Removal of Chromium, Copper, and Nickel Ions Using Bidentate Polymeric Ligand Derived from 4-Aminophenol and Salicylaldehyde

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ABSTRACT: The monomer 5-(4-acryloyloxyphenylazo)-salicylaldehyde [5,4-APASAL] was prepared and polymerized in dimethylformamide (DMF) at 70°C using benzoyl peroxide as free radical initiator. Poly5-(4-acryloyloxyphenylazo) salicylaldehyde [poly(5,4-APASAL)] was characterized by infrared and nuclear magnetic resonance spectroscopic technique. The molecular weight of the polymer was determined by gel permeation chromatography method. Cu(II), Ni(II), Cr(III), and Cr(VI) complexes of poly(5,4-APASAL) were prepared. Elemental analysis of polychelates suggests that the metal to ligand ratio is about 1 : 2. The polymer metal complexes were also characterized by XRD, magnetic moment, and thermal analysis. The effect of pH and electrolyte concentration in the metal uptake behavior of the polymer was also studied. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3600–3605, 2012

Key words: 4-aminophenol; azo polymer; electronic spectra; hexavalent chromium

INTRODUCTION

Functional chelating polymer has been found widespread application in the field of separation, recovery, and monitoring of heavy metal ions.[1–4] Heavy metal ion removal from aqueous waste is most important issues in today's world because they are nondegradable and thus persistent.[5] Chromium, copper, and nickel compounds have been used for commercial process in wide range. Such process is electroplating, leather tanning, dyeing, painting, and pigment manufacturing industries, and these waste water are disposed in an unregulated condition that leads to the contamination of the environment.[6,7] The use of chelating polymers for effective sorption of metal ions is an attractive field of research. The chelate forming ability of polymeric ligand largely depends on the nature of donor atom present in polymer matrix like nitrogen, oxygen, sulfur, and phosphorous. Various methods have been used to recover metal ions from water and waste water treatment process, such as ion-exchange, chemical precipitation, electrodialysis, biosorption, membrane filtration, and chelating polymers.[8–10] Among these chelating polymer has been used long time for metal removing process.[11,12] Salicylaldehyde is an important class of chelating ligands, which is used in numerous applications as highly selective reagent for separation and determination of number of metal ions and also used an intermediate in much organic synthesis, medicines, as antimicrobial, antituberculosis, antitumor, and antimycotic drugs.[13,14] Coordination ability of metals with such ligand also exhibit in various biological activities.[15] In the present study, synthesis and characterization of salicylaldehyde incorporated polymeric ligand and its Cu(II), Ni(II), Cr(III), and Cr(VI) complexes are investigated. Structure of the complexes and metal ions sorption on different factors such as effect of pH and presence of electrolytes are also investigated.

EXPERIMENTAL

Materials

5-(4-hydroxyphenylazo)salicylaldehyde was prepared according to the Dincalp et al.[16] Benzoyl peroxide was recrystallized from chloroform/methanol mixture. Acrylolchloride was prepared by a reported procedure.[17] Copper acetate and nickel acetate (Fluka), chromium chloride and potassium dichromate (Aldrich) were used as received. All the solvent was purified as standard method.
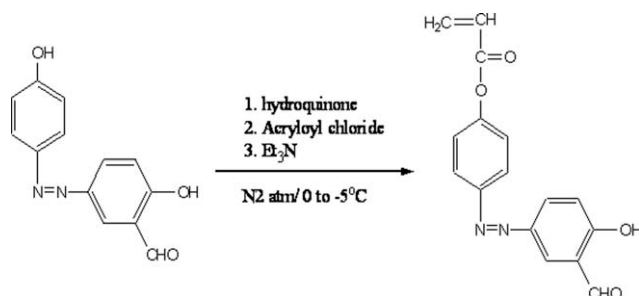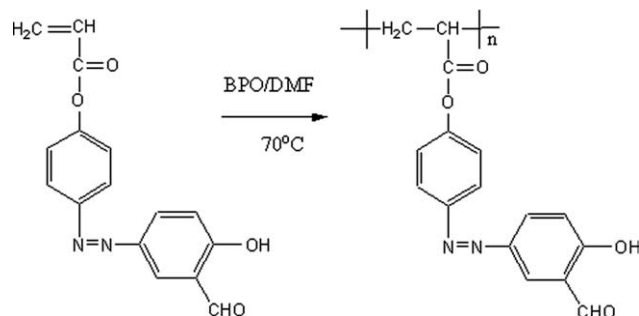
Scheme 1 Synthesis of 5-(4-acryloyloxyphenylazo) salicylaldehyde.

