New Polymeric Schiff Base and Its Metal Complexes

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ABSTRACT: A novel polymeric Schiff base was synthesized by the reaction of a Schiff base from 2,4-dihydroxy benzaldehyde and aniline with acryloyl chloride and was polymerized in methyl ethyl ketone at 70°C with benzoyl peroxide as a free-radical initiator. Polychelates were obtained in an alkaline solution of poly(2-hydroxy-4-acryloyloxy-N-phenylbenzylidine) with aqueous solutions of metal ions such as Cu(II), Ni(II), Co(II), Ca(II), Cd(II), Mn(II), and Zn(II). The polymeric Schiff base and polychelates were characterized with elemental analysis and spectral studies. The elemental analysis of the polychelates suggested that the metal-to-ligand ratio was 1:2. The IR spectral data of the polychelates indicated that the metals were coordinated through the nitrogen and oxygen of the phenolic —OH group. Diffuse reflectance spectra, electron paramagnetic resonance, and magnetic moment studies revealed that the polychelates of the Cu(II) complex were square-planar, those of the Ni(II), Mn(II), and Co(II) complexes were octahedral, and those of the Ca(II), Cd(II), and Zn(II) complexes were tetrahedral. X-ray diffraction studies revealed that the polychelates were highly crystalline. The thermal properties of the Schiff base and polychelates were also examined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 494–500, 2004

Key words: metal–polymer complexes; Schiff base

INTRODUCTION

A polymeric Schiff base with multidentate coordination sites or groups is known to form complexes with transition-metal ions readily. The basic properties of Schiff base polymers are due to the linkages of C=N in the backbone.[1] Schiff base polymers have been researched because of their high thermal stability,[2] complex-forming ability,[3,4] and semiconducting properties.[5,6] The radical polymerization of Cu(II) complexes with a Schiff base ligand containing a vinyl group and the radical polymerization of methacrylate monomers coordinated to Co(III) have been studied.[7] Polymeric Schiff base chelates based on naphthaldehyde and Mannich bases have been investigated.[8] The incorporation of transition-metal ions into polymeric Schiff bases not only affects the physical characteristics, such as the strength, but also the chemical activity. The catalytic activities of Schiff base complexes of transition-metal ions in a variety of organic reactions have been known for a long time. However, when the metal ions are complexed with functional polymeric Schiff bases, the activity of the metal complexes changes because of a polymeric effect. Lei and Wang[9] indicated that the polymeric support and polymeric end groups affected the catalytic activity and selectivity of these complexes in a hydrogenation reaction. Transition-metal/polymer complexes of bidentate or tetradentate polymeric Schiff base ligands are always of interest: they lead to novel structural types and display a wide variety of magnetic properties. El-Sonabati and El-Bindary[10] found that polymeric Schiff base ligands played a key role in understanding the coordination chemistry of transition-metal ions. The syntheses and studies of a series of polymeric ligands and their metal complexes were reported earlier.[11–15] In a continuation of our research in this domain, this article deals with the synthesis and characterization of a novel polymeric Schiff base and its metal complexes. The spectral and magnetic properties, conductivity, and type of geometry around the metal center are discussed.

EXPERIMENTAL

2,4-Dihydroxybenzaldehyde was recrystallized from ethanol. Benzoyl peroxide was recrystallized from a methanol/chloroform mixture. Acryloyl chloride was prepared according to the procedure of Stempel et al.[16] The solvents were purified with standard procedures before use.

Synthesis of 2,4-dihyroxybenzaldehyde-*N*-phenylimine

2,4-Dihydroxybenzaldehyde-*N*-phenylimine was synthesized by the reaction of 2,4-dihydroxybenzaldehyde (5.1 g) in ethanol and a mixture of aniline (5.6 g) and ethanol (50 mL). The mixture was refluxed in a water bath for 6 h. The resulting products were poured into cold water; this resulted in the precipita-

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TABLE I
Elemental Analysis Data for 2PH4ABI, Poly(2PH4ABI), and Its Metal Complexes

