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## ORIGINAL ARTICLE

# Biodegradable coordination polymer: Polycondensation of glutaraldehyde and starch in complex formation with transition metals Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)



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## KEYWORDS

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Polycondensation;  
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Glutaraldehyde;  
Biodegradable polymers

**Abstract** Starch a biopolymer, possesses many unique characteristics features accompanied with some shortcoming simultaneously. Some synthetic compounds are of great help to these demerits of starch and so by an addition of all these alternatively may acquire the tailor made features of starch-based compounds. By combining the individual advantages of starch and some other compounds and elements, starch-based biodegradable polymers were prepared for potential applications in biomedical and environmental fields. In this research, the structural analysis and characterization studies of starch glutaraldehyde polycondensed polymer were undertaken, and then the formation of polymer metal complexes with transition metal in coordinated form are carried out. FT-IR spectroscopy and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy were used to analyze the functionality of the synthesized compound. CHN of the synthesized compound was supported by FT-IR and NMR which again proved helpful for structural analysis. Electronic spectroscopy confirmed the geometry of the synthesized compounds. Thermal studies were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Besides this the biodegradable studies were carried out by ASTM standards of biodegradable materials by  $\text{CO}_2$  evolution in respirometric titration method. All the polymers showed good thermal strength and reduced biodegradation on attachment of transition metals, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

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## 1. Introduction

Synthetic or biobased biodegradable polymers have been a major focus of interest, especially by the use of natural polysaccharides such as cellulose, chitosan and starch. Starch is a primary choice for the development of sustainable material because of its abundance and cost. This polysaccharide is biodegradable, renewable and edible, which makes it ideal as food

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packaging materials (Arvanitoyannis and Biliaderis, 1998; ASTM D882-88, 1989; Cyras et al., 2006). Plastic films from edible biopolymer is one of the most important applications in utilizing them as packaging material. It is primarily used to extend the shelf-life and quality of foods by preventing changes in aroma, taste, texture or handling characteristics (García et al., 2002). These substances can provide additional nutrient content and enhance sensory characteristics, and sometimes may be consumed along with food without, fear of any form of poisoning. The biofavourable plastics, primarily composed of polysaccharides or proteins, have suitable mechanical and optical properties, as well as good gas barrier properties for gases such as O<sub>2</sub> and CO<sub>2</sub> when used in coating applications. Starch, is one of the most important and applicable polysaccharide in nature, that has led it to be the subject of numerous researches (Nimni et al., 1988). It is widely used in different industries to provide functional properties such as gelling, thickening, bonding and adhesion. It has also been extensively used in non-edible or edible film preparations (Sung et al., 1996; Noishiki et al., 1989; Shepherd et al., 2000). Pure native starch films are brittle compared with synthetic polymers such as polyethylene, and usually need to be cross linked. The use of cross linkers is to provide the enhanced mechanical properties. Various crosslinking reagents, including formaldehyde, glutaraldehyde, dialdehyde starch, and epoxy compound, have been used, that give an immense capability to starch in being used for fixing biological tissues. Glutaraldehyde is one of the best known cross linkers worldwide. Crosslinking is an important method to increase both viscosity and gelation (Wurzburg and Raton, 1987a) in aqueous food and non-food applications. Crosslinking of starch reinforced the film by chemical bonds that act as bridges between molecules, and it has been proved to be a valuable way for providing maximum film strength (Wurzburg and Raton, 1987b). Thus, crosslinked starches were used in the preparation of starch xanthates as ion-exchangers for water treatment, stilt materials for microencapsulated coatings and anti-blocking agent for films in the food, textile and paper industry (Noishiki et al., 1986). Glutaraldehyde and an epoxy compound that has been used extensively in developing bioprostheses (Sung et al., 1993; Noishiki et al., 1993) were used as controls. In this part of research we have provided cross linking to starch with glutaraldehyde and again with some transition metals in coordinated form to provide even better mechanical strength, thermal resistivity and controlled biodegradation.

## 2. Experimental

### 2.1. Materials

Manganese(II) acetate tetra hydrate [Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O], Copper(II) acetate monohydrate [Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O], Nickel(II) acetate tetra hydrate [Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O], Cobalt(II) acetate tetra hydrate [Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O] and Zinc(II) acetate dihydrate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] were used without further purification. Starch, glutaraldehyde, ethanol, sodium hydroxide, were provided by MERCK (Mumbai). Acetone, DMF, DMSO and methanol (s.d. fine chemicals) were purified by standard procedure before use and used as solvents. A.M.U., Agriculture and Microbiology Department, Aligarh,

provided the required microorganisms for biodegradation studies used in compost pile inoculums.

