Synthesis and Properties of some Transition Metal Complexes with Water Soluble Hydroxy Functionalized Polyacrylonitrile

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A B S T R A C T

Polyacrylonitrile (PAN) was converted to polyacrylonitrile-monoethanolamine (PAN-MEA), through reaction with 2-aminoethanol (MEA) in a simple and one step method. The obtained polymer was hydrosoluble and hydroxy-functionalized. The polymer-metal complexes were prepared in an aqueous solution in different pHs via two different methods, namely precipitation and dialysis tube. In all cases, increasing the pH values raised metal sorption capacities of PAN-MEA. The maximum metal sorption capacity was obtained for Fe(III) at pH 3 with 100.7 mg and the minimum for Ni(II) at pH 2 with 22.34 mg per one gram PAN-MEA metal complex. The selectivity of polymer for the adsorption of Fe(III) is greater than that of Cu(II) in the mixture of these ions and in the mixture of Zn(II) and Ni(II) the adsorption is greater for Zn(II). FTIR Spectra of polymer-metal complexes showed wavenumber shifts due to metal complex formation. UV-Vis spectroscopy studies showed the presence of metal ions in polymer-metal complexes due to the absorption in the region between 400 nm to 800 nm. Also, thermal gravimetry analysis of polymer-metal complexes confirmed the presence of metal in the final polymer complexes.

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INTRODUCTION

Polymers with complexing properties have gained considerable importance due to their potential application in chemistry and technology. Besides investigations on the complexation of metal ions with insoluble polymers, recently a method for the application of polymeric complexing materials in homogeneous phase has been developed. In general, polymer metal ion complexation can be prepared either by derivatization of a basic polymer (precursor) with the desired ligand or by polymerization of the corresponding monomeric ligand derivative. Ligand polymerization embraces all classical methods of polyreaction. There are two criteria for developing functional polymers for the complexation of metal ions. First, the polymer back-

bone must be compatible with the complexation process, and second, the selective ligands must be found for certain metals and then bound to the polymer [1,2].

Polyacrylonitrile (PAN) as a precursor polymer is a commercially important polymer because of its unique and well-known properties including hardness and rigidity, chemical resistance, compatibility with certain polar substances, and low gas permeability [3].

The chemical modification of PAN has been the object of numerous studies and those investigating the use of amino compounds are of special interest since these modifications lead either to the improvement of the physico-mechanical properties of the polymeric materials or to the obtainment of polymers with new properties [4-7]. Functionalized polyacrylonitriles specially amine containing polyacrylonitriles are useful in the seperation, preconcentration, determination, recovery, and purification of a wide range of metal ions and humic acid adsorption [8-11]. Adsorption is one of the methods commonly used to remove heavy metal ions from various aqueous solutions with relatively low metal ion concentration that could be toxic and carcinogen.

In the present study, PAN was modified by 2-aminoethanol to obtain polyacrylonitrile-monoethanolamine (PAN-MEA), which is hydrosoluble and hydroxy-functionalized polymer. The polymer-metal complexes were prepared in an aqueous solution and in different pHs by precipitation and using dialysis tube. The polymer-metal complexes were characterized by UV-vis and FTIR spectroscopy and thermal gravimetry analysis (TGA). The complexing capacity of functional polymer was determined in relation to pH dependency for Cu^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+} using atomic absorption method.

EXPERIMENTAL

Materials and Instruments
Polyacrylonitrile (PAN) purchased from Polyacryl Co. (Isfahan), and monoethanolamine purchased (MEA) from Merck and used without purification. Dialysis tube was from Sigma (D-7884, 2000 molecular mass cut-off). FTIR Spectra were performed on a Unicum 4600 spectrometer (KBr pellets). UV-Vis spectra were recorded on a Shimadzu (UV-256F. W) spectrophotometer. TGA was performed using Dupont 651 US. The scanning rate of TGA was 10 centigrade per minute in air atmosphere. The metal absorption capacities of polymers were measured by atomic absorption spectrophotometer AA-3600A Shimadzu at room temperature in an aqueous solution.

Chemical Modification of PAN with MEA (PAN-MEA)
Functionalization of PAN was conducted by MEA according to Todorov et al. procedure (Figure 1) [12].

