the presence of $\beta\%$ value indicated the covalent nature of the compound. The polymer metal complex SLys–Ni(II) was expected to be paramagnetic owing to the two unpaired d-electrons, and the experimental magnetic moment was found to be 2.85 BM. The electronic spectrum showed three bands at 25189, 14577, and 11148 which were assigned with ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, and ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ transition. The calculated values of 10Dq , B , β° , and $\beta\%$ are 4607.7, 1023.94, 0.95, and 5% which is in favour of octahedral geometry for SLys–Ni(II). The reduction in the free ion value of 1080 to 1023.94 and the presence of calculated $\beta\%$ value indicated the covalent nature of the compound. The above discussion of all polymer metal complexes was strongly an indication of an octahedral geometry around the central metal ion. For the formation of an octahedral environment, two coordinating sites out of six were occupied by H_2O molecule. SLys–Cu(II) corresponded to transition of ${}^2\text{A}_{2g} \leftarrow {}^2\text{B}_{1g}$ and charge transfer with observation of broad bands at 15639 cm^{-1} and 25000 cm^{-1} and indicated square planar geometry. The observed magnetic moment value of polymer metal complex of SLys–Cu(II) is 1.67 BM, which is in accordance with square planar geometry.

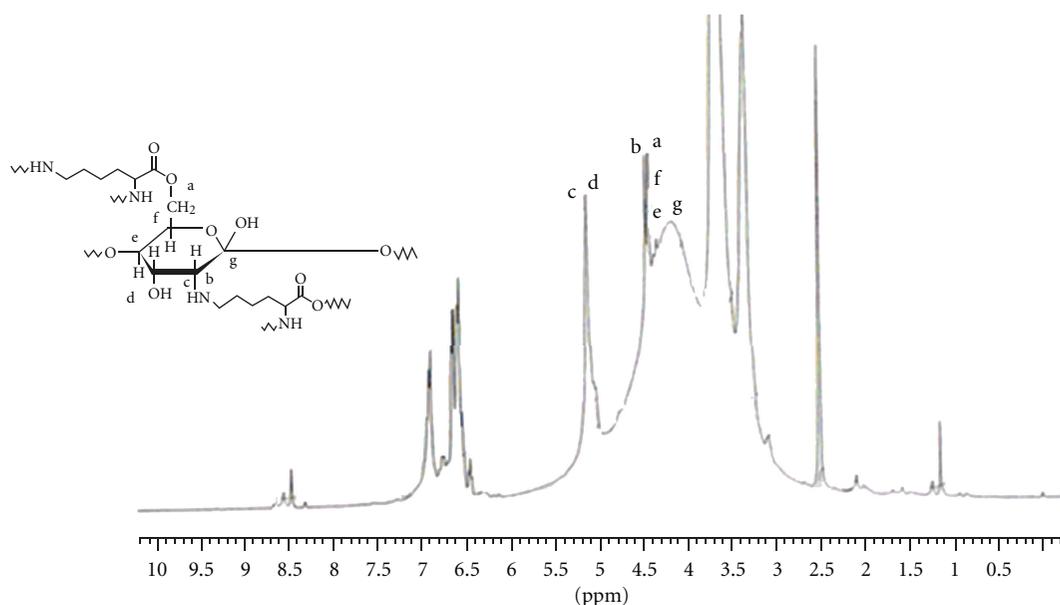


FIGURE 1: ¹H-NMR spectrum of polymeric ligand (SLys).