## 3. Synthesis

### 3.1. Synthesis of polymeric resin

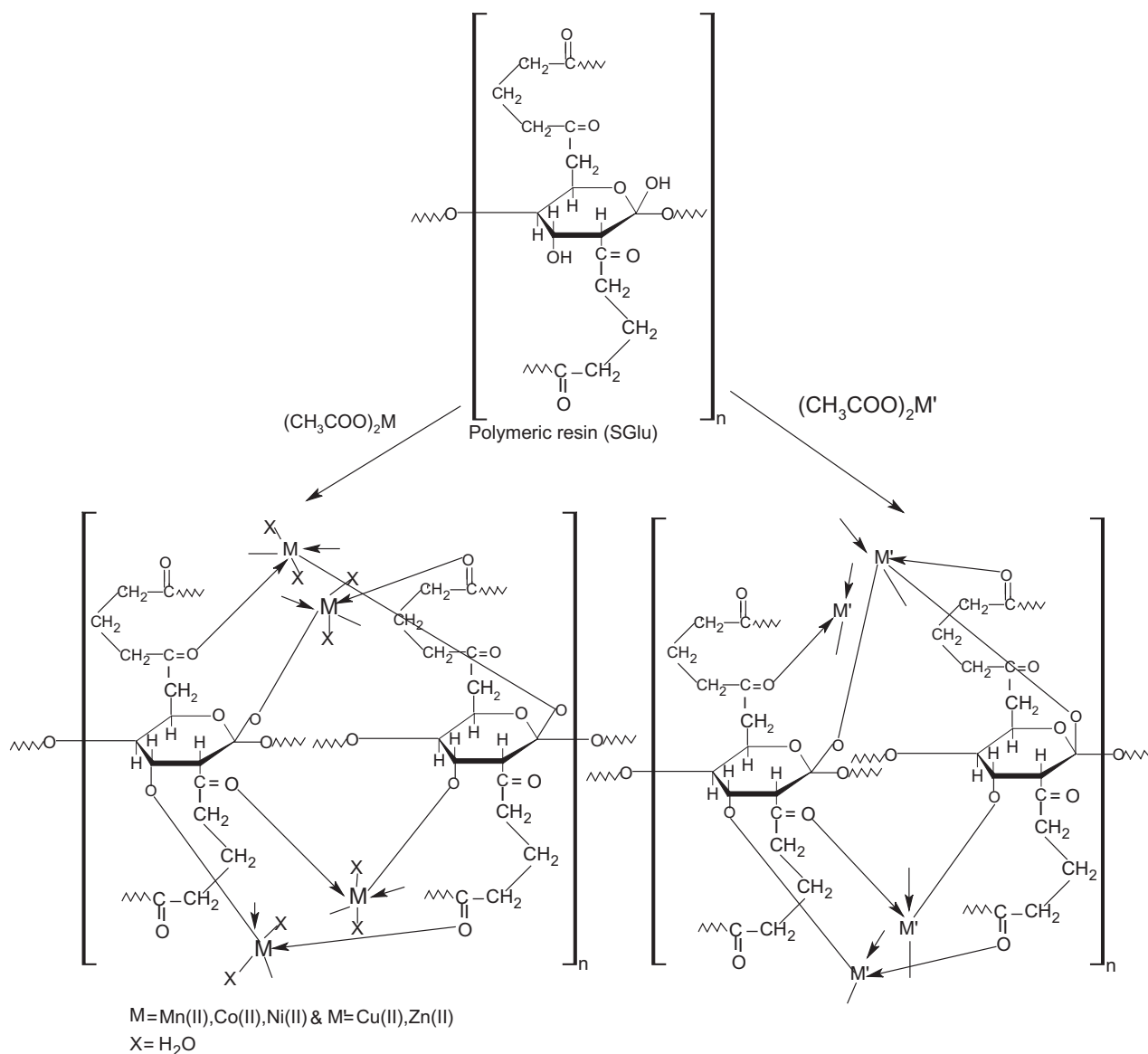
Polycondensation method of polymerization was undertaken for the reaction of glutaraldehyde and polymeric starch in a basic medium and the molar ratio was 2:1 which synthesized the products as given in Scheme 1 (Haaksman et al., 2006). NaOH was used to set the pH at 8. A dark brown colored highly viscous product was obtained, when this reaction was carried out in a condenser fitted three necked round bottom flask, in which was poured a distilled water up to 250 mL. 0.02 mol (2 g) glutaraldehyde and 0.01 mol (1.62 g) of starch were used. Stirring was done with very high speed (> 1000 r/min) in a stabilized temperature water bath for 3 h at 98 °C. TLC (thin layer chromatography) was used at frequent intervals for proper monitoring of the reaction and the eluent used in it was ethanol. Viscous product on continuous washing with acetone and ethanol was then left to dry in a vacuum oven under reduced pressure at 60 °C for a whole day. Seventy-three percent of the final product was obtained. Solubility was found in distilled water at high temperature and DMSO and insoluble in some common organic solvents like ethanol, methanol, carbon tetrachloride etc.

### 3.2. Synthesis of metal complexes

Preparation of Cu(II) complex was the initiation step for the formation of polymer metal complexes. 0.01 mol (2.62 g) of poly-SGlu and 0.02 mol (3.98 g) of Cu(II) salt were individually dissolved in a minimum quantity of DMSO (40 mL each). Mixing of both solutions was done in the hot condition of DMSO with a constant high stirring for 4 h at 60 °C. A parrot green colored product was obtained which was reprecipitated in distilled water. The product was washed and filtered and dried in vacuum desiccator on calcium chloride. Seventy-one percent yield was obtained and found soluble in DMSO only. Seventy to seventy-four percent yield and solubility in DMSO was obtained when the similar procedure was provided for the synthesis of the other metal complexes such as poly-SGlu–Mn(II), poly-SGlu–Co(II), poly-SGlu–Ni(II) and poly-SGlu–Zn(II).