		Elemental analysis (wt %)								
		Carbon		Hydrogen		Oxygen		Nitrogen		Metal	
Abbreviation	Empirical formula	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]	Found
(2PH4ABI)	$C_{16}H_{13}O_3N$	71.91	71.86	4.86	4.89	17.97	17.99	5.26	5.26	—	—
Poly(2PH4ABI	$(C_{16}H_{13}O_3N)_n$	71.91	71.86	4.86	4.89	17.97	17.99	5.26	5.26	—	—
Poly(2H4ABPI)–Cu(II)	$(C_{16}H_{13}O_3N)_x$–Cu(II)	65.08	65.05	4.06	4.09	16.27	16.22	4.75	4.78	9.84	9.86
Poly(2H4ABPI)–Ni(II)	$(C_{16}H_{12}O_3N)_x$–Ni(II)(H$_2$O)$_y$	65.32	65.30	4.08	4.06	16.32	16.36	4.76	4.71	9.52	9.57
Poly(2H4ABPI)–Co(II)	$(C_{16}H_{12}O_3N)_x$–Co(II)(H$_2$O)$_y$	65.53	65.50	4.09	4.11	16.38	16.39	4.77	4.71	9.23	9.29
Poly(2H4ABPI)–Mn(II)	$(C_{16}H_{12}O_3N)_x$–Mn(II)(H$_2$O)$_y$	65.97	65.95	4.12	4.14	16.49	16.46	4.83	4.85	8.59	8.60
Poly(2H4ABPI)–Zn(II)	$(C_{16}H_{12}O_3N)_x$–Zn(II)(H$_2$O)$_y$	64.86	64.81	4.05	4.07	16.22	16.25	4.73	4.71	10.14	10.76
Poly(2H4ABPI)–Cd(II)	$(C_{16}H_{12}O_3N)_x$–Cd(II)(H$_2$O)$_y$	61.15	61.13	3.83	3.85	15.28	15.29	4.46	4.47	15.28	15.26
Poly(2H4ABPI)–Ca(II)	$(C_{16}H_{12}O_3N)_x$–Ca(II)(H$_2$O)$_y$	67.15	67.16	4.19	4.16	16.78	16.80	4.89	4.91	6.99	6.97

[a] Calculated percentage of C, H, N, and O and metal ions for polymer–metal complexes based on the value of $x = y = 2$. Found: $x = 2.02$, and $y = 2.01$.

tion of the Schiff base, which was later dried under reduced pressure. The yield was 89%. The product was confirmed by elemental analysis.

ELEM. ANAL. Calcd.: C, 73.21%; N, 6.59%; H, 5.14%; O, 15.06%. Found: C, 73.23%; N, 6.57%; H, 5.16%; O, 15.04%.

### Synthesis of 2-hydroxy-4-acryloyloxy-*N*-phenylbenzylidine (2H4ABI)

2H4ABI was synthesized with acryloylchloride and 2,4-dihydroxy-*N*-phenylimine. Acryloyl chloride (12.03 mL), along with 25 mL of methyl ethyl ketone, was added slowly to a mixture containing 2,4-dihydroxy-*N*-phenylimine (16.8 g) and triethylamine (10.2 mL) in a methyl ethyl ketone (100 mL) solution maintained at $0 \pm 5°C$. After the addition of acryloyl chloride, the temperature was maintained at room temperature for 2 h. The resulting solution was thoroughly washed with water and a 5% sodium hydroxide solution and then was dried over anhydrous sodium sulfate. Finally, the solvent was evaporated, and the crude product was recrystallized from ethanol.

Polymerization

Poly(2-hydroxy-4-acryloyloxy-*N*-phenylbenzylidine) [poly(2H4ABI)] was prepared as a $4M$ solution in methyl ethyl ketone with benzoyl peroxide as an initiator at 70°C in a thermostatic water bath. The entire system was kept in an inert atmosphere with a continuous passage of nitrogen. The polymer was precipitated by the addition of a nonsolvent such as methanol and was purified by dissolution in chloroform and reprecipitation in methanol. The purification procedure was repeated twice, and the product was finally dried *in vacuo*. The yield was 75%.

