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Synthesis and Characterization of Novel Polymer-Metal Complexes of Cu(II), Ni(II) and Co(II) Derived from Poly(4,5-dihydroxy-2,7-naphthalene Disulfonic Acid)

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In this study, poly(4,5-dihydroxy-2,7-naphthalene disulfonic acid) was prepared by means of an oxidative polycondensation reaction of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt (monomer) in aqueous alkaline medium with NaOCl as the oxidant at 90 °C. Average molecular weights of the polymer were determined by gel permeation chromatography. The monomer and the polymer were characterized by elemental analyses, gel permeation chromatography, thermogravimetric analyses and UV-visible, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic studies. In addition, the new Cu(II), Ni(II) and Co(II) complexes of the polymer were characterized by elemental analyses, UV-visible, FT-IR, and AAS, TGA and magnetic susceptibility measurements. The results suggested that the polymer and metal ions in 2:1 molar ratio produced mononuclear complexes with oxygen donor atoms. All synthesized polymer-metal complexes have dimeric structures formed by the polymeric ligand units. The thermal stability of the polymer-metal complexes is higher than that of the polymer. Magnetic susceptibility studies showed that polymer-metal complexes have various configurations. The metal ion uptake studies were conducted using the batch technique. The barium salt of the polymer was determined to be effective in removing some metal ions *via* the batch technique.

Keywords: Oxidative polymerization, Metal complexes, Metal ion uptake.

INTRODUCTION

Heavy metal ion extraction from waste water is very important for environmental applications. It is known that solid phase extraction is an attractive technique based on the use of sorbent that retains analytes. The complex-forming polymeric ligands are characterized by their ability to coordinate to different heavy metal ions that have been usually studied[1]. These materials frequently show selectivity to certain metal ions, facilitating their use for preconcentration and separation of trace metal ions from saline and non-saline water samples at an appropriate pH range[2]. Metal complexes of polymers have useful properties such as paramagnetism, metal ion uptake, antimicrobial activity, good solubility and antistatic ability[3-5].

Some general methods have been used to overcome the limited solubility of polymers, such as insertion of flexible bonds between main chain aromatic rings and attached water-soluble groups such as carboxyl, sulpho groups[6-8]. Due to the reagents used for the reaction process, the oxidative polycondensation may also be regarded as a good example of an environmentally benign for synthesizing polymeric materials. Compared with other synthesis methods, oxidative polycondensation of phenols has significant advantages such as halogen-free monomers, moderate reaction temperatures and water as a by-product[9]. Polymers and polymer-metal complexes have been prepared because of their ability to bind toxic and heavy metal ions, thermal stability, and exhibition of catalytic and photoluminescent properties[10-13]. Some of the polymer-metal complexes obtained from Ni(II), Co(II) and Ti(II) act as efficient heterogeneous catalysts for polymerization of butadiene[14]. Some natural polymers (humic acid and fulvic acid) are used to remove heavy metal ions from waste water[15].

In this study, we present the preparation and characterization of Cu(II), Ni(II) and Co(II) chelates with the new polymer (Fig. 2). The polymer was characterized by ^{1}H (^{13}C) NMR, FT-IR, UV-visible spectroscopy, TGA and analytical methods. The synthesized polymer-metal complexes were characterized using a number of modern techniques. The metal ion uptake studies of the polymer were conducted using the batch technique after. The magnetic properties of the polymermetal complexes were determined by the Faraday method. The chelation of the polymer and the geometry around the metal center were discussed.