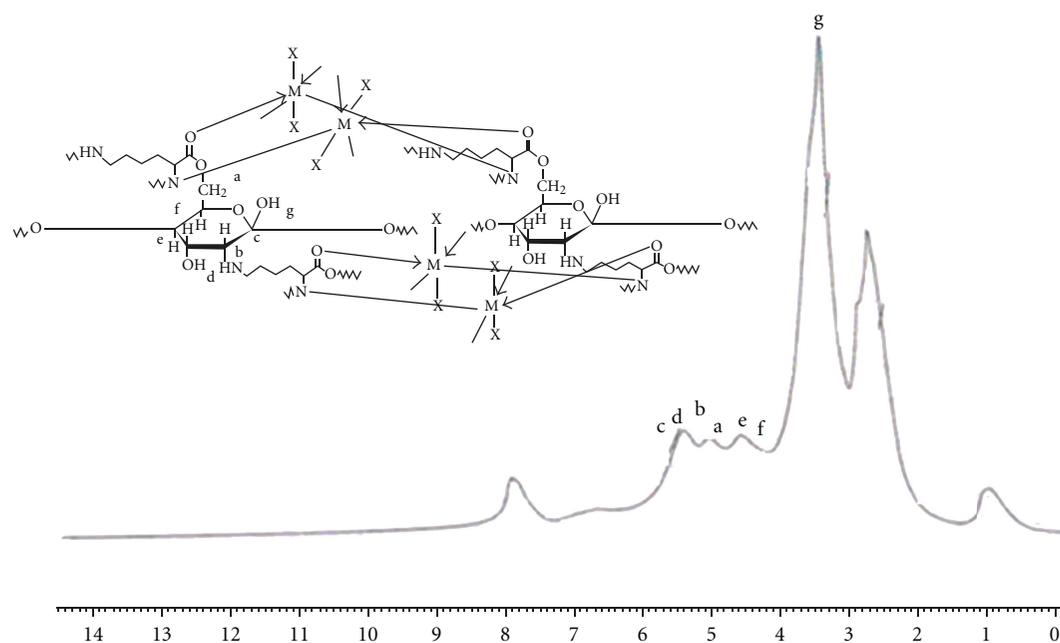


FIGURE 2: ¹H-NMR spectrum of polymer metal complex of SLys-Zn(II).

4.5. *Thermogravimetric Analysis.* Thermogravimetric method (TGA) was used to analyse the thermal decomposition of poly-SLys and its polymer metal complexes. The thermogravimetric curves of poly-SLys and its polymer metal complexes are depicted in Figure 5 and the thermal analytical data are listed in Table 4. Weight loss of only 1-2% occurred at 100°C, and this can be due to loss of solvent. At higher temperatures of more than 100°C, the mass loss was mainly related to some side products or the actual breaking of cross-linking in the resin. Up to 150°C the weight loss was slow, but after an increase or rise of

temperature beyond that, the decomposition was fast, and when the temperature reached to 200°C, the major part of decomposition has already been done. So at 200°C the poly-SLys loses its major stability. However, in case of polymer metal complexes, the thermal stability was enhanced and it overcame the thermal stability state of its parent ligand. This may be favoured due to the formation of coordination bond with the poly-SLys. Polymer metal complex started to decompose with weight loss only of 0.5-1% at 100°C, and the decomposition rate of polymer metal complexes was very slow up to 250°C, but above 250°C weight loss became

TABLE 3: Electronic spectra, magnetic moment, and ligand field parameters of polymer metal complexes.

Abbreviation	Magnetic moment (BM)	Electronic spectral data		10Dq	B	β°	$\beta^{\%}$
		Electronic Trans. (cm^{-1})	Assignment				
SLys-Mn(II)	5.93	20492	${}^4E_g(G) \leftarrow {}^6A_{1g}$	16317	777	0.81	19
		15949	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$				
		11299	${}^4T_{1g} \leftarrow {}^6A_{1g}$				
SLys-Co(II)	4.21	26316	${}^4T_{1g}(F) \leftarrow {}^4A_{1g}(F)$	18467.2	923.36	0.95	5
		19608	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$				
		15016	${}^4A_{2g}(F) \leftarrow {}^4A_{1g}(F)$				
SLys-Ni(II)	2.85	25189	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	4607.7	1023.9	40.95	5
		14577	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
		11148	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$				
SLys-Cu(II)	1.67	25000 15639	Charge transfer ${}^2A_{2g} \leftarrow {}^2B_{1g}(F)$				
SLys-Zn(II)	Diamagnetic	No transitions					

TABLE 4: Thermal behaviors of SLys and their polymer metal complexes.

