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First Example of Schiff Bases Containing Poly(Acryl Amid) in the Synthesis and Characterization

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A novel polymeric-Schiff base derived from the condensation reaction poly(acryl amid) and indole-3-carboxaldehyde has been synthesized and their Co(II) and Ni(II) complexes have been prepared. Mol ratio of acrylamid group and Schiff bases group was estimated by means of height of -CH multiple peaks and -CH = N- peak in ¹H-NMR spectrum. The studied substances were characterized by molar conductance, magnetic susceptibility, electronic and IR spectral studies. In addition, main units have been suggested with elemental analysis for these substances, and than the weight average molecular weight (M_w) has been suggested. The number average molecular weight (M_n) was determined with a vapor pressure osmometer. Polydispersity index (PDI) found to be ca 1.7 from M_w/M_n for poly-Schiff bases and their Co(II) and Ni(II) complexes. PAA-Schiff bases were found to have the highest thermal stability compared to that of the Co(II) and Ni(II) complexes. The conductivities of the PAA-Schiff bases and their complexes were measured by the four-probe technique and were found in the range $10^{-5} - 10^{-6} S cm^{-1}$.

Keywords poly-Schiff bases, poly condensation, thermal stability, polymeric-complexes, poly(acryl amid), conductivity

Introduction

In the past decade, there has been much interest in the coordination chemistry of polymers due to their high thermal stability and semiconducting or conducting properties (1–3). Metal-polymer complexes attracted the attention of researchers long ago and still hold a noteworthy place in modern chemistry (4, 5). Poly(acryl amid) (PAA) as a water-soluble synthetic polymer has found a significant role in many industrial applications as a coating in the textile and building industry. This significant role depends on the degree of amin and carboxyl group. PAA has the capability to change some of their behavior, i.e., permeability and mechanical strength, with small changes in structure (6, 7). Developing the properties of individual polymers can be an important approach for to use in new fields. For this reason, I chose PAA and indole-3-carboxaldehyde as aldehyde (Figure 1) and attempted to prepare polymer-Schiff bases by polycondensation.

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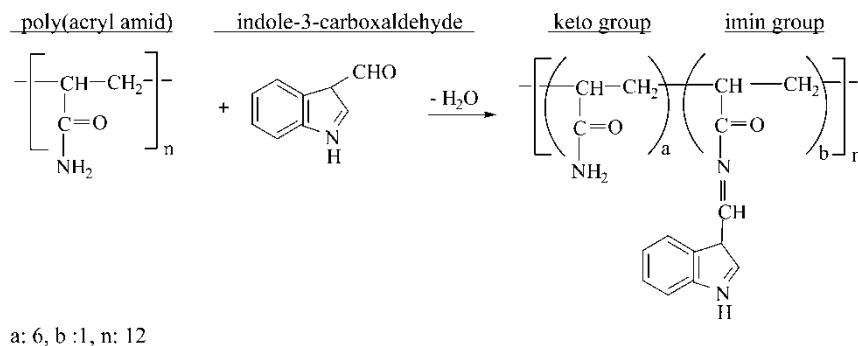


Figure 1. Structure of poly(acryl amid) and aldehyde.

In this way, derivatives new of PAA may be useful in the polymer network. PAA-Schiff bases may be have conjugate bonding with a new active group, therefore, studied substances may have semi conductivity or conductivity (8, 9), chemical sensors (10), corrosion protection (11, 12), thermostabilizers.

Experimental

Materials

The solvents used in this study were analytical grade. All the other materials (poly(acryl amid), indole-3-carboxaldehyde, metal (II) salts and solvents) were reagent grade (Sigma-Aldrich Company).

Apparatus

^1H and ^{13}C -NMR spectra of the ligands were recorded with a Bruker Spectrospin Avance DPX-400 using TMS as internal standard and DMSO- d_6 as solvent. IR spectra in the 4000–400 cm^{-1} ranges were recorded using KBr discs on a Mattson 1000 FTIR spectrophotometer. Carbon, hydrogen, and nitrogen values were obtained using a LECO-9320 analyzer. Metals were determined with a Philips PU 9285 model AAS spectrophotometer. Chlorine was determined titrimetrically by the Mohr method. The weight average molecular weight (M_w) was suggested from this element analyses. The number average molecular weight (M_n) was determined with a vapor pressure osmometer using Vescor 5520X. The TGA curves were obtained on a General V4.1C Du Pont 2000 between 30–600°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere. Conductivity measurements were carried out at 20°C in 10^{-3} M DMF using a Siemens WPA CM 35 apparatus. The room temperature magnetic moments were measured with a MK-1 model Gouy Balance (Christison Scientific Equipment Ltd.).