PAN (5.3 g, 0.1 mol) and MEA (48.9 g, 0.8 mol) were mixed in a three-necked flask (250 mL) equipped with stirrer, condenser, and thermometer. The reaction mixture was stirred in the heating bath (120°C). The initial dispersion was gradually transformed into a gel and then dissolved. The resulting clear, viscous solution indicates completion of the reaction, taking place within 60 min. The reaction product was cooled to room temperature, diluted with ethanol to the appearance of a light brown solution. The mixture was poured into the five-fold excess of acetone for the precipitation of the product. The precipitation was washed with Soxhlet using acetone. The light yellow powder was dried in vaccum at 60°C.
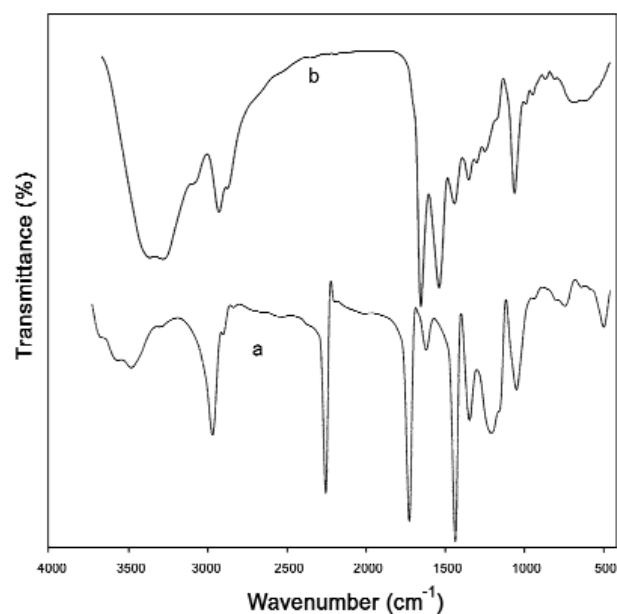

Figure 1. FTIR Spectra of: (a) PAN, and (b) PAN-MEA.

Preparation of Polymer-metal Complexes

Method A

A solution of 2 mmol metal salt (FeCl$_3$.6H$_2$O or CuCl$_2$.2H$_2$O) in 5 mL water was added to 200 mg PAN-MEA dissolved in minimum volume of water (about 5 mL). The pH of solution was adjusted at 1-4, and then the solution was poured into ethanol to obtain polymer-metal precipitation. Finally, the precipitate was collected using centrifuge and dried in vaccum.

To study selectivity, the complexation of PAN-MEA in the presence of two metal salts (equal mole of each metal ion), was performed at pH 3.

Method B

A solution of 2 mmol metal salt (NiCl$_2$.6H$_2$O or ZnCl$_2$) in 5 mL water was added to 200 mg PAN-MEA dissolved in minimum volume of water (about 5 mL). The pH of solution was adjusted at 2, 4 and 6. Then, the solution was located in dialysis tube (2000 molecular mass cut-off) for 24 h. Finally, it was dried in oven at 50ºC. The same method was applied to study the selectivity for equal molar mixture of two metal salts as mentioned above.

RESULTS AND DISCUSSION

PAN-MEA was prepared by a simple reaction between PAN and MEA at 120ºC for 1 h (Scheme I). FTIR Spectra of PAN and PAN-MEA as shown in Figure 1 indicate that the CN groups in PAN are omitted in PAN-MEA.

According to Todorov et al., the reaction temperature and mole ratio of MEA/PAN have important effects on the content of basic groups (expressed as amine index-mmol NH/g polymer) of prepared functional polymer (PAN-MEA). At the molar ratio MEA:AN= 2:1, a soluble polymer is not formed even after 20 h, which is probably due to cross-linking resulting in the formation of imide bridges between the polymer chains. The obtained maximum amine index is 0.91 mmol NH/g polymer at the molar ratio of 8:1, temperature of 120ºC and reaction time of 60 min [12].

PAN-MEA was brought into contact with aqueous solutions of metal ions such as Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} in the range of pH 1-6 via two different methods and their mixtures, respectively. The metal sorption capacities of PAN-MEA were measured with atomic absorption methods. The findings are shown in Tables 1 and 2.