EXPERIMENTAL

Monomer, metal salts ($CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$), HCl, EDTA, NaOCl neocuprion and dimethyl

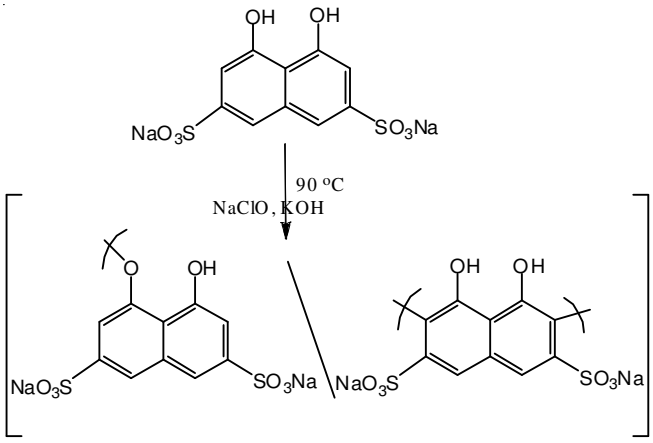

Fig. 1. Proposed structures of polymer

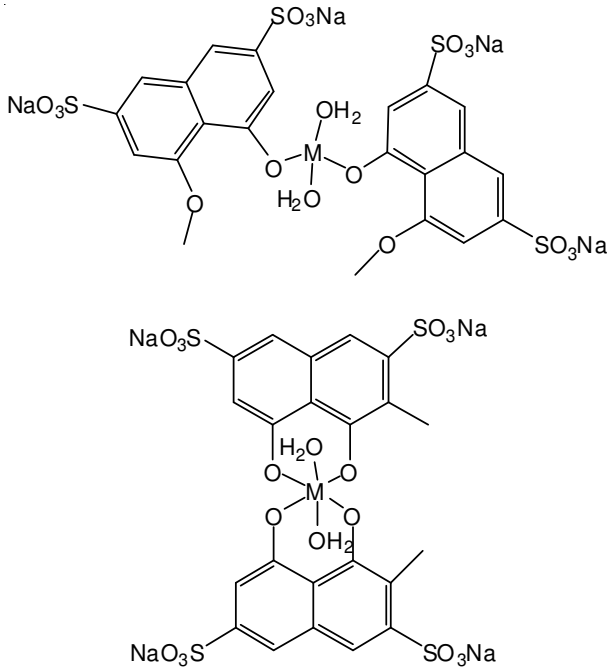

Fig. 2. Bidentate structure polymer with Ni(II) or Co(II)

glyoxime were obtained from Merck (reagent grade). The solvents used were methanol, EtOH, THF, DMF and DMSO. Monomer was recrystallized from EtOH/H_2O (1:1), followed by the addition of HCl to pH 3. Doubly distilled water was used for the preparation of all solutions, titrations, and metal ion uptake studies. Standard solutions were prepared by dissolving an appropriate amount of Cu(II), Co(II) and Ni(II) salts in EtOH. After acidic decomposition of the polymer-metal complexes, the levels of metal ion content were determined by potentiometric titrations and AAS.

The infrared and UV-visible spectra were measured using Jasco 300 FT-IR and Shimadzu UV-160 instruments, respectively. The FT-IR spectra were recorded using KBr discs (4000-400 cm^{-1}). UV-visible spectra (200-800 nm) of the monomer, the polymer and the polymer-metal complexes were determined by using distilled water and DMSO. The monomer and the polymer were characterized using ^1H NMR and ^{13}C NMR spectra (Bruker AC FT-NMR 400 MHz spectrometer) recorded at 25 °C using DMSO-d_6 as the solvent. Elemental analyses (C, N, H and S) were performed using a CHNS-932 (Leco). Percentages of the metal ions of the complexes were determined using an Ati-Unicam model-929 A.A.S. TGA was performed with a Shimadzu DTA-TGA-50. The TGA were made between 30 and 900 °C (in nitrogen, rate 10 °C min^{-1}). Average molecular weights of the polymer were determined by gel permeation chromatography. The columns were calibrated using different molecular weight PS. The flow rate of the THF was maintained at 1 mL through the experiments, and 1 wt. % (10 mg in 1 mL) of polymer solution was injected for obtaining the gel permeation chromatography. Melting points were determined by a Gallenkap apparatus. Magnetic measurements were carried out at 25 °C using a Sherwood Scientific magnetic susceptibility balance with $CuSO_4 \cdot 5H_2O$ as the standard. Magnetic susceptibility were calculated as Bohr Magneton (B.M.) using the $\mu_{eff} = 2.82\sqrt{X_m.T}$ equation. The molar conductivity of the polymer and polymer-metal complexes were determined in distilled water (10^{-3} M) at 25 °C using a Tacussion conductivity meter. Potentiometric titration and pH adjustments were carried out in a Selecta model equipped with a combined glass electrode.