Preparation of the Polymeric-Schiff Bases

A solution of poly(acryl amid) (0.001 mol) in hot water (15 mL) was added drop wise to a solution of the indole-3-carboxaldehyde (0.012 mol) dissolved in CH_3OH solution (20 mL). The stirring was continued until the solution was dense *ca.* 4 d. The mixture was evaporated until about the ratio 1:3 of its original volume and cooled.

A crystalline yellow precipitate was obtained. Then the crystalline solids were filtered, washed with a mixture of water-methanol (1:1) and methanol-ether (1:1). Finally, it was dried *in vacuo* (over P_4O_{10}).

Anal. Calcd for $[C_{30}H_{40}N_8O_7]$ in the main unit: Calcd.: C: 57.69; H: 6.41; N: 17.95; Found: C: 56.11; H: 6.61; N: 18.50. UV-Vis (λ_{max}): 221, 264, 230 and 336 nm. FT-IR (major I.R. absorption; KBr cm^{-1}): $\nu(NH)_{ring}$, 2937 m; $\nu(NH_2)_{asym}$, 3201; $\nu(NH_2)_{sym}$, 3423; $\nu(CN) + \delta(NH)$, 1518; $\delta(NH)$, 1256; $\nu(C=O)_{(out-of\ planes)}$, 483; 1H NMR (DMSO- d_6); δ (ppm); [$-C-NH_2$, 7.62(s, 2H), $-CH$, 2.93(m 1H), $-CH_2$, 2.67(t, 2H)]_{keto}; [$-C-NH$, 7.27(s, 2H), $-CH$, 2.44(m, 1H), $-CH_2$, 2.31(t, 2H)]_{enol}; $-N=CH$, 9.56(s, 1H), $CH_{(arom)}$, 7.92–7.80(s, 2H) and 6.45–6.28 (m, 4H), NH_{ring} , 8.16 (s, 1H), $-CH_2$ (imin group), 3.23 (m, 2H), $-CH$ (imin group), 3.52(m, 1H), ^{13}C NMR (DMSO- d_6); δ (ppm); $-C=O$, 165.01, $-C=O$ (imin group), 196.30, $-CH$ (keto and enol), 40–45, $-CH_2$ (keto and enol), 33–38, $-N=CH$, 196.30, $C_{(arom)}$, 112.72, 125.90, 123.40, 122.54, 132.77, 120.84, 138.34, 113.26.

Synthesis and Isolation of Complexes

First Step: Preparation of Metal-Aldehyde Complexes. The aldehyde (indole-3-carboxaldehyde) complexes of Nickel (II) and Cobalt (II) were prepared by mixing aqueous solutions of metal chlorür with ethanolic solutions of the aldehydes at 1:2 mol ratio (13). The resulting solutions was stirred for *ca.* 1 h, filtered, and allowed to stand. On standing for further 8 h, the golden-yellow solid complexes formed was collected by filtration, washed with a small volume, then dried in a desiccator over $CaCl_2$ (Figure 2).

Elemental analyses of metal-aldehyde complexes: found (calcd) %: $[Co(L)_2Cl_2]$; C:50.98 (51.44), H: 2.37 (3.33), N, 6.51 (6.67), Co: 13.79 (14.03); decom. $> 200^\circ C$. UV-Vis (λ_{max}): 221, 264, 332 and 552 nm. FT-IR (KBr, cm^{-1}): $\nu(NH)$ 3142 m, $\nu(CHO)$ 1728 s, $\nu(M-O)$ 412 m, $\nu(M-N)$ 507 m. $[Ni(L)_2Cl_2]$; C: 40.82 (54.47), H: 2.37 (3.33), N, 7.09 (6.67); Ni: 13.79 (13.99); decom. $> 200^\circ C$. UV-Vis (λ_{max}): 221, 263, 338 and 447 nm. FT-IR (KBr, cm^{-1}): $\nu(NH)$ 3140 m, $\nu(CHO)$ 1721 s, $\nu(M-O)$ 417 m, $\nu(M-N)$ 512 m.