In all cases, by increasing the pH values, the metal sorption capacities of PAN-MEA were raised. In high pH values, the protonation of ligand on the polymer backbone (especially in imine and amine groups) decreased, which led to a higher metal absorption. Metal sorption capacity of the prepared polymer in comparison with other water soluble complexing polymers was acceptable [2,13,14]. The maximum metal sorption was observed for Fe(III) at pH 3 by using method A. In the mixture of two metal ions (Fe^{3+} and Cu^{2+}), the metal sorption capacity of polymer to adsorb Fe(III) was higher than Cu(II).

The lowest metal content was observed for Ni(II) by dialysis tube. Moreover, using the mixture of two
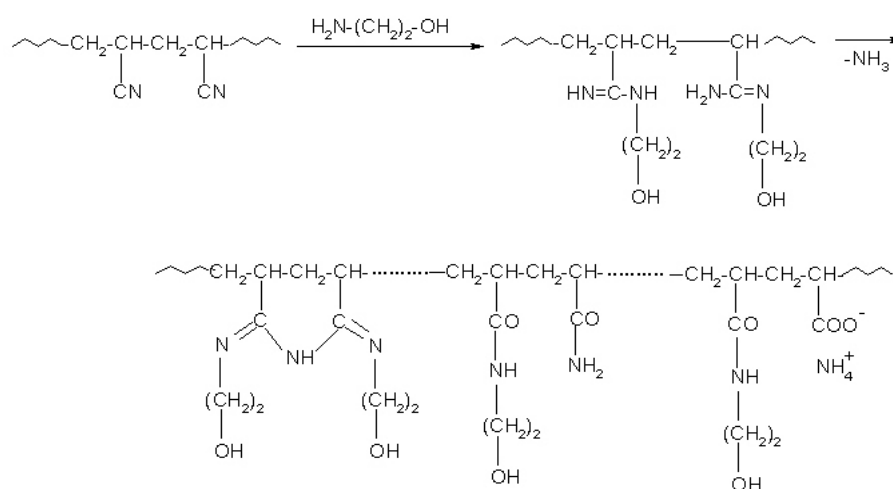
Scheme I. Preparation of PAN-MEA.

Table 1. Adsorption data of polymer-metal complexes prepared through method A.

Polymer	Metal salt	pH	Colour	Metal sorption capacity (mmol/g)	Metal sorption capacity (mg/g)
PAN-MEA-Cu	CuCl$_2$.2H$_2$O	3	Light green	0.51	32.47
		4	Green	1.3	82.55
PAN-MEA-Fe	FeCl$_3$.6H$_2$O	1	Light brown	0 .96	53.91
		2	Brown	1.31	73.48
		3	Dark brown	1.79	100.7
PAN-MEA-(Fe-Cu)	CuCl$_2$.2H$_2$O and FeCl$_3$.6H$_2$O	3	Dark brown	0.37(Fe)* 0.15(Cu)*	21.25(Fe)* 9.87(Cu)*

(*) Metal sorption capacity in the mixture of ions.

Table 2. Adsorption data of polymer-metal complexes prepared through method B.

Polymer	Metal salt	pH	Colour	Metal sorption capacity (mmol/g)	Metal sorption capacity (mg/g)
PAN-MEA-Ni	NiCl$_2$.6H$_2$O	2	Yellow	0.36	22.34
		4	Yellow-Green	0.71	41.83
		6	Yellow-Green	0.79	46.25
PAN-MEA-Zn	ZnCl$_2$	2	Light brown	0.85	55.27
		4	Yellow	1.01	66.1
		6	Yellow	1.06	69.76
PAN-MEA-(Ni-Zn)	NiCl$_2$.6H$_2$O and ZnCl$_2$	4	Yellow	(Ni)*0.30 (Zn)*0.57	(Ni)*18.02 (Zn)*37.31

(*) Metal sorption capacity in the mixture of ions.

metal ions, we observed that metal sorption capacity of polymer to adsorb Zn(II) is more than that of Ni(II).

Figures 2 and 3 illustrate the changes in metal sorption capacities based on mmol/g and mg/g versus pH. FTIR Spectra data of the metal complexed PAN-MEA in comparison with those of the non-complexed showed wavenumber shifts for absorption bands of C=O, C-O and C-N corresponding to polymer-metal complex formation (Table 3).