Synthesis of 5-(4-acryloyloxyphenylazo) salicylaldehyde

5-(4-hydroxyphenylazo)salicylaldehyde (64 mmol, 16 g), triethyl amine (64 mmol, 8 mL), hydroquinone (0.5 g), and dimethylformamide (DMF) (25 mL) were placed in a three-necked flask fitted with stirrer, thermometer, and dropping funnel. The content in the flask were cooled to −5°C. Acryloylchloride (64 mmol, 5.4 mL) in 20 mL of DMF was added drop wise with constant stirring and cooling. The reaction mixture was allowed to room temperature and stirring was continued for 2 h. The quaternary ammonium salt was filtered and the filtrate was washed with distilled water, solid was collected, and recrystallized from $EtOH/CH_2Cl_2$ (1 : 3). The monomer was dried under vacuum at 40°C for 24 h (yield 85%). The IR and ^1H NMR spectra were consistent with the assigned structure of the monomer (Scheme 1).

Polymerization

5-(4-acryloyloxyphenylazo)salicylaldehyde (35 mmol, 10 g) in dry DMF (20 mL) and benzoyl peroxide (0.05 g) were placed in standard reaction tube and deoxygenated by passing dry Nitrogen gas for 30 min. The reaction tube was closed and kept in a thermostat at 70°C for 8 h. The content were cooled and poured over methanol (100 mL). The precipitated poly5-(4-acryloyloxyphenylazo)salicylaldehyde
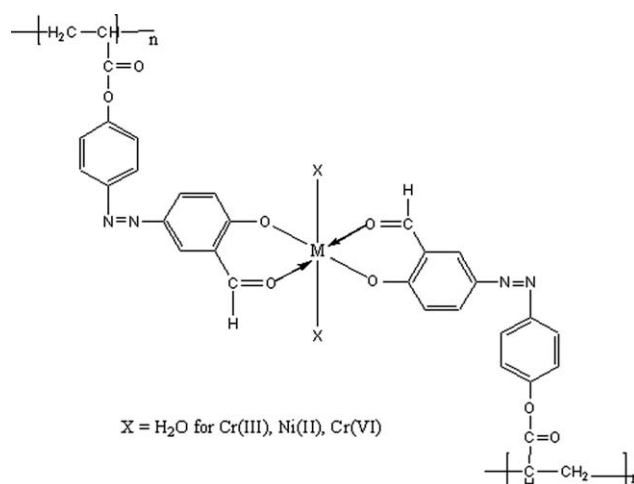
was collected and washed with methanol. Polymer was purified by precipitated with methanol (3 times) repeatedly, and dried under vacuum at 45°C for 48 h (yield 72%). The structure of the polymer was confirmed by IR and ^1H-NMR studies (Scheme 2).

Preparation of polychelates

The Polymer (6 mmol of repeating unit) was dissolved in 30 mL of DMF. An aqueous solution of metal salt (3 mmol) was added drop-wise with constant stirring, pH of the solution was adjusted to 7–8 with dilute ammonium hydroxide. The resulting mixture was digested on hot water bath for 2 h and kept overnight at room temperature. The precipitated polymer metal complexes were filtered and washed with ethanol, dried under vacuum at 50°C for 24 h, (Scheme 3) yield 90%.