### 3.3. Measurements

Perkin-Elmer infrared spectrometer model 621 by using KBr pellets was used to record the infrared (IR). The JOEL-FX-100 FT NMR instrument in dimethylsulfoxide (DMSO) solution and tetra methyl silane (TMS) as an internal standard was used to record the NMR spectra. Perkin-Elmer model-2400 elemental analyzer was used to carry out the elemental analysis of carbon, hydrogen and nitrogen (CDRI, Lucknow). Complexometric titration against EDTA after decomposing it with concentrated nitric acid (HNO<sub>3</sub>) was used to determine the percentage of metals. The solubility of polymeric ligand and its metal polychelates was checked at room temperature in different solvents. TA analyzer 2000 at a heating rate of 20 °C per minute under nitrogen atmosphere was used to evaluate the thermal stability of polymer and its metal polychelates by recording thermograms. PYRES DIAMOND DSC instrument



**Scheme 1** Synthetic route of the polymeric metal complex of (SGlu).

has been used to evaluate the glass transition temperature ( $T_g$ ) and decomposition temperature ( $T_m$ ) of the synthesized polymeric resin (SGlu) and its metal complex. Perkin-Elmer Lambda-EZ 201 was used to find out the electronic spectra of the metal complexes and vibrating sample magnetometer recorded the magnetic susceptibility measurements.  $\text{CO}_2$  evolution method of ASTM standards was used in the biodegradable testing of the compounds and was done in the laboratory itself.

#### 4. Results and discussions

Polycondensation process of polymerization in the molar ratio of 2:1 in basic medium was used for synthesizing polymeric resin (poly-SGlu) as provided in Scheme 1 and polymer metal complexes were prepared by the reaction of poly-SGlu with metal acetate in 1:2 M ratio. The obtained yield was good for all the products. The polymeric resin was found to be soluble in water and DMSO and for solubility in both solvents,

two stages were involved: in the first place, the polymer swelling, and next the dissolution step itself, while all the polymer metal complexes were soluble in DMSO only, as with the involvement of coordination the polymer metal complexes tended to be more in crosslinking and with DMSO, as a better solvent in dissolving transition metal salts, it was found soluble in DMSO only and that too again in a two steps as swelling and dissolution, and insoluble in common organic solvents like methanol, ethanol, THF, DMF,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  etc. Spectral characterization and elemental evaluation provided good coherence of the compounds to be 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.

##### 4.1. FT-IR spectra

Table 2 lists all the the important FT-IR spectral bands of all the polymeric compounds with their respective assignments

**Table 1** Elemental analysis and yields of the synthesized polymeric compounds.

Compounds	Yield (%)	D.T. (°C)	Elemental analysis		
			% C	% H	% M
SGlu	73	202	56.46	5.92	–
			56.100	4.640	–
SGlu–Mn(II)	70	258	36.93	5.03	21.11
			36.190	5.020	22.220
SGlu–Co(II)	74	257	36.38	4.96	22.31
			35.570	4.110	21.650
SGlu–Ni(II)	70	269	36.41	4.96	22.24
			36.100	4.360	21.100
SGlu–Cu(II)	71	265	41.29	3.89	27.30
			42.100	3.317	28.123
SGlu–Zn(II)	73	258	40.98	3.86	27.89
			40.701	3.208	27.330

**Table 2** IR bands of polymeric ligand (SGlu) and its polymer metal complexes.

Compounds	O–H	C–Ostr	C=Ostr	CH <sub>2</sub> sci	C–C	M–O
SGlu	3404	1050	1712	1417	1048	–
SGlu–Mn(II)	–	1011	1653	1413	1047	609
SGlu–Co(II)	–	1012	1654	1414	1047	608
SGlu–Ni(II)	–	1013	1652	1416	1045	607
SGlu–Cu(II)	–	1015	1655	1415	1046	605
SGlu–Zn(II)	–	1016	1653	1415	1044	603

and are also provided in the text below. In the IR spectra of poly-SGlu stretching bands appeared in the region  $3404\text{ cm}^{-1}$  which may be attributed to  $\nu\text{OH}$ . The stretching frequencies for  $\nu\text{C–O}$  and  $\text{CH}_2$  scissoring appeared at 1050 and  $1417\text{ cm}^{-1}$  for poly-SGlu. The vibrational band for  $\nu\text{C=O}$  appeared at  $1712\text{ cm}^{-1}$  for poly-SGlu. A stretching band at  $1048\text{ cm}^{-1}$  was observed which may be assigned to  $\nu\text{C–C}$  in poly-SGlu. In case of polymer metal complexes of SGlu the stretching frequencies of  $\nu\text{C=O}$  and  $\nu\text{C–O}$  shifted to the lower region from  $1712$  to  $(1652\text{--}1655)\text{ cm}^{-1}$  and  $1050$  to  $(1011\text{--}1016)\text{ cm}^{-1}$  which indicate the coordination of  $\text{C=O}$  oxygen to metal ion and this can be explained by the donation of free electrons from oxygen to metal atom. This is also supported by appearance of (M–O) bond at  $609\text{--}603\text{ cm}^{-1}$ . The shifting in  $\nu\text{C–O}$  was related to the loss of a proton from all the OH group for coordination. In poly-SGlu metal complexes the stretching frequency band of  $\nu\text{OH}$  has been disappeared due to involvement of proton of  $\text{–OH}$  group in coordination. Another stretching vibrational band at  $895\text{ cm}^{-1}$  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. NMR spectra ( $^1\text{H}$ and $^{13}\text{C}$ )

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR band ranges of polymeric resin and its polymer metal complex with Zn(II) are given in text below and also presented in Fig. 1–4. The poly-SGlu resin observed a vibrational band at  $3.555\text{ ppm}$  for  $\text{CH}_2\text{C=O}$  protons of methylene group. The bands appeared at