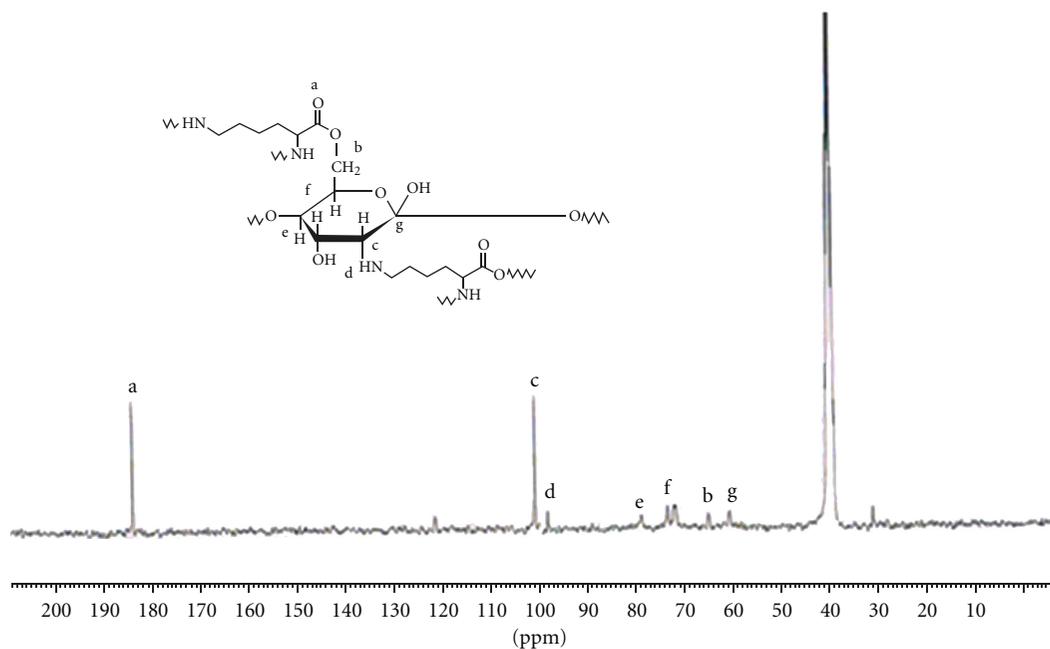
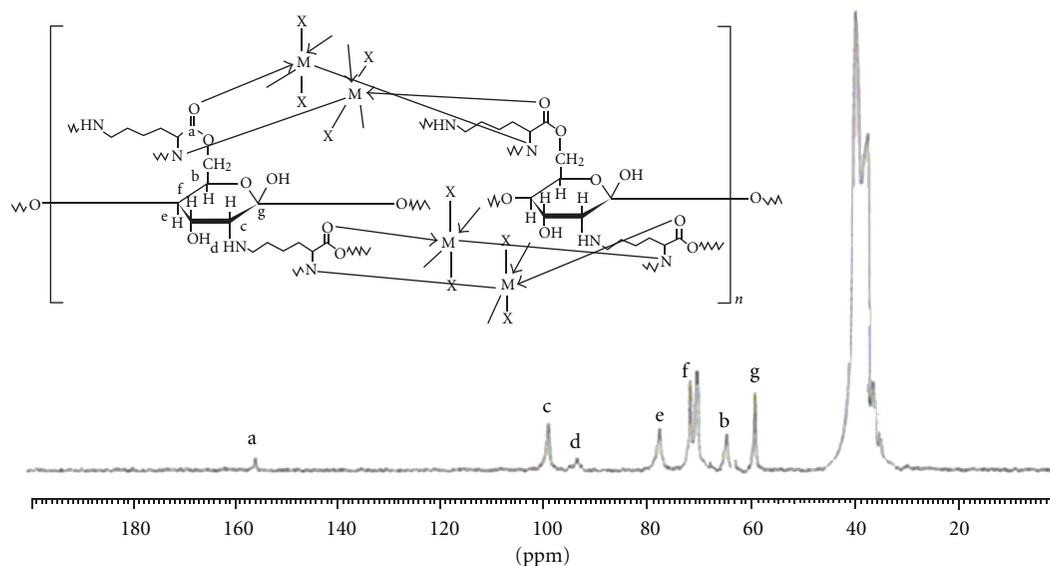
Compound/temperature ($^{\circ}\text{C}$)	Weight loss (%)								
	100	150	200	250	300	400	500	600	700
SLys	1	5	18.5	14	11	5.5	20	11	13.5
SLys-Mn(II)	1	1	7.5	5.5	22	5	3	17	22
SLys-Co(II)	2.5	3	2.5	10	23.5	8	3	13	24
SLys-Ni(II)	2	2	2	9.5	23	6	4	12	23
SLys-Cu(II)	0.5	0.5	1.5	3.5	23	8.5	4	13	23
SLys-Zn(II)	1	1	1.5	3	22	11.5	15	3	23