Metal uptake studies of polymer in the presence of electrolytes

The adsorption of metal ions in presence of electrolyte solution was conducted by following method. The polymer sample (25 mg in 25 mL of DMF) was added in an electrolyte solution (25 mL of NaCl) of known concentration. The pH of the solution was adjusted to 7–8. The solution was stirred for 24 h at room temperature. To this solution 10 mL of known concentration of metal ion was added. The mixture was again stirred at 25°C for 24 h and filtered. The solid was washed and left out Cu(II), Cr(III), and Cr(VI) contents were determined iodimetry and Ni(II) by gravimetry analysis. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiment. The experiments were also performed in the presence of Na_2SO_4 electrolyte.

Scheme 2 Synthesis of poly(5-(4-acryloyloxyphenylazo) salicylaldehyde).

X = H$_2$O for Cr(III), Ni(II), Cr(VI)

Scheme 3 Synthesis of polymer metal complexes.

TABLE I
Elemental Analysis of Polymer and Its Metal Complexes Found (Calculate) Values

Compounds	Carbon	Hydrogen	Nitrogen	Oxygen	Metal
Polymeric ligand	64.82(64.86)	4.04(4.05)	9.42(9.46)	21.60(21.62)	–
Cu(II) complex	55.69(55.73)	3.76(3.77)	8.11(8.12)	22.92(23.22)	9.21(9.22)
Ni(II) complex	56.19(56.14)	3.77(3.80)	8.15(8.18)	23.43(23.39)	8.61(8.58)
Cr(III) complex	53.95(54.10)	3.12(3.09)	7.85(7.87)	18.03(18.0)	7.14(7.19)
Cr(VI) complex	56.26(56.72)	3.81(3.84)	8.25(8.27)	23.18(23.24)	7.54(7.53)

Effect of pH on metal ion uptake

The optimum pH of the metal ion uptake was determined with a batch equilibrium technique. Excess of metal ions (10 mL, 0.1 mmol) were shaken with 25 mg of polymer for 24 h. The pH of the solution was adjusted before equilibration over a range of 5–10, with weak acid/base. The complex was filtered off and the concentration of remaining Cu(II), Cr(III), and Cr(VI) ions was determined by titrimetry and Ni(II) ion by gravimetry analysis.

Measurements

Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The metal content in complexes was determined by chemical method after the polymer was decomposed with concentrated sulfuric acid and nitric acid. The viscosity measurements were made in THF with Ubbelohde suspended level viscometer at 30°C. Molecular weight of the polymer was determined by gel permeation chromatography method (Water model 401). The infrared red spectra were recorded on a Shimadzu FTIR 8300/8700 spectrometer in the frequency range 4000–400 cm^{-1}. The measurements were made using almost transparent KBr pellets, contain fine powder sample at room temperature. The ^{1}H-NMR spectra of the ligand in DMSO-d$_6$ solution were recorded on a Bruker 400 MHz spectrometer. The Diffuse reflectance spectra were recorded in absorbance mode at room temperature in the range of 200–2000 nm on a Shimadzu UV-2450 PC instrument, using BaSO$_4$ pellet as the reference. The magnetic moment data were performed by Gouy method. The EPR measurement was recorded at room temperature on a JES-JOEL-TES 100 X-band frequency spectrometer. X-ray powder diffraction data for powder samples were collected on an 800 W Philips (PANANALYTICAL, Netherland) powder diffractometer using an etched glass plate sample holder by rotating anode diffractometer using Cu-$K\alpha$ irradiation. Themogravimetric analysis was carried on SDT Q600 V20.5 Build 15 Universal V4.5A TA Instruments at heating rate of 10°C/min in nitrogen.

RESULT AND DISCUSSION

The azo group containing monomer was prepared and polymerized in DMF using benzoyl peroxide as free radical initiator. Polymer-metal complexes were obtained in a DMF containing polymer and aqueous solution of metal ions. All the complexes were found to be stable in air and insoluble in common organic solvent. The polymer was soluble in THF, DMF, and DMSO. All the complexes were partially soluble in DMF and DMSO. The results of elemental analysis (Table I) data were shown that the metal to ligand ratio of the complexes is 1 : 2. The intrinsic viscosity [η] of poly[5-(4-acryloloxyphenylazo)salicylaldehyde] was obtained by extrapolating η_{sp}/C to zero concentration. The intrinsic viscosity was found to be 0.218 dL/g. This result reveals that the polymer was high molecular weight. The number average ($M_n = 1.75 \times 10^4$) and weight average ($M_w = 3.26 \times 10^4$) of polymer were determined by gel permeation chromatography method. The calculated polydispersity index is 1.86.