Synthesis of the polymer by oxidative polycondensation: Polymer was synthesized through the oxidative polycondensation of metal in aqueous solutions with NaOCl (Fig. 1). The metal (0.01 mol) was dissolved in an aqueous solution of KOH (10 %, 0.01 mol) and placed into a 250 mL three-necked, round-bottomed flask. It was fitted with a condenser, a thermometer and a stirrer, in addition to a funnel containing NaOCl. After heating to 70 °C, NaOCl (0.01 mol) was added dropwise over about 0.5 h. The reaction mixture was stirred at 90 °C for 18 h. The mixture was neutralized with 0.01 mol diluted HCl (37 %) at room temperature. All organic impurities were then extracted by washing with small portions of diethyl ether and EtOH. Then, the polymer was filtered and dried in a vacuum oven at 90 °C. Colour: black; D.p: 305 °C; yield: 51 %; ^1H NMR (DMSO-d_6, δ = ppm): 6.6-7.5 (m, Ar-H), 11.2 (s, OH); ^{13}C NMR (DMSO-d_6, ppm): 107.4-145.1 (for naphthalene ring carbons), 161.3 (C-O-C carbons). The decomposition points, FT-IR, UV-visible, TGA, gel permeation chromatography and analytical data of the polymer are given in Tables 1, 3 and 4.

TABLE-1
SOME ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE POLYMER AND POLYMER-METAL COMPLEXES

Compounds	Decomposition temp. (°C)	Yield (%)	Found (Calcd.) %				
			C	H	S	Metal	Λ_M[a]
$P(C_{10}H_6Na_2O_8S_2)_n \cdot 2.3H_2O$	305	51	33.3 (29.6)	2.9 (2.6)	17.4 (15.8)	–	16
$[Cu(C_{10}H_6Na_2O_8S_2)_2 \cdot 2H_2O] \cdot 3.4H_2O$	335	58	27.5 (27.2)	2.4 (2.6)	14.8 (14.5)	7.0 (7.2)	19
$[Ni(C_{10}H_6Na_2O_8S_2)_2 \cdot 4H_2O] \cdot 6H_2O$	370	54	24.6 (25.0)	2.9 (3.3)	13.1 (13.3)	6.4 (6.1)	28
$[Co(C_{10}H_6Na_2O_8S_2)_2 \cdot 4H_2O] \cdot 5H_2O$	340	57	25.6 (25.4)	3.5 (3.2)	13.2 (13.5)	6.6 (6.2)	20

[a]Ohm^{-1} cm^2 mol^{-1}

Synthesis of metal complexes of polymer: Polymer-metal complexes were synthesized by the addition of the appropriate metal salts (1 mmol, in 25 mL absolute EtOH) to a hot solution of the polymer (1 mmol, in 30 mL distilled water). The resulting solutions were stirred and heated in a water bath at 80 °C for 6 h. The product was collected by filtration, washed with EtOH, diethyl ether and finally dried under vacuum at 90 °C. Polymer-metal complexes were prepared by the same method and isolated as powdered material. All organic impurities were then extracted by washing with small portions of diethyl ether and EtOH. The geometry of the complexes was confirmed by magnetic moment measurements and absorption spectra. Elemental analyses, TGA, FT-IR and UV-visible and AAS confirmed the compositions of the complexes. Analytical and spectral data for all complexes are given in Table-1 and 4, respectively.