Absorption band in 1656 cm^{-1} for PAN-MEA corresponds to imine and amine, after complex formation shift to 1647 and 1638 cm^{-1} for Cu^{2+} and Fe^{3+}, respectively. With the sorption of metal on polymer, the new band appears at 1728 and 1798 cm^{-1} for polymer copper and iron complexes, respectively. A small shift was observed for C-O stretching band from 1065 cm^{-1} in parent PAN-MEA to 1063 cm^{-1} and

Table 3. FTIR Absorption signals (cm^{-1}) for PAN-MEA and its metal complexes in maxmum metal sorption (numbers represent pH in which maximum metal sorption was obtained).

Assignment	PAN-MEA	L-Cu 4	L-Fe 3	L-Ni 6	L-Zn 6
O-H, N-H	3286	3429	3413	3431	3407
C-H	2934	2935	2928	2930	2929
C=O amide, imine	1656	1647	1638	1647	1654
C-O	1253	1261	1262	1248	1250
C-N	1065	1063	1060	1060	1060

L= PAN-MEA
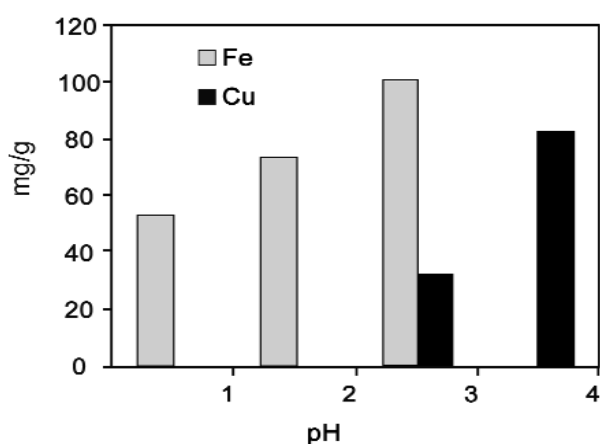
Figure 2. Metal sorption capacity of PAN-MEA for Fe(III) and Cu(II) in various pHs, prepared according to method A.

1060 cm^{-1} in copper and iron complexes, respectively (Figure 4).

For polymer-Ni^{2+} and Zn^{2+} complexes, it was
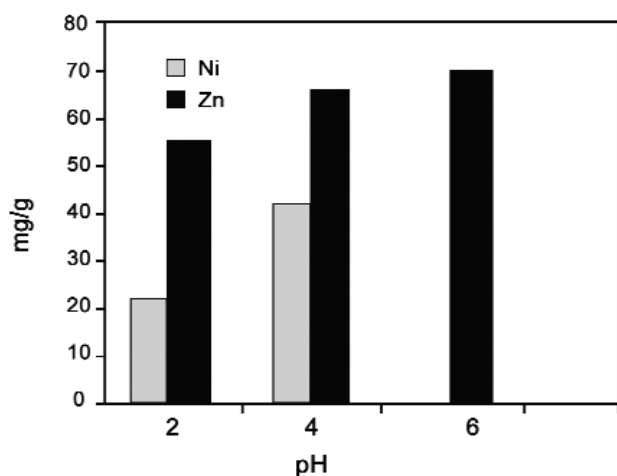
Figure 3. Metal sorption capacity of PAN-MEA for Ni(II) and Zn(II) in various pHs, prepared according to method B.

found that the wavenumbers shift from 1656 cm^{-1} to 1647 cm^{-1} and 1654 cm^{-1}, respectively. This shift increases with a decraese in pH. The same behaviour was observed for C-O stretching band, 1065 cm^{-1} shifts to 1060 cm^{-1} for two complexes (Figure 5).

On the other hand, in all cases, the new band appears at 1726-1798 cm^{-1}, corresponding to the hydrolysis of glutarimidine cycle to amide, if pH is decreased [15].