Second step: Preperation of Coordination Polymers. A solution of poly(acryl amid) (4 mL, 0.001 molL) in water (25 mL) was added to a solution of metal-aldehyde complexes (0.006 mmolL) in methanol (25 mL). These solutions were stirred until viscous and the solution changed color, *ca* 4 d. After cooling, the complexes were washed repeatedly with a mixture of ether-methanol (1:1) and then dried *in vacuo* (over P_4O_{10}). The coordination polymers were colored, crystalline solids, soluble in water, DMSO and DMF (Table 1).

Elemental analyses of (PAA-SB) – complexes: found (calcd.) %: $Co(PAA-SB)$; C:51.98 (52.43), H: 4.37 (5.66), N, 16.51 (15.86), Co: 3.79 (4.77), Cl: 5.69 (5.74); UV-Vis (λ_{max}): 221, 264, 330, 337 and 672 nm. FT-IR (KBr, cm^{-1}): $\nu(NH)_{ring}$ 2939 m, $\nu(NH_2)_{asym}$ 3203 m, $\nu(NH_2)_{sym}$ 3426 m, $\nu(M-O)$ 448 m, $\nu(M-N)$ 521 m.

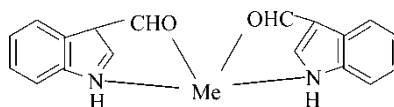


Figure 2. Reaction of metal-aldehyde complexes (Me: Ni(II), Co(II)).

Table 1
M_n, M_w and terminal unit of PAA-Schiff bases and their metal complexes

Abbreviation ^a M _n ; M _w , chemical formula	Heterojenic index	Main unit (a: ^a 6,10 n : 1) λ _M (ohm ⁻¹ cm ² mol ⁻¹)	Color Yield% μ _{eff} , BM
(PAA-SB) 6810; 7488, a: 6, n:12 [(C ₃ H ₅ ON) _a (C ₁₂ H ₁₀ ON ₂) _n]	1.1	^a [(C ₃ H ₅ ON) _a (C ₁₂ H ₁₀ ON ₂) _n [624] _n]	Yellow 63 4.2
Co(PAA-SB) 4360; 7415.4, a: 10, n:6 [(C ₃ H ₅ ON) _a (C ₂₄ H ₂₀ O ₂ N ₄ Co)] _n · 2nCl	1.7	[(C ₃ H ₅ ON) _a (C ₂₄ H ₂₀ O ₂ N ₄ Co)] _n · 2nCl [1235.9] _n 128	Deep blue 74 4.33
Ni(PAA-SB) 4120; 7414.2, a: 10, n: 6 [(C ₃ H ₅ ON) _a (C ₂₄ H ₂₀ O ₂ N ₄ Ni)] _n · 2nCl	1.8	[(C ₃ H ₅ ON) _a (C ₂₄ H ₂₀ O ₂ N ₄ Ni)] _n · 2nCl [1235.7] _n 125	Green 64 3.18

^aMeasurements are according to vapor pressure osmometer.

Ni(PAA-SB); C: 52.82 (52.43), H: 5.37 (5.66), N, 14.09 (15.86); Ni: 3.79 (4.77), Cl: 5.62 (5.74); UV-Vis (λ_{max}): 221, 263, 338 and 448 nm. FT-IR (KBr, cm⁻¹): ν(NH)_{ring} 2941 m, ν(NH₂)_{asym} 3206 m, ν(NH₂)_{sym} 3421 m, ν(M-O) 439 m, ν(M-N) 541 m.

Solid State Conductivity Measurements

Solid state electrical conductivities (σ) were measured with a Nippon NP-900 multimeter using a four-probe technique. The four-probe technique used for measuring the solid-state conductivity of pressed pellets was developed by van der Pauw (14). The pellets of the Schiff bases and the complexes were prepared at a loading of *ca.* 9 tons and thickness of *ca.* 0.04 cm.