$4.01\text{ ppm}$ , due to protons of  $\text{CH–OH}$  group in poly-SGlu. The vibrational bands of the protons of pyranose ring of Starch appeared at  $5.070, 4.768, 4.332, 3.472$  and  $3.414\text{ ppm}$  in poly-SGlu. In the spectrum of poly-SGlu–Zn(II) complex, the band for  $\text{CH–OH}$  has been reduced to  $\text{CH–O}$  and observed a shifting at  $3.767\text{ ppm}$ , due to the loss of all of the protons of hydroxyl group in coordination, which is also supported by appearance of  $\text{M–O}$  band in FT-IR spectrum. Vibrational bands of pyranose ring of Starch protons also observed a lowering of chemical shift values in the complexes of poly-SGlu. The  $^{13}\text{C}$  NMR bands of poly-SGlu observed a vibrational bands at  $191.61\text{ ppm}$  due to the carbon of aldehydes group. The vibrational band of  $\text{–CH}_2\text{C=O}$  appeared at  $30.55\text{ ppm}$  for poly-SGlu. The pyranose carbons of starch molecules in the polymeric resin observed stretching bands in the region  $101.63, 98.999, 85.39, 73.40$  and  $67.05\text{ ppm}$ , respectively for poly-SGlu. In case of metal complex of SGlu with Zn(II) bands  $\text{C=O}$  band observed a shifting and was assigned at  $185.5\text{ ppm}$ . This was due to coordination by free electron of oxygen of  $\text{C=O}$  group, which was also supported by  $\text{M–O}$  band in FT-IR spectrum. Carbon of pyranose ring also observed a little lowering in chemical shift values.

#### 4.3. Electronic spectra and magnetic susceptibility measurement

Dimethyl sulfoxide was used as a solvent for molar solution of polymer metal complexes and as well as reference solvent for recording the electronic spectra of all the polymer metal complexes. The electronic spectral bands and their magnetic moment measurement are depicted in Table 3. SGlu–Mn(II) exhibited three bands at  $20283, 14534$  and  $11415\text{ cm}^{-1}$  at transition of  $^4\text{A}_{1g}(\text{G})\leftarrow^6\text{A}_{1g}(\text{F})$ ,  $^4\text{T}_{2g}(\text{G})\leftarrow^6\text{A}_{1g}(\text{F})$  and  $^4\text{T}_{1g}(\text{G})\leftarrow^6\text{A}_{1g}(\text{F})$ . Graphical evaluation of these data were used to calculate crystal field parameter and the values of  $10\text{Dq}$ ,  $B$ ,  $\beta^\circ$  and  $\beta\%$  are  $19864\%$ ,  $520\%$ ,  $0.541\%$ ,  $45.84\%$ . SGlu–Mn(II) has a magnetic moment value  $6.10\text{ BM}$ , which is close to the calculated value of high spin state of the metal ion. On the basis of electronic spectral bands, an octahedral geometry is proposed for polymer metal complex of SGlu–Mn(II) (Kulkarni et al., 2009). SGlu–Co(II) has a magnetic moment value  $4.77\text{ BM}$  due to four unpaired electrons and showed three bands at  $25445, 18416, 16583\text{ cm}^{-1}$  which were assigned to  $^4\text{T}_{1g}(\text{P})\leftarrow^4\text{T}_{1g}(\text{F})$ ,  $^4\text{A}_{2g}(\text{F})\leftarrow^4\text{T}_{1g}(\text{F})$  and  $^4\text{T}_{2g}(\text{F})\leftarrow^4\text{T}_{1g}(\text{F})$  transition, respectively, and suggested octahedral environment around the Co(II) ion. The calculated values of  $10\text{Dq}$ ,  $B$ ,  $\beta^\circ$  and  $\beta\%$  are  $16869.8\%$ ,  $702.91\%$ ,  $0.724\%$ ,  $27.6\%$  (Chaudhary and Shelly, 2011). The three bands are observed for SGlu–Ni(II) at  $28011, 16583, 11890.6\text{ cm}^{-1}$  which were assigned to  $^3\text{T}_{1g}(\text{P})\leftarrow^3\text{A}_{2g}(\text{F})$ ,  $^3\text{T}_{1g}(\text{F})\leftarrow^3\text{A}_{2g}(\text{F})$  and  $^3\text{T}_{2g}(\text{F})\leftarrow^3\text{A}_{2g}(\text{F})$  transition, respectively. The calculated values of  $10\text{Dq}$ ,  $B$ ,  $\beta^\circ$  and  $\beta\%$  are  $9804\%$ ,  $933.71\%$ ,  $0.86\%$ ,  $14\%$ . The observed magnetic moment value for this compound is  $2.87\text{ BM}$  and suggested an octahedral structure (Agwara et al., 2011). The reduction in the free ion value and the  $\beta\%$  value indicate the covalent nature of the compound.  $\text{H}_2\text{O}$  occupied the two coordinating sites out of six around the central metal ion which strongly suggest an octahedral geometry. For SGlu–Cu(II) the absorption spectrum of the polymer metal complexes exhibited broad band at  $15650$  and  $24000\text{ cm}^{-1}$  which were assigned to  $^2\text{A}_{2g}\leftarrow^2\text{B}_{1g}$  and charge transfer, and which indicate square-planar geometry around the central metal ion. In the present study the magnetic moment values of