Figure 6 represents FTIR spectra of PAN-MEA-(Fe-Cu) prepared at pH 3. As expected, the presence of higher amount of Fe(III) in polymer complex compared to Cu(II) FTIR spectra reveals the same pattern as PAN-MEA-Fe. Also, due to the presence of more Zn in polymer complex, it was observed that FTIR
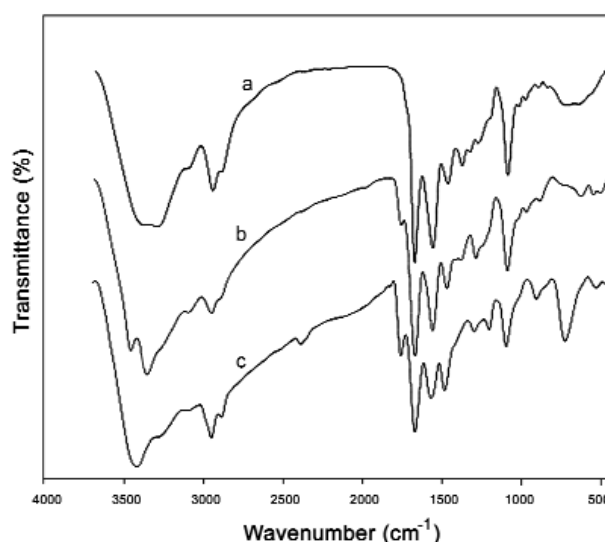
Figure 4. FTIR Spectra of: (a) PAN-MEA, (b) PAN-MEA-Cu 4, and (c) PAN-MEA-Fe 3 (numbers represent pH in which maximum metal sorption was obtained).
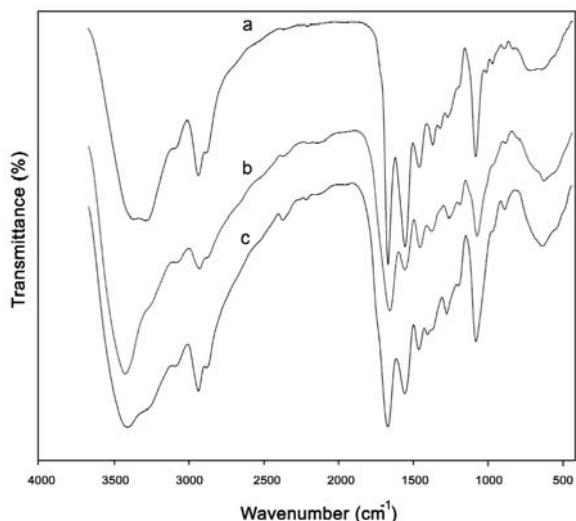
Figure 5. FTIR Spectra of: (a) PAN-MEA, (b) PAN-MEA-Zn 6, and (c) PAN-MEA-Ni 6 (numbers represent pH in which maximum metal sorption was obtained).
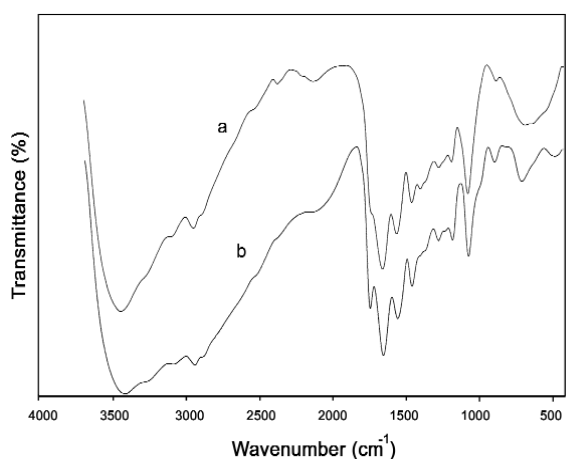

Figure 6. FTIR Spectra of: (a) PAN-MEA-(Fe-Cu) 3, and (b) PAN-MEA-(Zn-Ni) 4 (numbers represent pH in which maximum metal sorption was obtained).

spectrum of PAN-MEA-(Ni-Zn) is similar to that of PAN-MEA-Zn.