Synthesis of the polymer–metal complexes

A series of polymer–metal complexes [Cu(II), Ni(II), Mn(II), Co(II), Cd(II), Ca(II), and Zn(II)] were prepared at room temperature in an alkali medium with poly(2H4ABAI). A typical procedure for the preparation of the poly(2H4ABAI)–Cu(II) complex was as follows. Poly(2H4ABAI) (1.095 g of the repeat unit) was dissolved in a $3M$ NaOH (100 mL) solution. An aque-
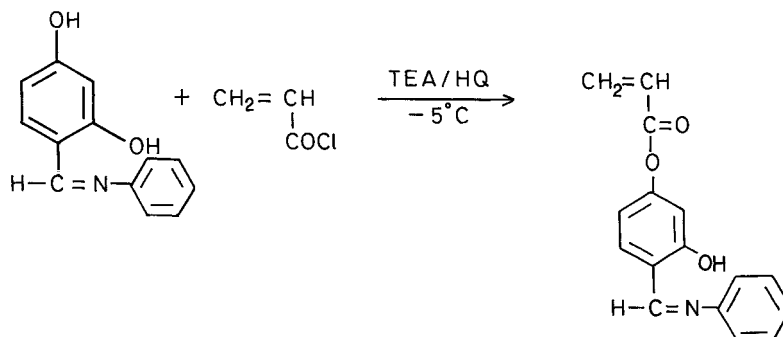
Scheme 1

TABLE II
IR Spectral Data of Poly(2H4ABPI) and Its Metal Complexes

Sample	Wave number (cm^{-1})			
	OH_{str}	$C=O_{ester_{str}}$	$C=N_{str}$	$M-N_{str}$
Poly(2H4ABPI)	3050–3400(b)	1780(m)	1600–1700(b)	—
Poly(2H4ABPI)–Cu(II)	—	1750(m)	1590–1650(b)	475(s)
Poly(2H4ABPI)–Ni(II)	3450(b)	1750(m)	1580–1650(b)	460(s)
Poly(2H4ABPI)–Co(II)	3400(b)	1740(m)	1610–1700(b)	395(s)
Poly(2H4ABPI)–Mn(II)	3350(b)	1750(m)	1600–1700(b)	425(s)
Poly(2H4ABPI)–Zn(II)	—	1750(m)	1590–1700(b)	400(s)
Poly(2H4ABPI)–Cd(II)	—	1760(m)	1575–1710(b)	425(s)
Poly(2H4ABPI)–Ca(II)	—	1750(m)	1570–1700(b)	435(s)

b = broad; m = medium; s = strong.

ous solution of copper(II) acetate (0.497 g) dissolved in distilled water (20 mL) was added dropwise to the polymer solution with constant stirring, and the pH of the solution was adjusted to 7 with an excess of a sodium hydroxide (1N) solution. The precipitated poly(2H4ABAI)–Cu(II) complex was filtered off, washed with hot distilled water and then with ethanol, and dried at 60°C *in vacuo*. A similar procedure was adopted for the preparation of the other polymer–metal complexes.

Measurements

The elemental analyses were carried out on a Coleman CHN analyzer. The metal content in the polymer–metal complexes was determined by a titration proce-

Figure 1   Representative FTIR spectra of (a) poly(2H4ABI), (b) poly(2H4ABI)–Cu(II), and (c) poly(2H4ABI)–Ni(II).

dure after the decomposition of the polymer with concentrated sulfuric acid and concentrated nitric acid. The results are shown in Table I. The viscosity measurements of poly(2H4ABAI) were made in an Ubbelohde suspended-level viscometer with dimethylformamide (DMF) at 30°C. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of poly(2H4ABAI) were determined by gel permeation chromatography (Waters 501) with tetrahydrofuran (THF) and polystyrene standard calibration. The IR spectra of poly(2H4ABAI) and its metal complexes were recorded on a PerkinElmer 782 spectrophotometer with KBr pellets. The ^{1}H-NMR spectrum of poly(2H4ABAI) was recorded on a Hitachi 90-MHz spectrophotometer in CDCl$_3$ with tetramethylsilane as the internal standard.