TABLE 5: % CO_2 mineralization of starch, SLys and its polymer metal complex.

Time (hrs)	% CO_2 mineralization		
	Starch	Polymeric resin	Polymer metal complex
24	—	5	4.1
44	1.6	7.5	5.6
68	2.2	10.30	8
92	3.7	13.5	9.35
110	5	18	12.8
136	9	22.80	13.5
160	15	25	16.2
187	18.5	26.4	16.3
200	18.6	28.8	16.5

TABLE 6: Biodegradability of starch, SLys, and Sly-Mn(II).

Materials	Biodegradability rate constant (k)	Total weight loss (gm)	Medium
Starch	0.001297	0.01081	Biotic
SLys	0.001461	0.01217	Biotic
SLys-Mn(II)	0.000791	0.006598	Biotic

FIGURE 3: ^{13}C -NMR spectra of polymeric ligand (SLys).FIGURE 4: ^{13}C -NMR spectra of polymer metal complex of SLys-Zn(II).

fast. This result revealed that coordinated-polymer has better thermal stability as compared to polymeric ligand, and, thus coordination is helpful in increasing thermal stability of polymer.

4.6. Scanning Electron Microscopy. Surface morphological analysis of starch, SLys, and SLys-Co(II) was confirmed by scanning electron microscopy (SEM) and is presented in Figure 7. The scanned surface reveals that starch granules were completely in strong adhesion. (a) Clearly uniform phases are visible in all the three figures. More even distribution of

polymer results from the compatibilized reaction in (b), (c). The increase in homogeneity can be explained through the philicity of the molecules in the reaction mixture. This can be an added technique to prove the occurrence of polymeric reaction of polymeric ligand and coordinated polymer metal complex as the final product.

4.7. Biodegradable Testing. Respirometric method in a biotic medium was used to perform the biodegradability test. Compost pile inocula were used [25], but there are preferences for users with different microbial environmental, with

TABLE 7: Antimicrobial activities of SLys and its polymer metal complexes.

	Zone of inhibition (mm) 50 μ g/disk					
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Candida albicans</i>	<i>Aspergillus niger</i>	<i>Fusarium spp</i>
SLys	—	—	—	—	—	—
SLys-Mn(II)	8	7	—	11	12	13
SLys-Co(II)	9	11	10	12	15	7
SLys-Ni(II)	10	9	11	13	8	10
SLys-Cu(II)	14	13	15	13	17	9
SLys-Zn(II)	6	7	9	10	6	5

18–30 mm = active, 10–17 mm = moderate, <10 = weak.

Standard = Kanamycin.

Solvent = DMSO.