Results and Discussion

PAA-Schiff bases and their metal complexes are prepared by a condensation reaction. Deviation from the theoretical values in the case of polymeric ligand may be due to the polymeric nature of the acryl amid. It is very well possible that the polydispersity of the ligand is not in a narrow range. The polymer-metal complexes were prepared from the reaction in PAA-Schiff bases with the corresponding metal salts also in methanol. The good solubility of metal complexes suggests their poly(acryl) amid nature in water and common organic solvents. Furthermore, the molar conductance values of the complexes were found to be 125–139.

Ω⁻¹cm² mol⁻¹ in a DMF solution (10⁻³ M), indicates the 1:2 electrolytic behavior, and suggests dissociations of main units according to the equilibrium (15).



The number average molecular weights (M_n) of the PAA-Schiff bases and their complexes were determined with a vapor pressure osmometer to be 6810, 4360, and 4120, respectively (PAA-SB), Co(PAA-SB) and Ni(PAA-SB). The number average and weight average molecular weights (M_w and M_n) of PAA-Schiff bases and polydispersity index (M_w/M_n) were given in Table 1. The polydispersity index of studied substances varied in the range of 1.01–1.80. These data clearly indicates that as metal (II) content in the main units increases, the molecular weight and polydispersity also increases.

Figure 3 was assumed for the polymeric-Schiff bases. Elemental analyses are consistent with a polymeric-Schiff base-to-metal ratio of 2:1 where $a = 10$ and $b = 1$. However, deviations from these values should be noted, and may be attributed to the polymeric nature of coordination polymers (16).

The assigned absorption bands are consistent with suggested structure polymeric-Schiff bases and their complexes. Bands in the region of $2937\text{--}2941\text{ cm}^{-1}$, $3202\text{--}3206\text{ cm}^{-1}$ and $3423\text{--}3426\text{ cm}^{-1}$ may be due to $\nu(\text{NH})$, $\nu(\text{NH}_2)_{\text{asym}}$ and $\nu(\text{NH}_2)_{\text{sym}}$ modes, respectively (17).

The observation of a medium new band at 1647 cm^{-1} may be attributed to the $\nu(\text{CH}=\text{N}-)$ stretching vibration (17). Bands appearing at 1515 cm^{-1} , 1255 cm^{-1} , and 485 cm^{-1} are assigned to $\nu(\text{CN}) + \delta(\text{NH})$, $\delta(\text{NH})$, and $\nu(\text{C}=\text{O})$ vibrations, respectively, for the polymeric-Schiff bases (17). These observations indicate that the aldehyde reacts with the polymer. On complexing, the $\nu(\text{CN}) + \delta(\text{NH})$, $\delta(\text{NH})$, and $\nu(\text{C}=\text{O})$ frequencies generally increase. Such frequency shifts, when compared to those of the