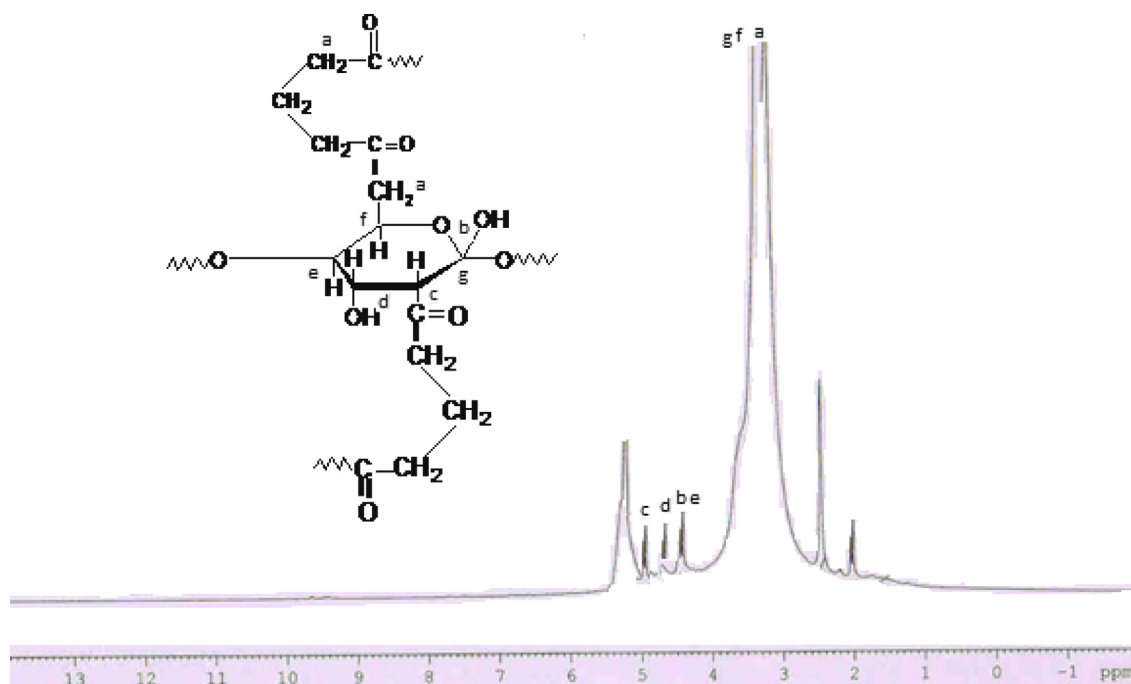


Figure 1  $^1\text{H}$  NMR spectrum of polymeric ligand (SGlu).

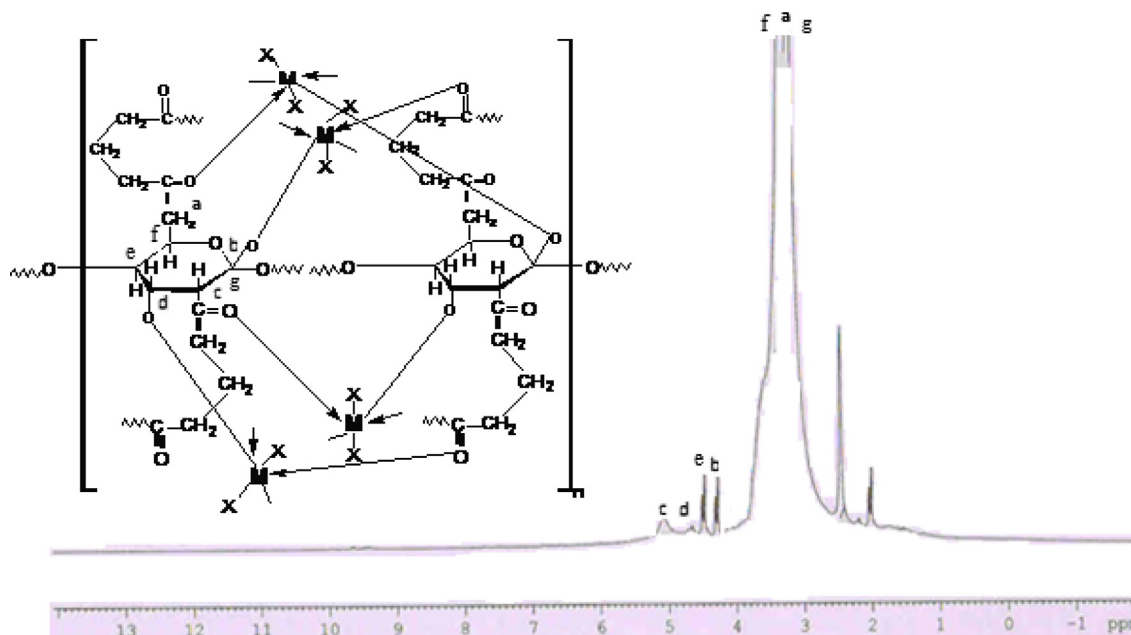


Figure 2  $^1\text{H}$  NMR spectrum of polymer complex of SGlu-Zn(II).

polymer metal complex of SGlu-Cu(II) is 1.79 BM, which is in accordance with square planar geometry (Raman et al., 2004). SGlu-Zn(II) was found to be diamagnetic.