Thermal Gravimetry Analysis

For comparison, TGA curves of PAN-MEA and its complexes with maximum metal sorption are shown in Figures 7 and 8. With an increase in metal content in polymer, the final decomposed residue increases as well. For polymer-Fe complex prepared at pH 3 with the highest metal content, the amount of residue is higher than others. However, for polymer-Ni complex

is low. A slow mass reduction was observed for Cu and Fe complexes which have high metal content. On the other hand, thermal behaviour of Cu and Ni complexes are similar to the parent polymer until 550°C. Considerable mass reduction was observed for Zn complex over 600°C. As reported in Table 4, the comparison of TGA data of Fe complexes at pHs 1 and 3 proves that the existence of more Fe in the complex
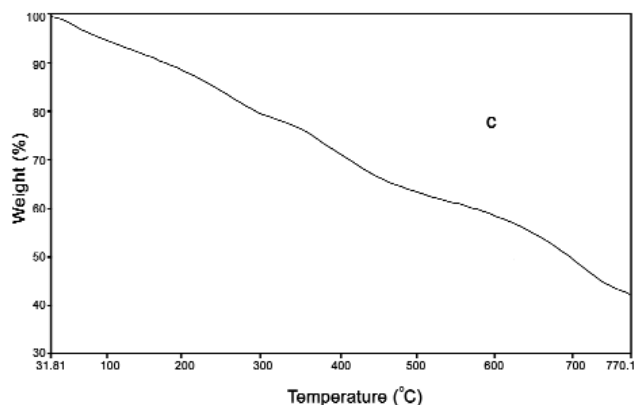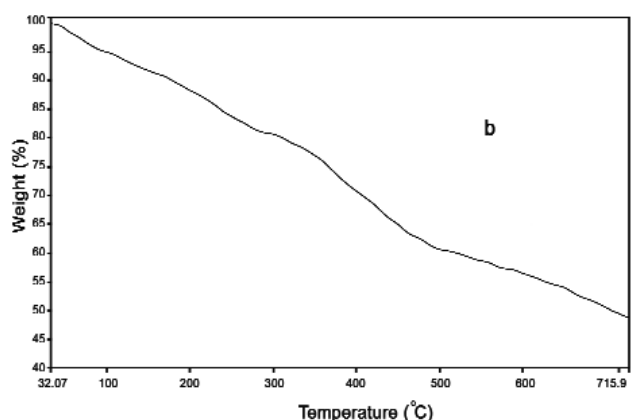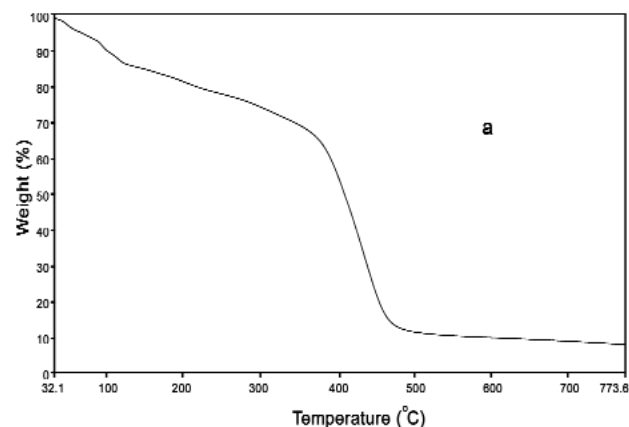