The IR spectra of polymer and its complexes were shown as the functional groups by proposed structure (Fig. 1). The IR spectra of polymer exhibit broad
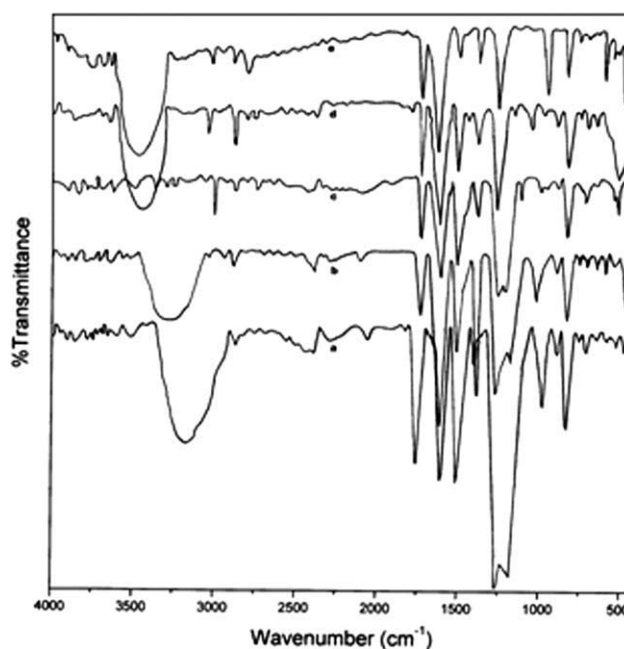

Figure 1　IR spectra of (a) polymeric ligand, (b) Ni(II) complex, (c) Cu(II) complex, (d) Cr(III), and (e) Cr(VI) complex.
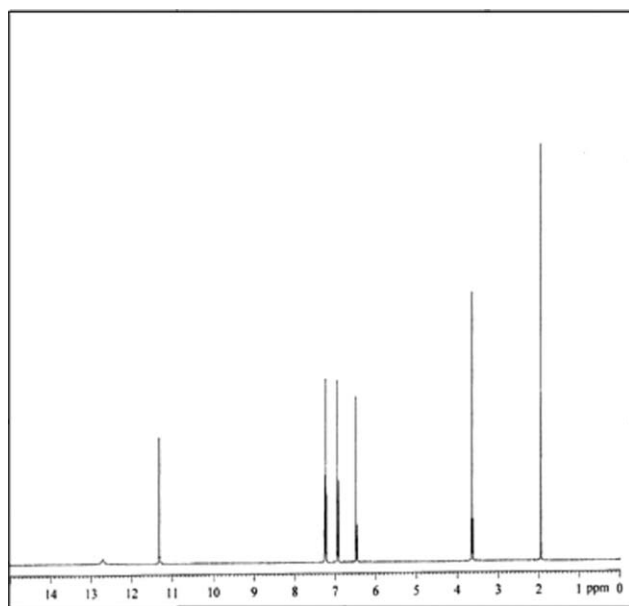
Figure 2 ^{1}H NMR spectra of polymer.

band at 3190 cm^{-1} are assigned to intermolecular hydrogen bonded —OH stretching.[18] This —OH stretching was disappeared in the polychelates suggested that the hydrogen was disappeared and coordination through oxygen. Ni(II), Cr(III), and Cr(VI) polychelates shows broad band between 3450–3300 cm^{-1} was assigned to coordinated H$_2$O molecules. This band was disappeared in the case of Cu (II) complex. Polymer and its complexes shows methylene C—H stretch at 2950–2835 cm^{-1}. Polymer shows strong band at 1734 cm^{-1} corresponds to C=O stretch in polychelates this band was shifted to lower frequency (1724–1718 cm^{-1}) because of involvement of coordination through oxygen. The polymer and its complexes shows strong stretching at 1510–1504 cm^{-1} was assigned to N=N. The phenolic C—O stretching was observed in the region 1270–1260 cm^{-1}. All the complexes show weak band in the region 470–425 cm^{-1} was assigned to M—O coordination covalent bond.[19]

