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Synthesis and Characterization of EDTA Functionalized Polyacrylonitriles and Their Metal Complexes

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ABSTRACT

Novel ethylenediaminetetraacetic acid (EDTA) functionalized polyacrylonitriles (PANs) were synthesized by direct reaction of ethylenediaminetetraacetic acid dianhydride (A-EDTA) with amine and hydroxyl functionalized polyacrylonitrile. The polymeric products were insoluble in water and common organic solvents and the maximum EDTA functionality was 3.2 mmol/g. The polymer-metal complexes were prepared by dispersing of the EDTA functionalized PANs in aqueous solutions of various metal ions such as Cu^{+2}, Ni^{+2}, Co^{+2}, and Cr^{+3} when the pH ranged from 1 to 5. The highest and lowest metal sorption were observed for Ni^{+2} in pH 5 and Co^{+2} in pH 1 which were 5.2 mmol/g and 1.5 mmol/g, respectively. The SEM micrographs show that there is a drastic variation in morphology of polymer surface when it forms complex with Cu^{+2}. It change from rougher surface to smoother surface.

Key Words:
functional polymer;
metal complex;
EDTA;
polyacrylonitrile.

INTRODUCTION

In recent years, preparation of polymer materials either soluble or insoluble in water with various functional groups has been developed, which can adsorb metal ions in aqueous and non-aqueous media. In general, functionalized polymers for metal ion complexation can be prepared either by derivation of a basic polymer (precursor) with the desired ligand or by polymerization of the corresponding ligand derivative [1-4].

Among functionalized polymers, those containing EDTA have attract-

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ed much attention. EDTA with aminocarboxylic acid groups can be introduced into or graft onto the backbone of polymer chains. Polymers bearing such groups have stable complexes with various heavy metal ions [5-10]. Therefore, we attempted to prepare new complexing polymer materials, which can be used in wastewater treatment.

In this work, polyacrylonitrile (PAN) was reacted with ethylenediamine (EDA) or monoethanolamine (MEA) initially, to obtain amine and hydroxyl functionalized polyacrylonitriles, PAN-EDA and PAN-MEA, respectively [11,12].

For the first time, functionalized polyacrylonitriles containing both carboxyl and amine groups were synthesized by reaction between PAN-EDA or PAN-MEA and ethylenediaminetetraacetic acid dianhydride (A-EDTA) to prepare EDTA functionalized polyacrylonitriles (PAN-EDA-EDTA and PAN-MEA-EDTA).

EDTA Functionalized polyacrylonitriles were dispersed in aqueous solutions of various metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} and their metal sorption capacities were measured by gravimetry, UV-Vis spectroscopy and atomic absorption techniques.

The prepared functionalized polymers and their metal complexes were characterized by FTIR spectroscopy, elemental and thermal analysis and electron scanning microscopy.

EXPERIMENTAL

Materials

Polyacrylonitrile was provided by Polyacryl Co. (Isfahan-Iran) with a moleculare weight of 60000 $g.mol^{-1}$ (15% acrylic acid, based on elemental analysis data). Ethylenediamine (EDA) and monoethanolamine (MEA) were purchased from Merck and used without purification. Ethylenediaminetetraacetic acid dianhydride (A-EDTA) was prepared according to method in literature [8,10]. Copper (II) nitrate [$Cu(NO_3)_2.6H_2O$], nickel (II) nitrate [$Ni(NO_3)_2.6H_2O$], cobalt (II) nitrate [$Co(NO_3)_2.6H_2O$] and chromium (III) nitrate [$Cr(NO_3)_3.3H_2O$] were provided by Fluka and were used directly. DMF and other solvents were purchased from Merck or Fluka and purified according to standard procedures.

Instruments

Elemental analysis of the polymers was carried out using a Heraeus instrument. The infrared spectra (4000-500 cm^{-1}) were obtained from Unicam 4600 spectrophotometer by using KBr pellets. The metal absorption capacities of polymers were measured by a AA-670 Shimadzu atomic absorption spectrometer and Shimadzu-120 (UV-Vis) spectrophotometer at room temperature in aqueous solution. The thermal stability of polymers was studied by a Dupont TGA-951 US thermogravimeter. The electron micrographs were obtained by using a scanning electron microscope LEO.