Figure 7. TGA Curves of: (a) PAN-MEA, (b) PAN-MEA-Fe 1, and (c) PAN-MEA-Fe 3 (numbers represent pH in which maximum metal sorption was obtained).
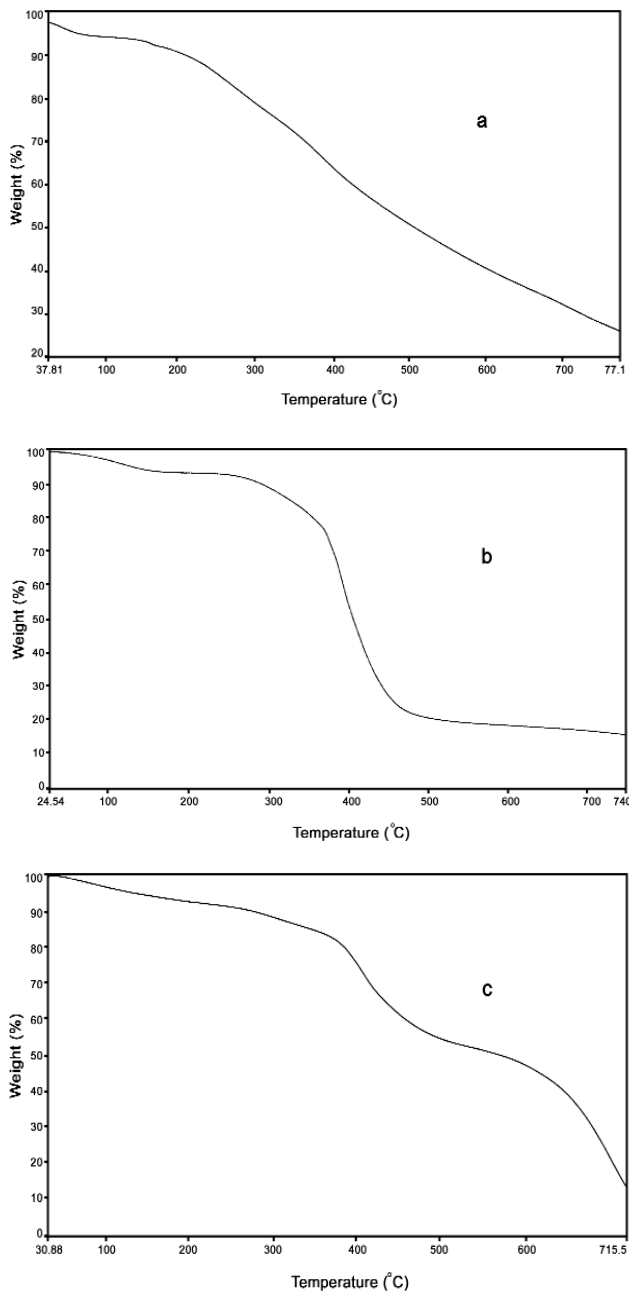
Figure 8. TGA Curves of: (a) PAN-MEA-Cu 4, (b) PAN-MEA-Ni 6, and (c) PAN-MEA-Zn 6 (numbers represent pH in which maximum metal sorption was obtained).

increases the thermal resistance of decomposed residue over 550°C.

UV-Vis Studies

The same UV-Vis spectrum pattern was observed for all polymers and metal-polymer complexes with maximum metal sorption (Figure 9). Maximum absorptions were obtained at 264 nm (λ_{max1}) and
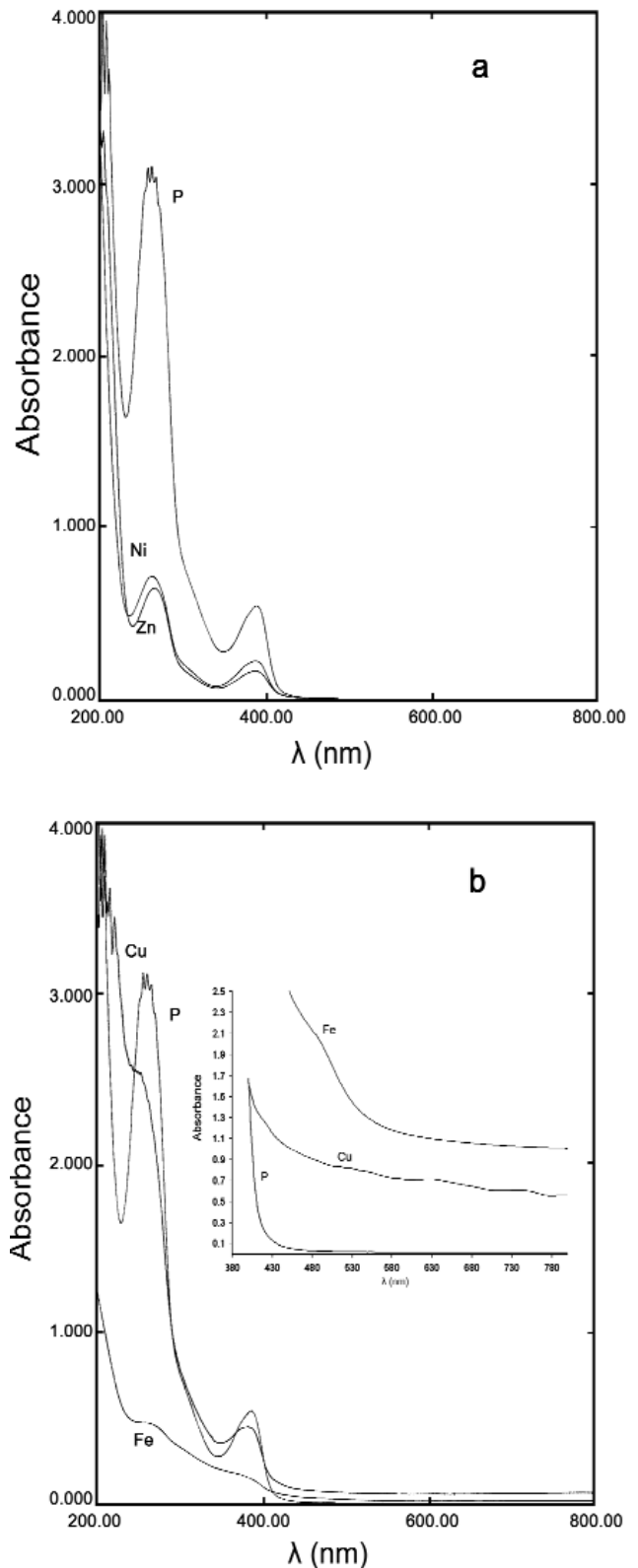