The ^{1}H NMR spectrum of poly (5-4APASAL) was measured in DMSO-d6 solution (Fig. 2). The ^{1}H NMR signal in the region 1.945 δ and 3.631 δ corresponds to methylene protons. The signal in the region 6.402–7.261 δ belongs to aromatic protons. The high field ^{1}H-NMR signal was observed at 11.38 δ, which may correspond to hydrogen bonded aldehyde proton. The phenolic —OH proton was observed at 12.731 δ.

Electronic spectrum of Cu(II) complex (Fig. 3) shows d-d band at 20,492 cm^{-1} corresponds to ^2E_g $(t_{2g})^6$ $(e_g)^3 \rightarrow ^2T_{2g}$ $(t_{2g})^5$ $(e_g)^4$ transition. The second band was observed in near visible region at 26,870 cm^{-1} corresponds to ligand to metal charge transfer transition. The magnetic moment of Cu(II) com-

plexes is 1.76 BM suggests the square-planar geometry.[20,21] Ni(II) complexes shows two weak d-d bands at 20,408 and 22,726 cm^{-1} was assigned to $^3A_{2g} \rightarrow$ $^3T_{2g}$ and $^3A_{2g} \rightarrow ^3T_{1g}$ transition. The intense band in the region 35,088 cm^{-1} corresponds to $^3A_{2g} \rightarrow$ $^3T_{1g}(P)$ ligand to metal charge transfer transition suggests spin free octahedral geometry.[22,23] The magnetic moment of Ni(II) ion is 3.28 BM Cr(III) complexes shows two weak d-d bands in the region at 20,745 and 25,974 cm^{-1} corresponds to $^4A_{2g} \rightarrow$ $^4T_{2g}$ and $^4A_{2g} \rightarrow ^4T_{1g}$ 'spin allowed' d-d transition between t_{2g} and e_g orbital of the complexes $(t_{2g}^2$ $e_g^1 \leftarrow t_{2g}^3)$. The intense short wave length band observed at 34,365 cm^{-1} corresponds to $^4A_{2g} \rightarrow$ $^4T_{1g}(P)$ ligand to metal charge transfer transition. Magnetic moment of Cr(III) ion is 3.74, indicate presence of octahedral geometry.[24] In case of Cr(VI) complex shows three intense charge transfer bands at 20,877, 26,590, and 33,898 cm^{-1}. CT band in visible region observed may be due to metal ion, which has higher oxidation state and low d-orbital population.[25]

The powder EPR spectrum of complexes was recorded at room temperature and it was shows in Figure 4. In Cu (II) complex exhibits two different 'g' values. Such values are g$^{||}$ = 2.38 and g$^\perp$ = 2.13. Observed these two different 'g' values are confirmed the existence of square-planar geometry. Ni (II) complex shows intense isotropic peak. The measured 'g'$_{iso}$ values are g$^{||}$ = 2.086 and g$^\perp$ = 2.09, respectively, these value indicates the octahedral geometry.[26] A Cr (III) complex shows broad band line and calculated g value is 1.98. The signal does not show hyperfine splitting.[27] This result consistent in the presence of octahedral complexes.
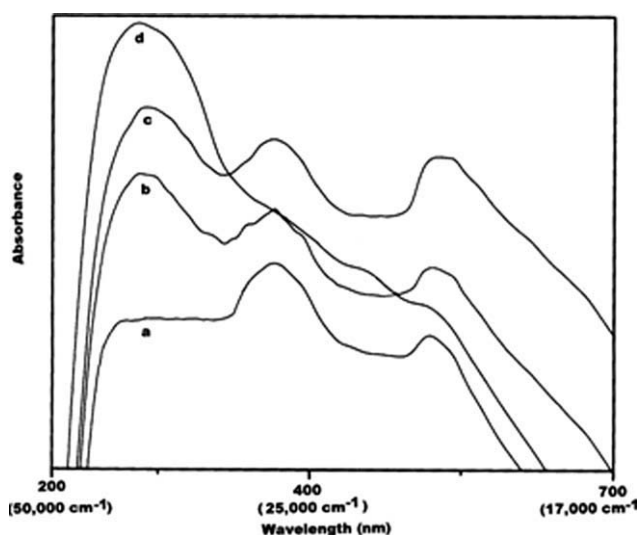