Metal ion uptake studies: Addition of the barium nitrate solution (0.1 M, pH = 7) produces the water-insoluble barium salt of the polymer. Therefore, the barium salt of the polymer was obtained and then filtered and dried *in vacuo*. The obtained polymer was used in metal ion extraction studies. The metal ion uptake studies were conducted using the batch technique[16]. The polymer was powdered, sieved (100 mesh, ASTM) and suspended over the water at pH 4 for one day. The polymer was filtered off, and two times washed with distilled water. The metal ion concentration in the filtrate and the washing collected was estimated following the neocuprion method for Cu(II), and the dimethyl glyoxime method[17] for Ni(II) from which the percentage of metal ion uptake by the polymer and distribution coefficient values (K_{ad}) were calculated. Percentage of Co(II) ions of complexes were determined by potentiometric titration after acidic decomposition.

RESULTS AND DISCUSSION

Polymer interacts with metal ions [Cu(II), Co(II) and Ni(II)] to form mononuclear complexes. Their suggested structures are shown in Fig. 2. All polymer-metal complexes are black-coloured compounds. Elemental analyses and AAS showed that the metal:ligand ratio of the polymer-metal complexes is 1:2 in every polymeric ligand unit, with various numbers of water molecules per complex. This polymeric ligand unit is monovalent or divalent (oxygen donors), since they form two bonds to the metal ions. In the case of a bidentate ligand, the vacant coordination sites are occupied by solvent molecules (water). The coordination may be constructed as bidentate for every polymeric ligand unit. Therefore, the polymer may bind metal ions such as Cu(II), Ni(II) and Co(II) to form a variety of complex structures. The special conformation of the polymeric ligand unit's with oxygen atoms in the naphthalene ring facilitates the formation of dimer complexes since the polymeric ligand unit's act like a bridge. polymer-metal complexes have satisfactory analytical data, and the instrumental studies suggest that the complexes are of the general formula $[(M)_n(L)_{2n}\cdot xH_2O]\cdot yH_2O$ (x = 2 or 4; y = 3, 4 and 6) where M is copper(II), nickel(II) or cobalt(II).

The polymer and polymer-metal complexes were soluble in several polar solvents such as DMF, DMSO and water. polymer-metal complexes were insoluble in other solvents. Conductivity of the polymer-metal complexes in distilled water (10-3 M) is shown in Table-1. polymer-metal complexes are non-electrolytes because their conductivity values ranged from 16 to 28 ohm^{-1} cm^2 mol^{-1}. The decomposition points, yields, analytical and magnetic moment data of the polymer-metal complexes are given in Table-1.

Molecular weight determination: The number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer was determined by gel permeation chromatography using polystyrene standards (PS) as reference in THF. The retention time is 12 h and yield 55 %. The M_n and M_w values of the polymer were found to be 5300 and 5800 g mol^{-1}. The formation of the polymer suggests that the oxidative polycondensation conditions used for the synthesis are highly effective. M_w/M_n was calculated as 1.09. The chromatogram of the polymer showed a bimodal distribution. These results corroborate the assumptions on the basis of ^{1}H NMR spectra.

Electronic spectra: It has been known that aromatic polymers are coloured compounds. The electronic spectra of the polymer-metal complexes were measured in DMSO and distilled water at room temperature. The wavelength of maximum absorbance and molar extinction coefficients are reported in Table-2. The energy of the π-π^* transition of the polymer is characteristic of an aromatic hydroxyl which

TABLE-2
UV-VISIBLE SPECTRAL DATA AND MAGNETIC MOMENTS OF THE POLYMER-METAL COMPLEXES

Compound	μ_{eff} (B.M.)[a]	λ_{max} (nm) (ε_{max}, M^{-1} cm^{-1})
$P(C_{10}H_6Na_2O_8S_2)_n$	–	268(72000), 370(4400), 410(40400)
$[Cu(C_{10}H_6Na_2O_8S_2)_2\cdot 2H_2O]$	1.42	261(83200), 376(3200), 495(45500), 660(1100)
$[Ni(C_{10}H_6Na_2O_8S_2)_2\cdot 4H_2O]$	1.51	264(81800), 485(41500), 375(2500), 645(980)
$[Co(C_{10}H_6Na_2O_8S_2)_2\cdot 4H_2O]$	2.11	266(85600), 455(39800), 386(2400), 664(891)