Figure 9. UV-Vis spectra of: (a) PAN-MEA, PAN-MEA-Zn 6, and PAN-MEA-Ni 6, and (b) PAN-MEA, PAN-MEA-Fe 3, and PAN-MEA-Cu 4 (numbers represent pH in which maximum metal sorption was obtained).

Table 4. TGA Analysis data for functionalized polymer and its metal complexes.

Products*	Reduced mass (wt%) of products at different tempreatures (ºC)													
Temperature (ºC)	100	150	200	250	300	350	400	450	500	550	600	650	700	750
PAN-MEA	10	15.1	19.8	22.4	25.7	28.3	44.2	78.5	89.1	91.1	91.1	91.1	91.1	-
PAN-MEA-Fe 1	2.8	7.6	11.2	15.6	19.2	22.8	29.6	36	41.2	43.2	45.6	49.2	52.4	-
PAN-MEA-Fe 3	4.1	7.6	10.3	14.4	19.3	22.9	27.4	32.4	36.4	39.6	42.3	46.8	52.2	56.7
PAN-MEA-Cu 4	5.2	6.8	8.8	13.1	19.7	27.5	35.8	44.2	51.4	57.7	63.4	68.1	71.7	72.8
PAN-MEA-Ni 6	2.6	5.9	7.2	10.5	15.1	43.5	73.9	78.5	79.8	81.1	81.2	82.5	83.1	-
PAN-MEA-Zn 6	2.6	5.2	7.2	9.9	11.8	15.1	24.4	39.6	47.5	50.8	56.1	63.3	81.8	-

* Numbers represent pH in which maximum metal sorption was obtained.

392 nm (λ_{max2}) that corrospond to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. The reduction in the ratio of absorption at λ_{max1} to absorption at λ_{max2} from polymer to metal-polymer complexes shows the presence of metals in polymer complexes. It also indicates that an increase in metal content in the case of Fe(III) and Cu(II) deforms the maximum peaks more than other complexes. Also, Figure 9b shows absorptions of PAN-MEA, PAN-MEA-Fe and PAN-MEA-Cu in concentrated solution at visible region. As it is observed, the presence of metal in polymer shows an absorption at 480 nm and 630 nm for Fe and Cu containing polymer, respectively.

CONCLUSION

By means of a simple and one step method, polyacrylonitrile was functionalized by monoethanolamine. The prepared functionalized polymer has good solubility in water and common solvents. Polymer-metal complex was prepared by the use of two different methods in an aqueous solution containing metal ions and in a defined pH. The highest metal content was obtained for Fe-polymer complex prepared by the precipitation method while the lowest metal content was observed for Ni-polymer complex prepared by dialysis tube. The results showed that changes in pH value affected the metal sorption capacity. FTIR and UV-Vis spectroscopies and TGA confirmed the presence of metal in final polymer-metal complexes. The present

study shows that the selectivity of polymer for the adsorption of Fe(III) and Zn(II) are greater than that of Cu(II) and Ni(II).

ACKNOWLEDGEMENT

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