The magnetic moments were measured by the Gouy method and were corrected for the diamagnetism of the component with Pascal's constant. The diffuse reflectance spectra (8000–26,000 cm^{-1}) were measured on a Karl-Zeiss VSU-28 spectrophotometer. The electron paramagnetic resonance (EPR) analyses were carried out at room temperature on a Varian spectrophotometer. The X-ray diffraction (XRD) experiments were performed on a Phillips PW 1820 diffractometer with a Staton camera with Cu Kα radiation (wavelength = 1.542 Å). The glass-transition temperatures (T_g's) of poly(2H4ABAI) and its metal complexes were determined by differential scanning calorimetry (DSC) on a DuPont 900 thermal analyzer at a heating rate of 15°C min^{-1} in air. The thermogravimetric analysis (TGA) was carried out on a Mettler TA 3000 thermobalance with a 0.5-mg sample at a heating rate of 15°C min^{-1} in air.

RESULTS AND DISCUSSION

The novel Schiff base 2H4ABAI was synthesized from 2,4-dihydroxy-N-phenylimine and acryloyl chloride in the presence of triethylamine and polymerized in methyl ethyl ketone with benzoyl peroxide as an initiator according to Scheme 1.
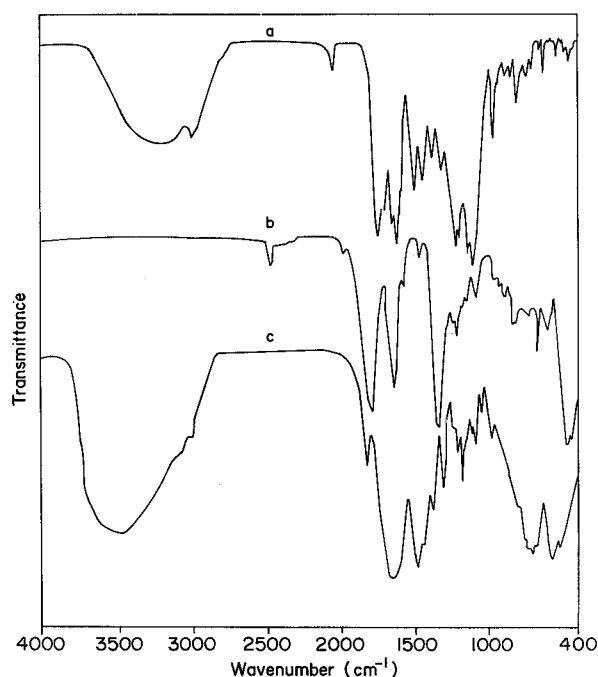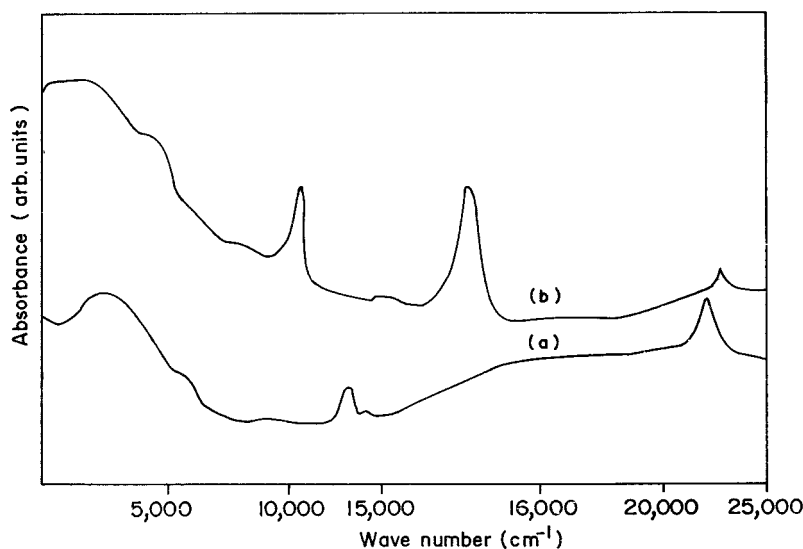
Figure 2 Diffuse reflectance spectra of (a) poly(2H4ABI), (b) poly(2H4ABI)–Cu(II), and (c) poly(2H4ABI)–Ni(II).