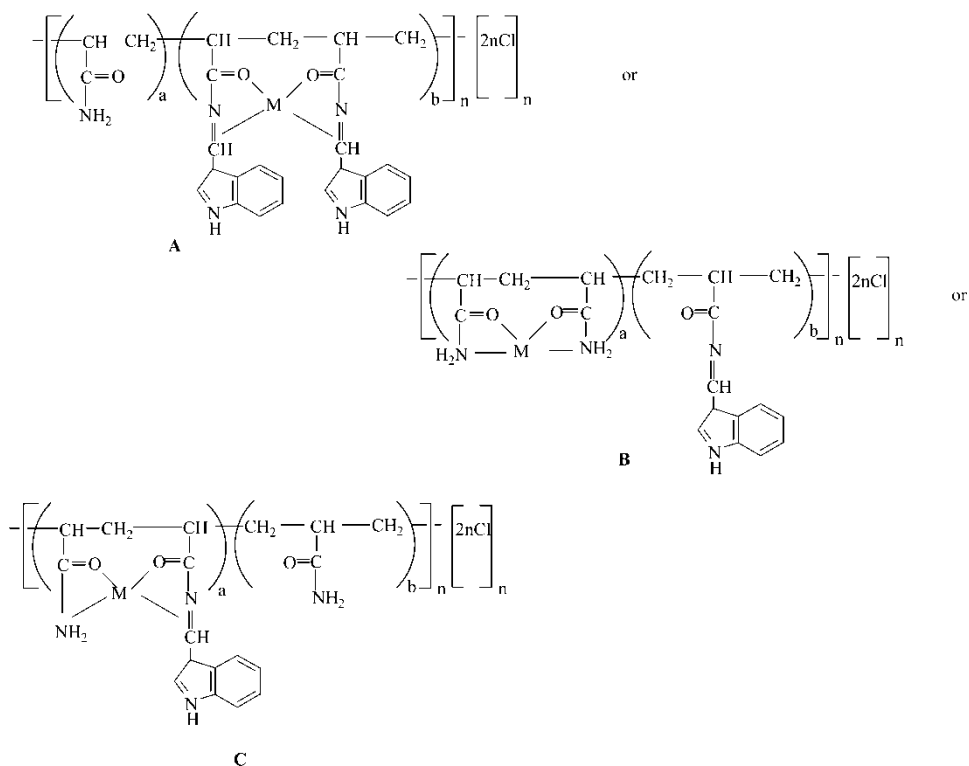


Figure 3. Suggestion structures for (PAA-SB)—metal (II) complexes.

polymeric-Schiff bases, may be attributed to coordination of the metal ion with the azomethine nitrogen and the imine oxygen of the carboxylate group. Furthermore, the appearance of new bands in the $410\text{--}420\text{ cm}^{-1}$ and $495\text{--}520\text{ cm}^{-1}$ can be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$, respectively (18, 19).

The $^1\text{H-NMR}$ spectra of the polymeric-Schiff bases exhibit three signals at 7.72 ppm, 7.62 ppm and 6.89 ppm, which are assigned to the $-\text{OH}$, $-\text{NH}$ and $-\text{NH}_2$ protons, respectively (Figure 4). The spectra strongly suggest that even in solution the keto and enol forms remain as two dominant species in polymeric-Schiff bases. Similar keto-enol tautomerism has been previously reported for other Schiff bases studies (20).

The $^1\text{H-NMR}$ spectra of the polymeric-Schiff bases exhibits a signals at 8.15 and 9.56 ppm due to the $-\text{NH}$ protons in indole ring and imine protons ($-\text{N}=\text{CH}-$), respectively. The ring proton signals appear at 7.92, 7.81, 6.68 and 6.28–6.45 ppm in the (PAA-SB). Most polydispersed polymers exhibit broad and multiple peaks in the NMR spectra (21). Multiple peaks are shown in (PAA-SB). Therefore, the δ values were reported in terms of data in the midpoint of multiple peaks. For (PAA-SB), signals at 3.68 ppm/3.52 ppm, 2.93/–2.67 and 2.44, 2.31 ppm are assigned to the $-\text{CH}/-\text{CH}_2$ of imine group and $-\text{CH}/-\text{CH}_2$ of keto and $-\text{CH}/-\text{CH}_2$ of enol group, respectively. These data strongly support the presence of keto and enol forms in polymeric-Schiff bases. Peak high (one unit) of imine proton ($-\text{CH}=\text{N}$) and total peak high (six unit) $-\text{CH}$ of keto-enol group were compared in the polymeric-Schiff base. From the $^1\text{H-NMR}$ spectrum it can be concluded that imine ($-\text{CH}=\text{N}-$)/acryl amid (keto group + enol group) can be 1/6 in the unit structure (Figure 4).

Since Co(II) complexes and Ni(II) complexes are paramagnetic, the $^1\text{H-NMR}$ spectra could not be obtained.

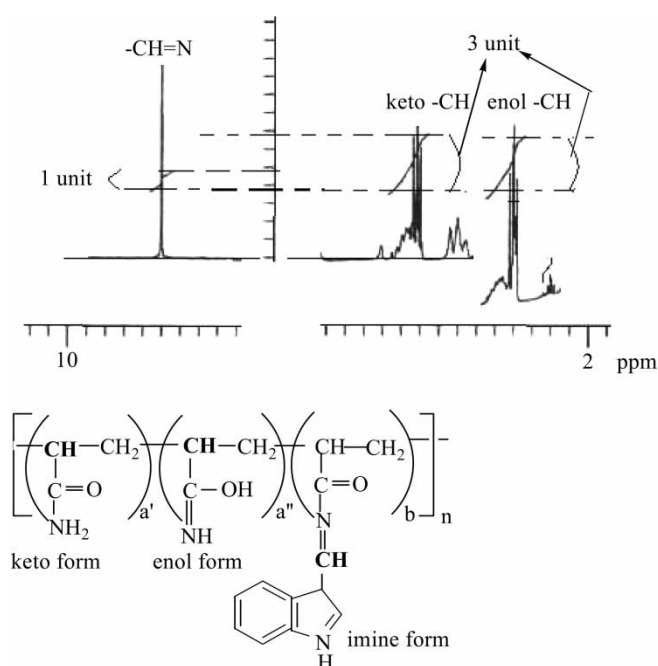


Figure 4. Evaluation of peak high in $^1\text{H-NMR}$ spectrum according to suggested unit.