Figure 3 Electronic spectra of (a) Cu(II) complex, (b) Cr(III) complex, (c) Cr(VI), and (d) Ni(II) complex.
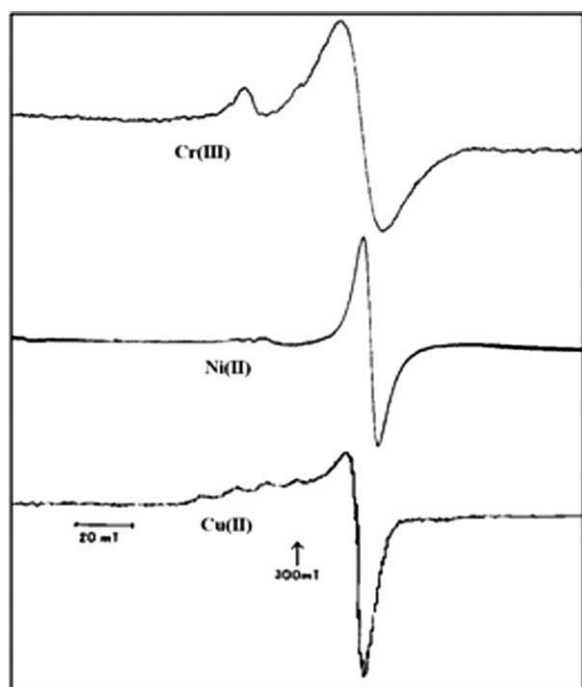
Figure 4 Powder EPR spectrum of complexes were recorded at room temperature. Frequency 9.34041.

The thermal decomposition behavior of chelating ligand and their complexes were shown in Figure 5. The initial decomposition of polymer commenced at 80°C; however, in case of polychelates it is 150°C. The polymer completely charred at 580°C with total weight loss about 97%. In case of all the polychelates lost 60–70% of their masses. The residues lefts correspond to the formation of respective metal oxides. The first decomposition of polymer and its complexes may be due to the rupture of weak linkage and volatilization of low molecular weight fragments. The second decomposition chelates at higher temperature than polymer may be due to the breakage of main chain accompanied by volatilization of cleaved products. The thermal property result clearly indicates the polymer possess and lower thermal stability than the corresponding metal complexes.

The X-ray diffraction studies of polymer and their complexes are shown in Figure 6. The X-ray studies indicate that polymer was amorphous and their complexes were crystalline nature. The crystalline nature of the complexes may not have any ordering of the complexes, may imply inter cross-linking between polymer chain and metal ions. From FTIR, ^{1}H-NMR, electronic spectra, magnetic moment, EPR, and elemental analysis result shown that the proposed structure of the complexes are shown in Scheme 3.

Effect of pH on metal-ion uptake

The adsorption of various transition metal ions (Cu(II), Ni(II), Cr(III), and Cr(VI)) on polymer at var-
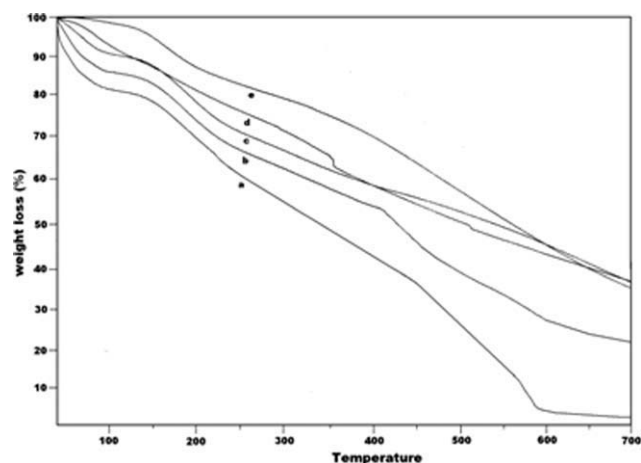
Figure 5 TGA spectra of (a) Polymeric ligand, (b) Ni(II) complex, (c) Cu(II) complex, (d) Cr(VI), and (e) Cr(III) complex.