The polymer was soluble in chloroform, THF, DMF, and dimethyl sulfoxide (DMSO) and insoluble in common organic solvents such as benzene, toluene, methanol, and water. The polymer–metal complexes were obtained when an alkaline solution of poly(2H4ABAI) was treated with aqueous solutions of metal ions in the presence of excess sodium hydroxide. The polychelates were insoluble in common organic solvents but were sparingly soluble in DMF. All the polymer–metal complexes were colored. The elemental analysis (Table I) showed that the ligand-to-metal ratio in all the polychelates was 2:1, in good agreement with the calculated values.

The intrinsic viscosity was obtained by the extrapolation of n_{sp}/C to a zero concentration. The intrinsic viscosity of poly(2H4ABAI) was found to be 0.417 dL

g^{-1}. The results revealed that the polymer had a moderately high molecular weight. M_n and M_w of poly(2H4ABAI) were obtained by gel permeation chromatography with THF ($M_n = 1.89 \times 10^4$ and $M_w = 3.26 \times 10^4$).

The polydispersity index (M_w/M_n) for poly-(2H4ABI) was 1.72. The result agreed with the viscosity. Table II shows the IR spectral data of poly(2H4ABI) and polymer–metal complexes. The absorption band near 3100–3500 cm^{-1} corresponded to phenolic —OH[17] (Fig. 1). The phenolic —OH stretching disappeared in the spectra of polychelates; this indicated coordination. Ni(II), Co(II), and Mn(II) polychelates showed strong absorption bands in the 3550-cm^{-1} region because of the coordination of water molecules to metal ions.[18] This band remained even when

TABLE III
Magnetic Moment, Diffuse Reflectance, and EPR Spectral Data of Polymer–Metal Complexes

| Polymer–metal complex	Magnetic moment (BM)	Electronic transition (cm^{-1})	Assignment	$g\|$	$g\perp$	Geometry
Poly(2H4ABPI)–Cu(II)	1.80	15,645	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.35	2.16	Square planar
		25,395	Charge-transfer			
Poly(2H4ABPI)–Ni(II)(H$_2$O)$_2$	3.32	9,750	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	2.26	2.15	Octahedral
		15,450	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$			
		25,500	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
Poly(2H4ABPI)–Co(II)(H$_2$O)$_2$	3.39	8,800	$^4A_2 \rightarrow {}^4T_1(F)$	2.38	2.23	Octahedral
		15,850	$^4A_2 \rightarrow {}^4T_1(P)$			
		25,050	Charge-transfer			
Poly(2H4ABPI)–Mn(II)(H$_2$O)$_2$	5.65	15,750	$^6A_{1g} \rightarrow {}^4T_{1g}(4G)$	2.62	2.18	Octahedral
		17,675	$^6A_{1g} \rightarrow {}^4T_{2g}(4G)$			
		22,745	$^6A_{1g} \rightarrow {}^4E_g{}^4A_{2g}$			
Poly(2H4ABPI)–Cd(II)	Diamagnetic	—	—	—	—	Tetrahedral
Poly(2H4ABPI)–Zn(II)	Diamagnetic	—	—	—	—	Tetrahedral
Poly(2H4ABPI)–Ca(II)	Diamagnetic	—	—	—	—	Tetrahedral
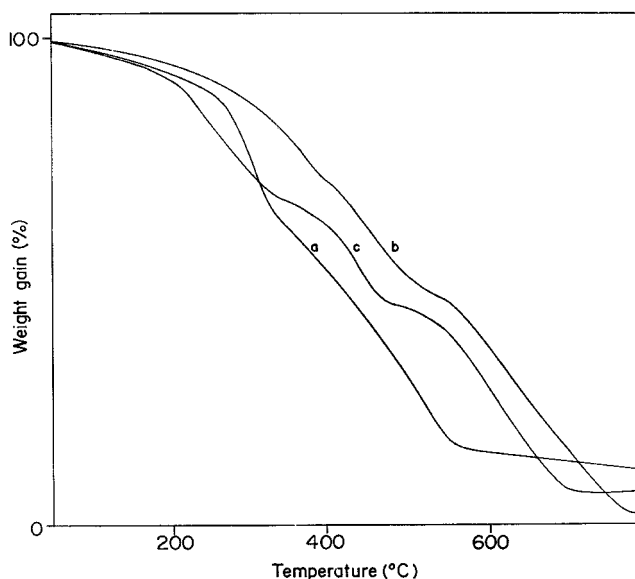
Figure 3 TGA curves of (a) poly(2H4ABI), (b) poly(2H4ABI)–Cu(II), and (c) poly(2H4ABI)–Ni(II).