[a]Per metal ion at room temperature

TABLE-3
FT-IR (cm^{-1}) DATA FOR THE OF THE MONOMER, POLYMER AND METAL-COMPLEXES

Compound	ν(OH)	ν(HO)	ν(C-O-C)	ν(-C=C-)	Arm. CH	ν(MO)
Monomer ($C_{10}H_6Na_2O_8S_2$)	3415 br	-	1224 m	1520 s	3050 s	-
$P(C_{10}H_6Na_2O_8S_2)_n$	3420 br	-	1280 m	1560 s	3075 s	-
$[Cu(C_{10}H_6Na_2O_8S_2)_2\cdot 2H_2O]$	3345 br	853 w	1297 m	1599 s	3065 s	612 m
$[Ni(C_{10}H_6Na_2O_8S_2)_2\cdot 4H_2O]$	3443 br	846 w	1293 m	1605 s	3060 s	638 m
$[Co(C_{10}H_6Na_2O_8S_2)_2\cdot 4H_2O]$	3435 br	857 w	1285 m	1596 m	3050 s	642 m

showed delocalized systems with intramolecular hydrogen bonding[18]. The bands at 370 nm were assigned to the aromatic ring π-π^* transition in the polymer. The absorption peak at 410 nm of the polymer showed around the visible region. This can be explained by conjugation of aromatic rings in the polymeric backbone.

The bathochromic shifts of the UV-visible spectra are observed in all the polymer-metal complexes. The absorption peak of the polymer at around 370 nm shifted to a slightly longer wavelength in the polymer-metal complexes. This means that the length of the π-electron conjugation is changed by complexation. These complexes showed broad and intense visible bands between 450-485 nm due to the metal binding to the polymeric ligand unit's. The electronic spectra of polymer-metal complexes show two major bands, which are more intense than those of the corresponding polymer in the region of 400-500 nm, which could be attributed to the charge transfer transitions. Therefore, we assumed that the polymer coordinated to the metal ion through the oxygen atoms. Also, electronic spectra of all the complexes were characterized by strong-intensity absorptions with shoulders around 600-700 nm, which can be associated to *d-d* transitions[19]. Complexation of Cu(II) and Ni(II) ions with the polymer showed at 460 nm and 545 nm, respectively, which indicates $t^5_{2g}\ e^0_g$ and $t^6_{2g}\ e^0_g$ configurations for Cu(II) and Ni(II) ion complexes.

Infrared spectra: FT-IR spectral data of all compounds are given in Table-3. The shift of certain bands in the spectra of polymer give an idea about of the polymerization. The infrared spectra of the monomer displayed a shoulder of a broad band of weak intensity around 2980-2730 cm^{-1}. This band was ascribed to the O-H stretching vibration, which is known to shift significantly to lower frequencies because of OH···O intramolecular hydrogen bonding[16]. The polymer showed a peak in the 3450-3260 cm^{-1} range, corresponding to the naphtholic hydroxyl and crystal water molecules. This band slimmed and shifted in the polymer due to polymerization by the oxygen. The infrared spectra of the monomer showed bands at 1224 cm^{-1} assignable to the naphtholic C-O vibration. However, in the spectrum of the polymer, the C-O-C band shifted to the higher region because of the polymerization *via* the oxygen atoms. The strong bands at around 1500 cm^{-1} are due to the C=C stretching of the aromatic ring. It also showed the presence of free hydroxyl groups at the polymer as indicated by OH stretching at around 3400 cm^{-1} as well as 1600 cm^{-1} for the quinone groups. This means that C-O-C type coupling is higher than C-C type coupling. Hydroxyl peaks in the polymer-metal complexes showed red shifts of 20-30 cm^{-1} compared to those of the polymer, indicating coordination of the oxygen atoms to the metal ions[20]. This feature can be explained by the withdrawing of electrons from the oxygen atom to the metal ion due to coordination.