#### 4.4. Thermal analysis (TGA & DSC)

The thermal decomposition of poly-SGlu and its polymer metal complexes was studied by the thermogravimetric method. The thermogravimetric curves of poly-SGlu and its polymer metal complexes are depicted in Fig. 5 and the average values

of the thermal analytical data are listed in Table 4. The thermal decomposition of polymeric ligand (poly-SGlu) and its polymer metal complexes was studied by the thermogravimetric method. Initial weight loss up to 100 °C in poly-SGlu was 7–8%. This loss was mainly due to absorbed solvent loss. The decomposition of both polymeric resin and side products mass loss occurred at higher temperature above 100 °C. The decomposition in both poly-SGlu was slow in the initial stage but at temperature above 200 °C weight loss was fast and the major weight was lost as the temperature reached 250 °C. The

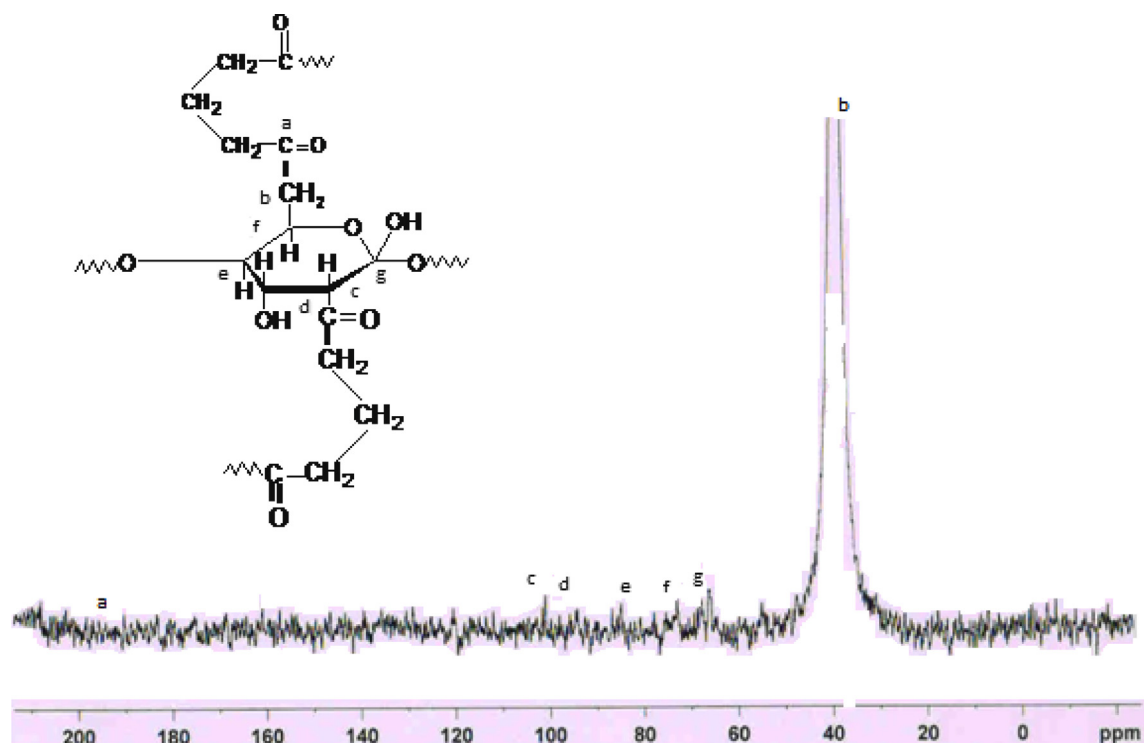


Figure 3  $^{13}\text{C}$  NMR spectra of polymeric ligand (SGlu).