the polychelates were heated up to 150°C. Poly(2H4ABI) displayed strong bands at 1740 and 1620 cm^{-1} that were ascribed to C=O of esters and C=N stretching, respectively. The band around 2760 cm^{-1} indicated intramolecular bonding, which occurred between the phenolic —OH and nitrogen of the azomethine group. The appearance of well-defined absorption in the range of 600–400 cm^{-1} was assigned to an M—N bond.[19]

The ^{1}H-NMR spectrum of poly(2H4ABI) showed broad multiple resonance signals at $\delta = 7.96$, which may be attributed to the phenolic —OH proton. A singlet around $\delta = 6.92$ corresponded to a substituted phenyl ring. The resonance signals around $\delta = 6.75$–7.62 were due to aromatic protons. The resonance signals at $\delta = 1.82$ and $\delta = 2.85$ were due to methylene and methine protons. The ^{13}C-NMR spectrum of poly(2H4ABI) showed a broad signal between $\delta = 20$ and $\delta = 50$ due to methylene and methane carbons. The ester carbonyl carbon signal appeared at $\delta = 175$.

The aromatic ring carbons produced a very broad single peak from $\delta = 100$ to $\delta = 150$.

The magnetic moment, diffuse reflectance (Fig. 2), and EPR spectral data are given in Table III. The results revealed that the structure of the Cu(II) complex was square-planar, where as the Co(II), Ni(II), and Mn(II) complexes were octahedral. Zn(II), Cd(II), and Ca(II) polymer–metal complexes were diamagnetic. The diamagnetic nature, coupled with elemental analysis data, suggested a tetrahedral environment of chelating ligands around the metal.[20–24]

The TGA traces of the polymeric Schiff base and its metal complexes are shown in Figure 3. The differential thermal analytical data are listed in Table IV. The polymeric Schiff base was stable up to 325 and 750°C; all the polymer–metal complexes lost about 97% of their weight. The Cu(II) metal complexes were more stable than the other polymer–metal complexes. The T_g values of the polymer and its metal complexes are listed in Table IV. The difference in the transition may be ascribed to the crystallinity of the polymer–metal complexes and agrees with the XRD studies (Fig. 4). IR, ^{1}H-NMR, cross-polarity/magic-angle-spinning ^{13}C NMR, EPR, electronic spectra, and magnetic moment studies confirmed that the chelation of metal ions could have occurred between two groups from different polymeric chains, as shown in Scheme 2.

The treatment of polymeric metal complexes with 7M HCl resulted in quantitative regeneration of the polymer. The dechelated polymer underwent complexation with the original efficiency. The reproducibility of the aforementioned results was established by the sequence being repeated several times; this revealed the good recyclability and stability of the polymer under acidic conditions. Finally, it may be concluded that the complex-forming ability of this polymer with various divalent metal ions in an aqueous medium at pH 7 could be effectively used for the removal of heavy metals from water and wastewater.