In the ^{13}C -NMR spectra of the polymeric-Schiff base, a new peak appears at 165.01 ppm. This behavior can be due to a change in the chemical state of C atom in the $-\text{C}=\text{O}$ (carbonyl) in (PAA-SB). Furthermore, C atoms of the $-\text{CH}=\text{N}$ (imin) group are observed at 196.30 ppm in PAA-Schiff base. The ^{13}C -NMR spectra data of the poly-Schiff base is also in agreement with the proposed structures (Figure 4).

LC mass spectra for the given $[\text{M}]^+ 79.1$ ($m/z = \% 38$) and $[\text{M}]^+ 195.1$ ($m/z = \% 37$) for (PAA-SB), $[\text{M}]^+ 79.1$ ($m/z = \% 32$), $[\text{M}]^+ 195.1$ ($m/z = \% 21$) $[\text{M}]^+ 464.7$ ($m/z = \% 12$), for Co(PAA-SB); $[\text{M}]^+ 79.1$ ($m/z = \% 31$), $[\text{M}]^+ 195.1$ ($m/z = \% 19$) $[\text{M}]^+ 464.2$ ($m/z = \% 11$), for Ni(PAA-SB). These results indicate that (PAA-SB) and their complexes have been synthesized according to the suggested structure (Figure 5).

The electronic spectra of the (PAA-SB) in water were recorded in the range of 200–800 nm. The strong absorption bands which appeared in the range of 221 nm, 264 nm, and 230 nm are due to intra-ligand electronic transition. The magnetic moment 4.34 BM is commensurate with tetrahedral geometry about Co(II) in the complexes (22). Electronic spectra of Co(II) complexes shows a medium intense assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ (448 nm) transition for tetrahedral coordination about Cobalt(II). The magnetic moment 3.18 B. M is commensurate with octahedral geometry around Ni(II) ion (22, 23). Nickel(II) complexes show two d-d bands between 693 nm and 397 nm, indicating an octahedral structure.

Thermal Analyses

The thermal analysis data of the three studied substances are given in Table 2. (PAA-SB), Co(PAA-SB) and Ni(PAA-SB) are thermally stable up to 115, 60, and 55, respectively. Polymeric Schiff base is thermally decomposed in two steps. The first one is consistent with the loss (*ca* 10%) of imine in the 'b' group molecules in the temperature range *ca* 115–230°C. The second one occurs in a wide temperature range (235–600°C) and corresponds to decomposition of $-\text{[CH(CONH}_2\text{)-CH}_2\text{]}-$ 'a' group molecules due to the polydispersity. In the decomposition process of the Co(PAA-SB), and Ni(PAA-SB) the mass losses corresponded to Cl, imin group and organic moieties leaving in the first, second and third