ious pH ranging from 5.0–10.0 at fixed time was investigated. At higher pH (8–10), deprotonation of ligand and ionization of metal ions become significantly increased and compete with polychelate formation. At lower pH H_3O^+ ion concentration interacted with metal ions and decreased for complex formation.[28,29] According to this study, the amount of metal adsorption on polymer is highly sensitive towards changes of pH.

Effect of electrolyte on metal ion-uptake

The effect of electrolyte solution (Cl^- and SO_4^{2-}) on chelating process a various concentration with fixed buffer of pH 7.0 was also investigated (Table II). To these study metal ions uptake increases when increases of anion concentration due to its significant changes of free energy of hydration and stabilized the metal complexes. This observation suggests that the chloride and sulfate anions possess good stability on polychelates.
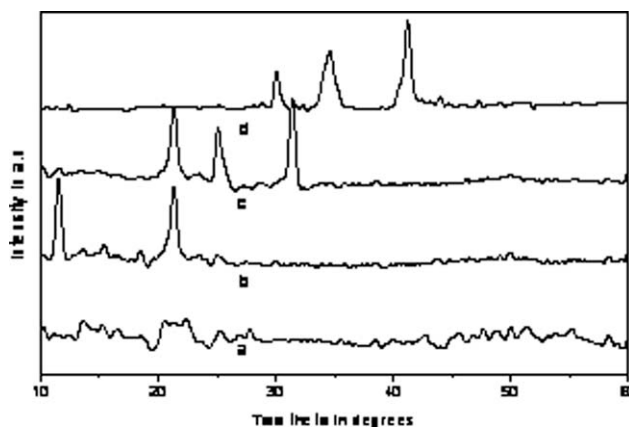

Figure 6 X-ray diffraction of (a) Polymer, (b) Ni(II) complex, (c) Cu(II) complex, and (d) Cr(III) complex.

TABLE II
Percentage Metal Uptakes of Poly(5-(4-acryloyolxyphenylazo)salicylaldehyde) with Different Electrolytes at pH 7–8

Metal ions	Electrolyte concentration (mol/L)	% Metal uptake in the presence of	
		NaCl	Na$_2$SO$_4$
Cu(II)	0.05	90.45	88.65
	0.1	93.73	91.86
	0.5	94.03	93.13
Ni(II)	0.05	90.02	88.85
	0.1	92.03	92.38
	0.5	93.13	92.42
Cr(III)	0.05	90.16	89.65
	0.1	94.26	93.12
	0.5	96.16	93.86
Cr(VI)	0.05	90.86	89.01
	0.1	94.48	94.25
	0.5	95.1	94.65

Regeneration of polymeric ligand

Regeneration of adsorbed metal ions from ligand were studied with the help of 7*M* HCl. Complexes were placed in 7*M* HCl for desorption of metal ions from polymeric ligand and the percentage of desorbed metal ions were calculated by titrimetric and gravimetric methods. More than 95% of metal ions desorbed from the polymeric ligand. This sequence was repeated for four cycles with same polymeric ligand, the results were found to be good that the polymeric ligand possess good recyclability under acidic condition.

CONCLUSION

The novel bidentate salicylaldehyde based chelating polymer and polychelates were synthesized and that the structure was determined using various spectroscopic techniques. The elemental analysis assigned metal to ligand ratio is 1 : 2. The IR spectral studies showed that the formation of azo compound and coordination involved through oxygen of ligand. Electronic and EPR spectra were determined octahedral structure of the Ni(II), Cr(III), and Cr(VI) complexes, and square-planar structure of the Cu(II) complex. Thermal studies revealed that the decomposition of ligand and its complexes. The maximum metal uptake efficiency of ligand with different parameter was also determined. The reusability of polymeric ligand was conducted and result was found to be good metal uptake even after four cycles.

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