TABLE IV
T_g and TGA of the Polymer and Polymer–Metal Complexes

| Sample	T_g (°C)	Temperature (°C)					Char (%) at 700°C
		10	30	50	70	90	
Poly(2H4ABPI)	135	310	405	480	635	685	0
Poly(2H4ABPI)–Cu(II)	225	375	420	570	635	635	9
Poly(2H4ABPI)–Ni(II)(H$_2$O)$_2$	195	370	435	530	615	650	6
Poly(2H4ABPI)–Mn(II)(H$_2$O)$_2$	120	330	375	380	410	505	5
Poly(2H4ABPI)–Co(II)(H$_2$O)$_2$	165	325	385	405	420	545	4
Poly(2H4ABPI)–Ca(II)	150	350	380	420	445	565	3
Poly(2H4ABPI)–Cd(II)	170	325	365	390	410	525	5
Poly(2H4ABPI)–Zn(II)	165	310	350	405	465	555	4
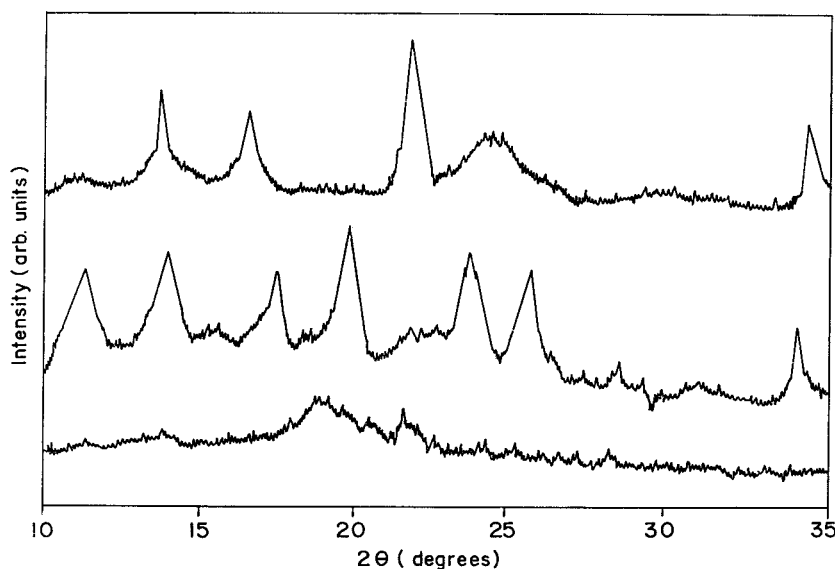
Figure 4 X-ray diffractograms of (a) poly(2H4ABI), (b) poly(2H4ABI)–Cu(II), and (c) poly(2H4ABI)–Ni(II).
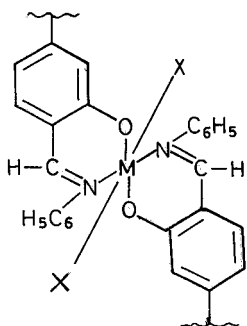
CONCLUSIONS

Acrylate containing Schiff base ligands with hydroxyl and azomethine functions underwent free-radical polymerization under an inert atmosphere and moderate conditions, giving polymers in good yields. The polymeric Schiff base was soluble in chloroform, THF, DMF, and DMSO and insoluble in benzene, toluene, and methanol, whereas the polymer–metal complexes were insoluble in all these solvents. The molecular weight of the polymer was moderately high, as evidenced by viscosity and gel permeation chromatography. Elemental analysis revealed that the ratio of the polymeric ligand to the metal ion was 2:1 in all cases. TGA and DSC studies revealed that polychelates were more heat-resistant than their respective polymer counterparts. The amorphous nature of the polymeric Schiff base, in contrast to the crystallinity of the respective polymer–metal complex, was indicated by DSC and XRD. As evidenced by IR, diffuse reflectance spectroscopy (DRS), EPR, and magnetic moment data, for Co(II), Ni(II), and Mn(II) polychelates, coordination with the metal ions involved nitrogen and oxygen of the —OH group along with two water molecules, leading to a octahedral structure. However, the structure of the Cu(II), Ca(II), and Cd(II) complexes were square-planar, and coordination with the metal ions was only through nitrogen and —OH groups. The recovery of the polymeric Schiff base from the polymer–metal complexes in an acid medium was good, the polymers being stable under that condition. This will be extremely valuable for water treatment [particularly Ca(II) complexes], hydrometallurgy, and the recovery of trace metal ions.

M = Cu, Ni, Mn, Co, Ca, Cd, Zn

X = H_2O for Ni, Mn, Co

Scheme 2

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