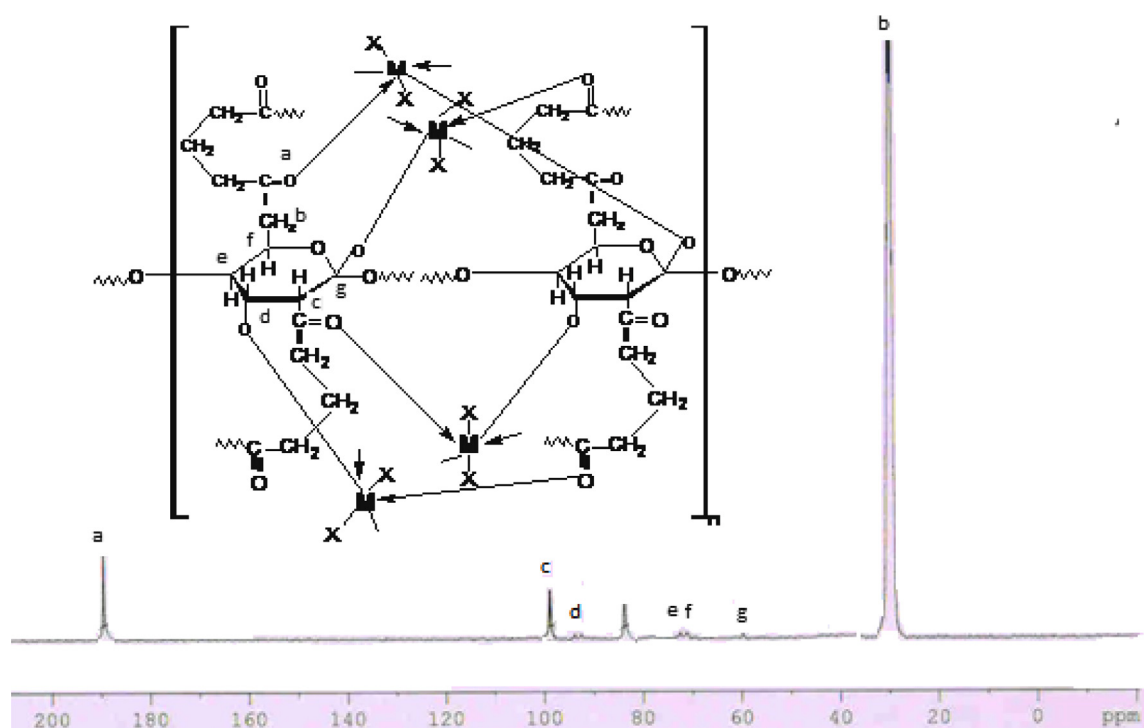


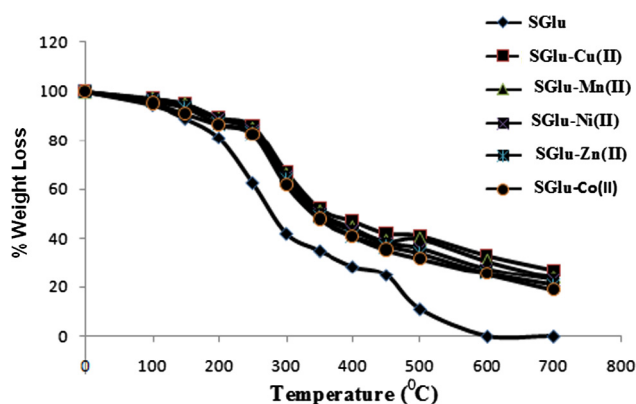
Figure 4  $^{13}\text{C}$  NMR spectra of polymer metal complex of SGlu-Zn(II).

decomposition in the polymer metal complexes was two step decomposition. In the first step lies the decomposition of uncoordinated part of the complexes, and in second step was the decomposition of the coordinated part. The coordination reduced the volatility in the polymer metal complexes

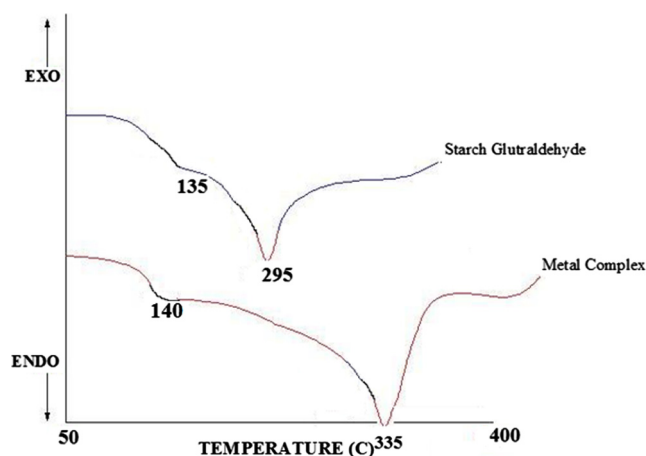
(poly-SGlu). In case of polymer metal complexes initial decomposition in octahedral complexes was due to water loss while in square planar and tetrahedral complexes suffered an initial mass losses due to absorbed solvent losses. Poly-SGlu complex started to decompose with weight loss of only 3–4%

**Table 3** Electronic spectra, magnetic moment and ligand field parameters of polymer metal complexes.

Abbreviation	Magnetic moment (BM)	Electronic spectral data		10Dq	B	$\beta^\circ$	$\beta\%$
		ElectronicTrans. ( $\text{cm}^{-1}$ )	Assignment				
SGlu-Mn(II)	6.10	20283	${}^4A_{1g}(G) \leftarrow {}^6A_{1g}$	19864	520	0.541	45.84
		14534	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$				
		11415	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
		25445	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$				
SGlu-Co(II)	4.77	18416	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	16869.8	702.91	0.724	27.6
		16583	${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
		28011	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$				
		16583	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
SGlu-Ni(II)	2.87	11890	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	9804	933.71	0.86	14
		24000	Charge transfer				
SGlu-Cu(II)	1.79	15650	${}^2A_{2g} \leftarrow {}^2B_{1g}(F)$				
SGlu-Zn(II)	Diamagnetic		No transitions				

**Figure 5** TGA curve of SGlu, SGlu-Mn(II), Ni(II), Co(II), Zn(II), Cu(II).

at 100 °C and this mass loss depicts the loss of coordinated water molecule. The decomposition rate of polymer metal complexes was very slow up to 250 °C, but above 250 °C weight loss became fast. This result revealed that all the polymer metal complex show better thermal stability than their parent resin (poly-SGlu) due to the coordination with metal ions. The order of thermal stability in the polymer metal complex of poly-SGlu-M(II) was found to be SGlu-Cu(II) > SGlu-Mn(II) > SGlu-Ni(II) > SGlu-Zn(II) > SGlu-Co(II). The DSC measurement was used to evaluate the glass transition temperature ( $T_g$ ) and decomposition temperature ( $T_m$ ) and for this, the calorimetric curves of the polymeric resin and its polymer metal complexes are reported in Fig. 6. The

**Figure 6** DSC curve of Starch Glutaldehyde and its metal complex.

decomposition temperature scattered typically at 295 °C for polymeric resin, and the  $T_g$  scattered at 135 °C for polymeric resin. This evolution could be ascribed due to the interaction between the starch and glutaraldehyde. The strong sigma bond formed between starch and glutaraldehyde, which overall decreased the chain mobility of starch polymer and consequently increased the synthesized matrix glass transition temperature, but for the case of polymer metal complexes the decomposition temperature and  $T_g$  increased. The decomposition temperature scattered typical range for polymer complex of Ni(II) is 335 °C and the  $T_g$  scattered is in the range of 140 °C. This indi-