The C-O-Cu frequency of the coordinated hydroxyl group of polymer which was detected as a strong band at 3335 cm^{-1} shifted +30 cm^{-1} from the free polymer. This feature can prove the involvement of the hydroxyl oxygen atom in the coordination. The polymer-metal complexes exhibited band at 3450-3335 cm^{-1}, which are attributed to OH of associated water molecules, while the band observed at approximately 857-785 cm^{-1} is assigned to coordinated water molecules[21]. These similar frequencies correspond to those observed in Ni(II) and Co(II) complexes. The most obvious transformations after the complexation were found in the 500-700 cm^{-1} range. In the polymer-metal complexes spectra, there were increased absorptions at this range. More signals were observed for the polymer-metal complexes than for the corresponding polymer. On the other hand, in the infrared spectra of the polymer-metal complexes, new absorption bands at 650-610 cm^{-1} were observed because of the M-O bonds[22].

^{1}H NMR and ^{13}C NMR spectra: The ^{1}H NMR spectra of the monomer and the polymer were recorded by using DMSO-d_6 as the solvent. The ^{1}H NMR spectrum of the monomer shows sharp peaks in the 6.8-7.9, 8.0 ppm range and 9.5 ppm. These peaks can be ascribed to the aromatic ring and hydroxyl protons of the monomer. The peak at 3.4 ppm is assigned to the H_2O impurity in the DMSO-d_6 solvent. According to the literature, the polymer exhibited signals in the 6.7-8.1 ppm range due to the aromatic ring proton with broadening[23]. The coupling of free phenoxy radicals under basic conditions and the coupling *via* coordinated phenoxy radicals would mainly lead to the C-O-C coupling.

The ^{1}H NMR spectrum of the polymer also showed the broad signal at 8.2 ppm corresponding to the hydroxyl proton; the multiplet broadened signal in the 6.7-7.9 ppm range indicates the aromatic protons. The weakly broadening of the peaks in the spectrum of polymer is attributed to the limited polymerization. The singlet at 11.1 ppm is attributed to the proton of the hydroxyl group in the naphthalene ring. Coupling of free phenoxy radicals under basic conditions and coupling *via* coordinated phenoxy radicals would mainly lead to the C-O coupling. The weakening of *o*-hydroxyl peaks of the polymer can be attributed to the participation in the polymerization reaction *via* one of the hydroxyl groups. This indicates that aromatic ring protons are participating in the coupling reaction at low rates. C-C coupling rates are lower than those of C-O-C type coupling probably due to the steric hindrance of the sulpho groups in the polymeric ligand unit's. The sharp peak at around 8 ppm is assigned to the non-polymerization *via* one of the oxygen atoms on the naphthalene ring. This hydroxyl peak shifted to the lower field due to the oxygen-bridged polymerization. In the ^{1}H NMR spectrum of the polymer, the integral ratio of the aromatic ring protons to the hydroxyl protons for the monomer and the polymer is 1.95 and 5.82, respectively. This indicates that one of the hydroxyl groups is participating in the polymerization reaction at the highest rates. The detailed analysis of ^{1}H NMR spectral data suggests that there are 67 % C-O-C (oxynaphthalene) and 33 % C-C type coupling types in the polymer structure. Also, coupling types and rates of polymers were determined by potentiometric titration.

The ^{13}C NMR spectrum of the monomer showed that signals between 112.5 and 181.2 ppm are due to the aromatic ring carbons. The relatively high upfield of two carbonyl carbons at 174.3 ppm is attributed to hydroxyl groups on the naphthalene ring. The ^{13}C NMR spectrum of the polymer indicated broad signals at 107.4, 113.6, 135.5, 147.9, 151.3, 125.5, 128.4, 145.1, 174.3 and 181.2 ppm, respectively. The chemical shift of the carbon that is bonded to the hydroxyl group is 174.3 ppm for the monomer, whereas it is 181.2 for the polymer,

indicating that hydroxyl oxygens are participating in the polymerization reaction. These similarities of the ^{13}C NMR spectra of the monomer and the polymer can be attributed to the protection of all monomer structures during the oxidative polycondensation reaction except hydroxyl groups. According to the FT-IR, ^{13}C NMR and ^{1}H NMR data, polymerization of the monomer occurs in the form of C-O-C coupling and C-C type coupling. The proposed structure of the polymer is given in Fig. 1.