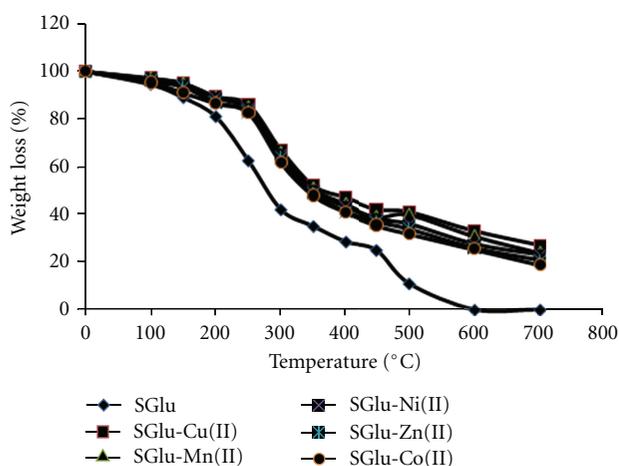
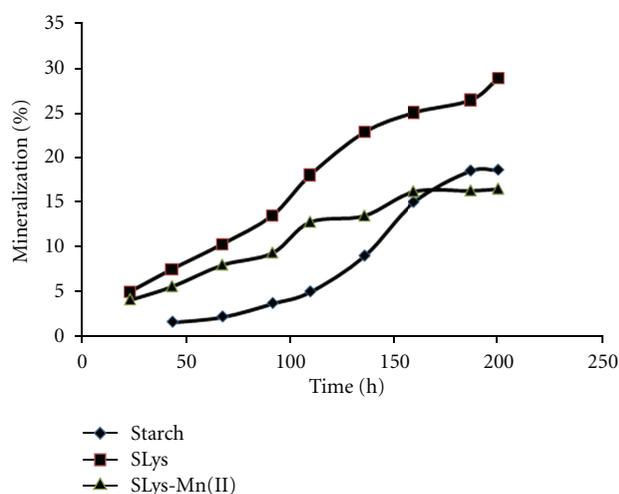


FIGURE 5: TGA curve of SLys and its polymer metal complexes.

FIGURE 6: %CO₂ mineralization of starch, Slys, and Slys-Mn(II).

certain typical polymers that are readily biodegradable or with biopolymer material. A specially designed flask is used for convenience (Anthony L. Andrady 1998 by Chapman and Hall London). Soil test has been preferred in this testing, although water test can also be preferred, but activated sludge is necessary in both situations to obtain complete mineralization. The inoculums must be placed for almost a month. The inoculums must be used the same day as collected and kept aerated until used. Also sufficient urea and potassium hydrogen phosphate (0.1 and 0.05% of weight of polymer substrate) are added to the medium to fortify it and to promote further microbial growth. The biodegradation rates of starch, poly-SLys, and poly-SLys-metal complex for a comparative study are shown in Figure 6 and predicted in Tables 5 and 6, respectively. From these data, it can be seen that the biodegradation rates of poly-SLys-metal complex were lower than those of starch polymer and poly-SLys since beginning and that the biodegradation rates of poly-SLys were higher than starch polymer at respective interval of hours.

4.8. *Antimicrobial Studies.* The antimicrobial activities of the synthesized poly-SLys and its polymer metal complexes (Poly-SLys-M(II), where M=Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)) were tested against three bacteria (*Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis*) and three fungi (*Candida albicans*, *Aspergillus niger*, and *Fusarium spp*), and the zone (zone of inhibition) inhibited by the use of synthesized polymer is given in Table 7. Presence of biodegradable starch limits the role of Slys in acting as antimicrobial, and so, the ligand SLys showed no inhibition against any bacterium and fungus. These microbes, but when then tested against polymer metal complexes, they showed a mild resistant against them as in case of SLys-Cu(II) showed 17 mm which was highest for all other metal complexes. The least resistance was shown by SLys-Zn(II) and that was only 5 mm and that is against the fungal species *Fusarium spp*. The drug used as a standard was Kanamycin and the solvent used was DMSO, (dimethyl sulphoxide). The polymer metal complexes were found to be mildly potential in their antimicrobial action. Biocidal capacity of complexes was medium when compared to standard drug Kanamycin.