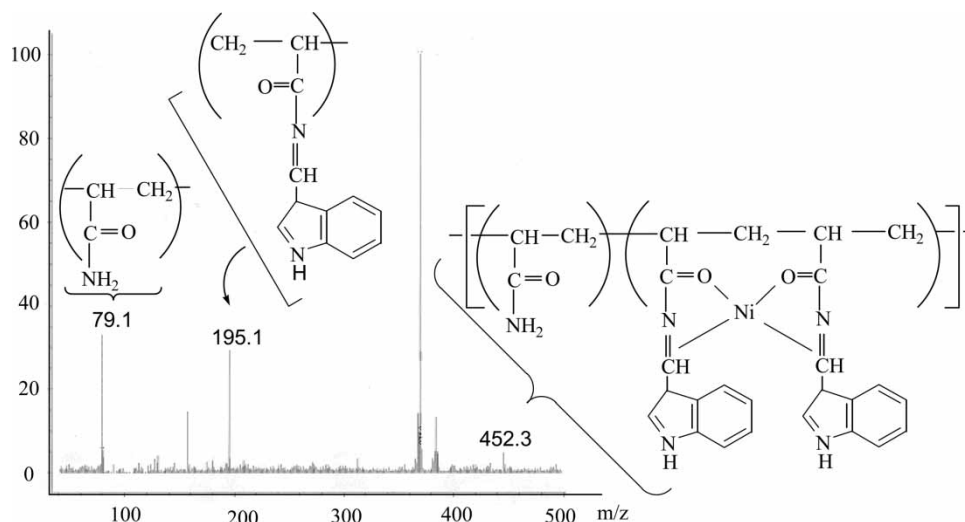


Figure 5. LC-MS spectrum for Ni(PAA-SB).

Table 2
Solid state conductivity measurements and thermal analysis data of the polymeric-Schiff base and it's complexes

Compound	σ (S cm ⁻¹) at 25 ± 0.1°C	Thermal analysis (°C)				NiO/CoO- carbon residue
		T _{start}	Weight loss 5%	Weight loss 16%	Weight loss 50%	
PAA	Nonconductivity					
(PAA-SB)	3.21 × 10 ⁻⁶	115	235, 9.7		330	18
Co(PAA-SB)	6.80 × 10 ⁻⁶	65	193	285	370	47
Ni(PAA-SB)	9.91 × 10 ⁻⁶	50	211	275	350	42

stages of the decomposition, respectively (24). In the first step, 5% weight loss was observed at 65°C and 50°C, respectively, Co(PAA-SB) and Ni(PAA-SB). This result shows that the polymer-complexes contain 12 mol Cl. The second step, 16% weight loss was observed in the temperature range 200–260°C due to loss of imin group with the aromatic ring.

The third step, the decomposition continued up to 310–600°C with weight loss corresponding to the loss of poly(acryl amid) group. The half degradation temperature of PAA-Schiff bases was higher than the complexes. There is no further weight loss beyond 600°C, which indicates thermo-oxidative degradation with the formation of stable NiO/CoO and carbon residue (Figure 6).

Solid State Conductivity Measurements

Solid state electrical conductivity of the studied compounds is given in Table 2. On the contrary, PAA is nonconductive, the complexes and polymeric-Schiff bases are

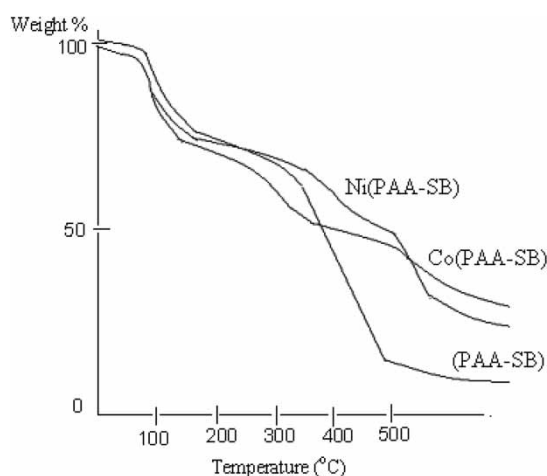


Figure 6. TG curves of (PAA-SB) and their complexes.

semiconductive. The conductivity range for semi-conducting materials is known to be 10^{-7} – 10^{-2} S cm⁻¹ (25). The conductivities of the (PAA-SB) is higher than the complexes. This may be ascribed to the conjugation length in the complexes arising from delocalization of π -electrons in the chelate ring. The conjugation length in the complexes may lead to higher conductivity (26). The conductivities of the nickel complexes are higher than the cobalt complexes. This may be ascribed to the conjugation ease in nickel complexes due to octahedral structure.

Conclusions

The first example of Schiff Bases Containing Poly(acryl amid) has been derived from the condensation reaction. Then, Ni(II) and Co(II) complexes of this PAA-Schiff bases have been synthesized. Chemical structures were investigated and solid state conductivities were compared. PAA do not conduct, but PAA-Schiff bases and their metal complexes have conductivity. This may be attributed to delocalization of π -electrons in the chelate ring. The conjugation length in complexes may lead to higher conductivity. So this study may be useful for various applications.

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