**Table 4** Thermal behaviors of SGlu and its polymer metal complexes.

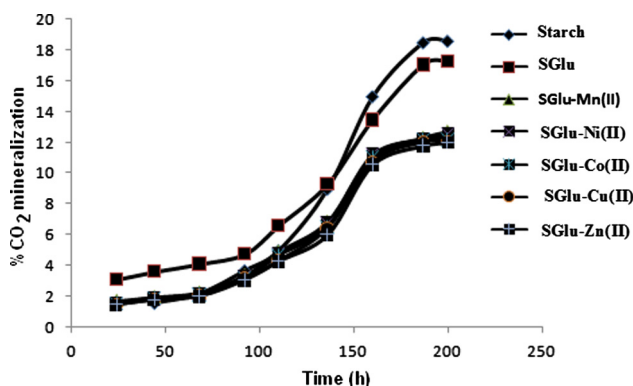
Compound/temperature (°C)	Weight loss (%)									
	100	150	200	250	300	400	500	600	700	
SGlu	5.5	5.5	8	18.5	20.5	14.5	16.5	11	0	
SGlu-Mn(II)	3	2	6.5	2.5	19	20	6	8	6	
SGlu-Co(II)	5	5	5	4	23	19	8	8	8	
SGlu-Ni(II)	3	3	3.5	5	22	17	6	8	9	
SGlu-Cu(II)	2	3	2	4	20	16	5	7	5	
SGlu-Zn(II)	4	4.5	5	6	21	19	6.5	7	11	

**Table 5** ASTM standards of biodegradable polymeric compounds.

Environment	ASTM	Microorganism
Single species	D 5247-92, G-21, G-22	Species of bacteria and fungi specified
Sewage sludge	D5209-91,D5271-92	Aerobic activated sludge organisms
Marine environment	D5437-93	Marine algae and invertebrates
Compost pile	D5338-93	Thermophilic microbes in compost
Anaerobic environment	D5210-92	Anaerobic microbes from activated sludge

**Table 6** % CO<sub>2</sub> mineralization of starch, SGlu and its polymer metal complex.

Time (h)	CO <sub>2</sub> mineralization %		
	Starch	Polymeric resin	Polymer metal complex
24	—	3.10	1.7
44	1.6	3.60	1.95
68	2.2	4.10	2.25
92	3.7	4.75	3.35
110	5	6.60	4.90
136	9	9.30	6.85
160	15	13.5	11.10
187	18.5	17.10	12.30
200	18.6	17.30	12.70

**Figure 7** %CO<sub>2</sub> mineralization of Starch, SGlu and SGlu–Mn(II), Ni(II), Co(II), Zn(II), Cu(II).

cates that the thermal stability is enhanced by the incorporation of metal into the organic backbone. The glass transition temperature of these polymers increased by metal incorporation and lower  $T_g$  and  $T_m$  are related to amount of starch and glutaraldehyde in the initial composition. This is the evidence that the entities are participating in the chemical polymerization reaction and making it part for macromolecular structure. In addition, the  $T_g$  variation of metal incorporated polymer depend on the amount of metal ions and also to the cross linking effect of polymer between two chains of starch and strong hydrogen bonding which affects on chain mobility of starch modified in different ways.

#### 4.5. Biodegradation

Among all the problems faced by the modern world, plastic degradation is one of the most critical ones. Biodegradable starch-based material, may however be a little help in solving the issues. Starch in its virgin form is incapable to provide a strength like plastics, but in crosslinking can be an effective substitute to plastics. Biodegradation in present research is checking the resistant time of synthesized biodegradable material, as an alternate to plastics. In this method compost pile inocula given in Table 5, was used as biotic medium for the laboratory respirometric method used in biodegradation studies (Andrady and Pritchard, 1998). Soil or water can be used as media for the required test but the soil test is preferred here. Activated sludge of suitable volume was used to attain the

**Table 7** Biodegradability of starch, SGlu and SGlu–Zn(II).

Materials	Biodegradability rate constant (k)	Total weight loss (gm)	Medium
Starch	0.000899	0.007489	Biotic
SGlu	0.00079	0.00659	Biotic
SGlu–Zn(II)	0.000606	0.00505	Biotic

complete mineralization of the sample for about a month successfully. Aeration of the inoculums was necessary until used. A trace amount of urea and potassium hydrogen phosphate are also added to the medium to strengthen it, and to promote further microbial growth. Complete and comparative data analysis of the biodegradation rates of starch, poly-SGlu and poly-SGlu–M(II) are obtained and shown in Fig. 7 and predicted in Tables 6 and 7, respectively. From these data, it can be seen that the biodegradation rates of poly-SGlu–Zn(II) were lower than those of poly-SGlu since beginning, and that the biodegradation rates of poly-SGlu were higher than starch polymer.

#### 5. Conclusion

The newly synthesized virgin polymeric ligand and its metal complexes were obtained in good yield and which is then characterized by various spectroscopic techniques. The polymeric ligand was found to be soluble in distilled water and DMSO and insoluble in benzene, toluene and methanol, ethanol and acetone whereas all the polymer metal complexes were soluble in DMSO and insoluble in water and common organic solvents. The incorporation of metal ion in the polymeric backbone enhances the thermal stability as well as reduced biodegradability. Because of the degradable nature of the prepared polymeric resin which is coordinated to metal ions and they may be used in various applications of biomedics, controlled drug release, waste water treatment, catalytic activity, hydrometallurgy, manufacture of plastic technology. The biodegradation of starch was decreased due to the cross linking with glutaraldehyde and the thermal efficiency was enhanced by addition of glutaraldehyde and even enhanced by complexation with transition metal cations.



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