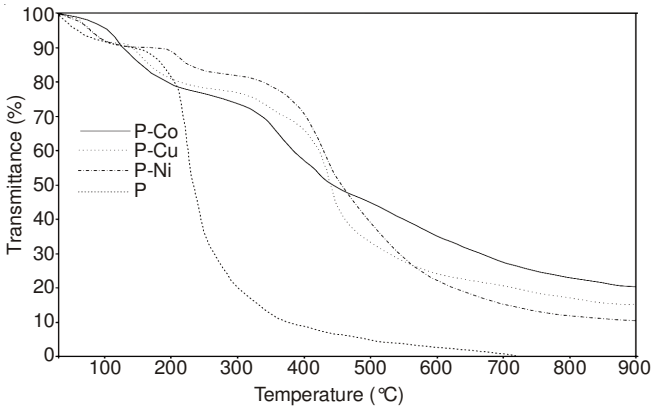

Fig. 3. TG curves of polymer and polymer-metal complexes

Magnetic moments (MM): The magnetic moment's of the polymer-metal complexes were measured by the Gouy method, and the diamagnetic corrections were made using Pascal's constants. The values of μ_{eff} of all the complexes of the polymer are nearly half of those reported in the literature[24]. The presence of metal ions in the big molecule probably causes decreased magnetism. The magnetic moment values of the polymer-metal complexes are given in Table-2. It was determined that all complexes were paramagnetic in character. The magnetic moment's of the P-Cu, P-Ni and P-Co were 1.42 BM, 1.51 BM and 2.11 BM, respectively, which was a clear indication that Cu(II), Ni(II) and Co(II) ion complexes were paramagnetic in nature. The magnetic moment and electronic transitions have suggested d^2sp^3 hybridization with distorted octahedral structure for Ni(II) and Co(II), and sp^3 hybridization tetrahedral geometry for the Cu(II) complexes. Probably the coordination sphere is completed by coordination of water molecules to the metal ions. The values of infrared spectra, elemental analyses and TGA studies showed the presence of crystal water molecules. The magnetic susceptibility measurements showed the existence of weak antiferromagnetic interactions for the polymer with Cu(II), Ni(II) and Co(II). Molecular models indicate that there are no severe steric strains as a result of the proposed geometries for the polymer-metal complexes.

Metal ion uptake studies: Metal ion uptake data for the polymer are shown in Table-4. The polymer has sulfo groups that aid in aqueous solubility. The addition of a barium nitrate solution (0.1 M, pH = 7) resulted in the precipitation of the barium salt of the polymer (insoluble in water), which were isolated by filtration, and dried *in vacuo*. The precipitated polymer was used for all metal ion uptake studies. The saturation time was obtained by plotting the percentage of metal ion uptake versus contact time, keeping initial metal ion concentration fixed (2500 µg per 30 mL). The effect of the metal ion concentration on the uptake behavior of the polymer was studied at the concentration range (500-2500 µg per 30 mL) of metal ions. In our work, the optimum pH of the adsorption of Cu(II), Ni(II) and Co(II) ions was 5.0, 6.5 and 7.0, respectively. A high concentration of metal ions enhanced the percentage of loading. However, a leveling effect was not observed at higher concentrations because of the available saturation coordination sites. In the polymer, the rate of Cu(II) adsorption is higher than that of Ni(II) and Co(II). The presence of a benzene ring in the C-O-C moiety presumably led to efficient molecular packing for Cu(II). Also the presence of hydroxyl groups in the polymer was responsible for a higher uptake percentage of metal ions. The polymer could be used conveniently in heavy metal chelation for environmental applications. The high stability of the polymer towards Cu(II) is remarkable.