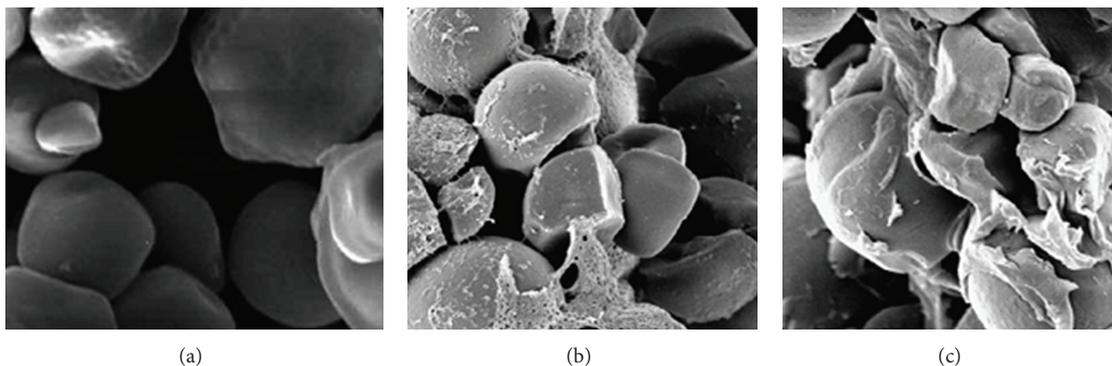


FIGURE 7: SEM micrographs of (a) Starch, (b) SLys, and (c) SLys-Co(II).

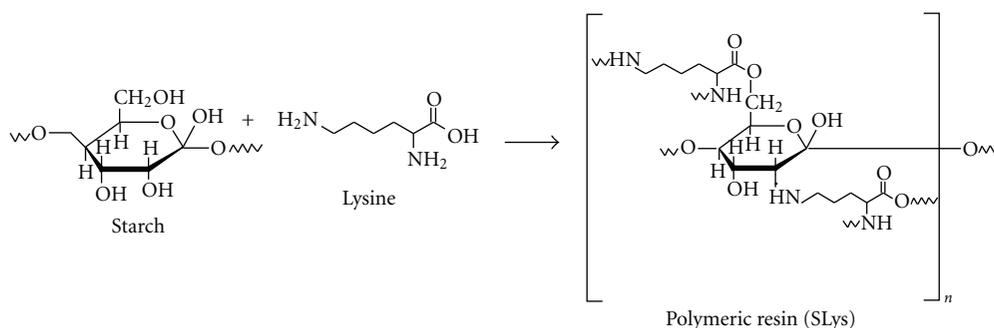


FIGURE 8: Synthesis scheme of ligand of starch and lysine (SLys).

High zone of inhibition values of SLys-Cu(II) complex as antimicrobial agent is purely attributed to its higher stability constant.

5. Conclusion

Synthesized polymeric ligand and its polymer metal complexes were obtained in potential yield. These polymers, when characterized by various instrumental techniques like FTIR, NMR, CHN, TGA, SEM, and biological activities, showed that the compound is polymeric, and the analysis was also in correlation with the occurrence of coordination in polymer metal complexes. CHN, ¹H-NMR, ¹³C-NMR, and FT-IR proved the structural formulae and the SEM showed the different morphological behaviour of starch, SLys, and SLys-M(II), and the uniformity in the phases at each step which is again is important for the occurrence of reaction at different steps. The polymeric ligand was found to be sparingly soluble in distilled water and DMSO and insoluble in benzene, toluene, methanol, ethanol, and acetone whereas all the polymer metal complexes were soluble in DMSO only and insoluble in distilled water and common organic solvents. The incorporation of metal ion in the polymeric backbone enhanced the thermal properties and showed that coordinated polymer is thermally better stable than the parent ligand, but the biodegradability was reduced and the coordinated complex was lesser in biodegradation than its polymeric ligand. Because of the degradable nature of the prepared polymeric resin which is coordinated to

metal ions, they can be used in various applications of controlled drug release, wastewater treatment, catalytic activity, hydrometallurgy, manufacture of plastic technology, and some biomedical applications.

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