Thermal studies: The thermal behavior of the polymer and its polymer-metal complexes were studied by using TGA in the range of 30-900 °C in nitrogen atmosphere. The TGA curves of the polymer and the polymer-metal complexes are given in Fig. 3. The results obtained from the TGA indicated that the decomposition of the polymer proceeds in two steps. The mass loss of the polymer in the range of 40-120 °C is due to the water molecules in the structure. After the removal of hydrated water molecules, the weight loss of the polymer began at 200 °C, which is lower than the 300 °C for the monomer. This observation is that the first decomposition point of the polymer has a lower stability than that of the corresponding monomer. This behavior can be explained from the C-O-C type conjugated structure of the main chain. A 50 % weight loss of the monomer and the polymer were observed at 220 and 270 °C. This may be due to a phase transition. The melting point of the polymer was not observed. However, as expected, the polymer had lower thermal stabilities at higher temperatures compared to the parent monomer. This is probably due to the dominantly formation of the C-O-C coupling (67 %) and the polymer backbone.

The studied polymer-metal complexes, after the elimination of the crystal water molecules at the range of 40-120 °C, decompose in two or three stages. The P-Ni complex has the greatest water content of all the complexes. The first decomposition of the P-Ni complex started at 380 °C after removing

TABLE-4
EFFECT OF pH ON THE ADSORPTION BEHAVIOR OF THE POLYMER FOR Cu(II), Ni(II) AND Co(II) IN BATCH TECHNIQUE

Metal ion	pH						
	3.5	4.0	5.0	5.6	6.5	7.0	8.1
Cu(II)	12.1	14.5	35.6	55.7	65.4	68.1	30.4
Ni(II)	3.5	6.7	8.8	21.6	60.8	68.4	22.1
Co(II)	4.7	8.8	12.4	16.5	20.7	29.4	15.4

[a]Metal ion concentration, 2500 mg per 20 mL; polymer quantity, polymer size, 100 mesh; Temperature 25 °C; contact time, 12 h

the water molecules. The decomposition was completed at 900 °C for all complexes. The initial decomposition temperature for the polymer begins at 245 °C, which is 100-120 °C less than that of the polymer-metal complexes. The 50 % weight loss of the polymer-metal complexes is between 300-400 °C higher than that of the polymer. This can be explained by the higher thermal stability of the polymer-metal complexes as compared to the polymer. The complexes had greater stabilities compared to the polymer, probably due to the formation of six-membered ring structures. The order of stability observed is P-Cu > P-Ni > P-Co. This behavior indicates that the polymer in the present study, which provides oxygen donor sites, exhibit a greater affinity towards copper than nickel and cobalt do. The weight losses of the P-Cu, P-Ni and P-Co complexes were found to be 90, 87 and 77 %, respectively. The final residues in the Ni(II), Cu(II) and Co(II) polymer complexes are NiO, CuO and Co_3O_4, respectively. The results were in good agreement with those calculated from the metal content using AAS and elemental analyses.

Conclusion

According to the FT-IR, ^{13}C NMR and ^{1}H NMR data, polymerization of monomer occurs dominantly in the form of C-O-C (67 %) and C-C (33 %) type coupling. These oxygen donor atoms are known as suitable electron donors to prepare polymer-metal complexes. The synthesized polymer was soluble in common solvents such as water, DMF and DMSO. These properties of the polymer are promising for their environmental and analytical usage. Analytical data, FT-IR spectroscopy and TGA indicate that polymer-metal complexes have coordinated and uncoordinated water molecules. Some important information was observed in this study. At first, polymer-metal complexes are thermally stable at high temperatures. An interesting observation is that the polymer-metal complexes have a higher stability than that of the corresponding polymer. The introduction of metal ion coordination in the polymer backbone results in an increase in thermal stability. Secondly, polymer is usable highly effective for metal ion extraction from waste water. The high stability of the polymer towards Cu(II) is remarkable. These properties of complexes are important for their technological and environmental usage.

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