Preparation of EDA and MEA Containing Polyacrylonitriles

EDA and MEA containing polyacrylonitriles were prepared according to Todorov et al. procedures as follows [11,12]:

PAN (2.65g, 0.05mol) and EDA (17 mL, 0.28 mol) or MEA (24.7 mL, 0.42 mol) were mixed in a 100 mL round-bottom flask equipped with stirrer and condenser. The reaction mixture was stirred continuously at 120°C for 2 h in a heating bath. The initial dispersion was gradually changed into a gel and further became considerably more viscous. Heterogeneous mixture with yellow colour was obtained for EDA and homogeneous, red brown colour mixture obtained for MEA. The reaction mixture was cooled to room temperature and was mixed with five-fold acetone. The precipitate was filtered, washed with acetone and dried in vacuum at 60°C.

The yields of PAN-EDA and PAN-MEA were 3.70 g and 3.32 g, respectively. Amine and hydroxyl functionality of PAN-EDA and PAN-MEA were measured by gravimetry analysis and gave 6.0 and 3.7 mmol/g, respectively.

Table 1. Experimental conditions for preparing EDTA containing polyacrylonitriles: reaction temperature 70-80°C, reaction time 24 h.

Polymer	PAN-EDA (g)	PAN-MEA (g)	A-EDTA (g.mmol)	DMF (mL)	Yield (g)	EDTA (mmol/g)
PAN-EDA-EDTA	0.650	-	1.5, 5.86	25	1.20	3.2
PAN-MEA-EDTA	-	0.325	0.55, 2.15	30	0.74	2.4

Table 2. Elemental analysis of functionalized polymers.

Polymer	Elemental analysis (%)			
		C	H	N
PAN	Calcd	64.80	5.61	21.39
	Found	65.34	5.46	21.75
PAN-EDA	Calcd	59.16	7.60	23.22
	Found	58.31	7.33	23.68
PAN-EDA-EDTA	Calcd	53.23	7.49	17.81
	Found	52.14	7.01	17.98
PAN-MEA	Calcd	56.21	9.42	16.81
	Found	54.82	8.53	15.21
PAN-MEA-EDTA	Calcd	50.36	7.67	13.41
	Found	49.93	7.00	12.09

PAN polyacrylonitrile with 15 mole percent acrylic acid units; PAN-EDA functionalized PAN with ethylenediamine (30 mole percent reacted nitrile groups); PAN-EDA-EDTA functionalized PAN-EDA with EDTA (54 mole percent reacted amine groups); PAN-MEA functionalized PAN with monoethanolamine (58 mole percent reacted nitrile groups); PAN-MEA-EDTA functionalized PAN-MEA with EDTA (66 mole percent reacted hydroxyl groups).

Preparation of EDTA Containing Polyacrylonitriles

In a 100-mL round bottom flask equipped with stirrer and condenser, a defined amount of PAN-EDA or PAN-MEA was dispersed in a clear solution of A-EDTA in DMF.

Reaction mixture was stirred continuously at 70-80°C in a heating bath under argon atmosphere for 24 h. The reaction mixture was cooled to room temperature and then mixed with 500-mL of water. The precipitate was filtered, washed with water and then with methanol and finally dried in vacuum at 60°C. The experimental conditions for preparing EDTA containing polyacrylonitriles (PAN-EDA-EDTA and PAN-MEA-EDTA) are presented in Table 1.

Preparation of Metal-polymer Complexes

The complexation of PAN-EDA-EDTA and PAN-MEA-EDTA was carried out with Cu^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} ions by batch equilibration method. The functionalized polymer (100 mg) was stirred with definite rate of excess metal salt for 30 min. The solution pH was set at 1, 3, and 5. After being left overnight the pH solution was set again. The metal-polymer complexes were collected by filtration, washed with aqueous solution at the same pH to remove non-complexed metal ions. The collected precipitates were dried at 60°C in vacuum.

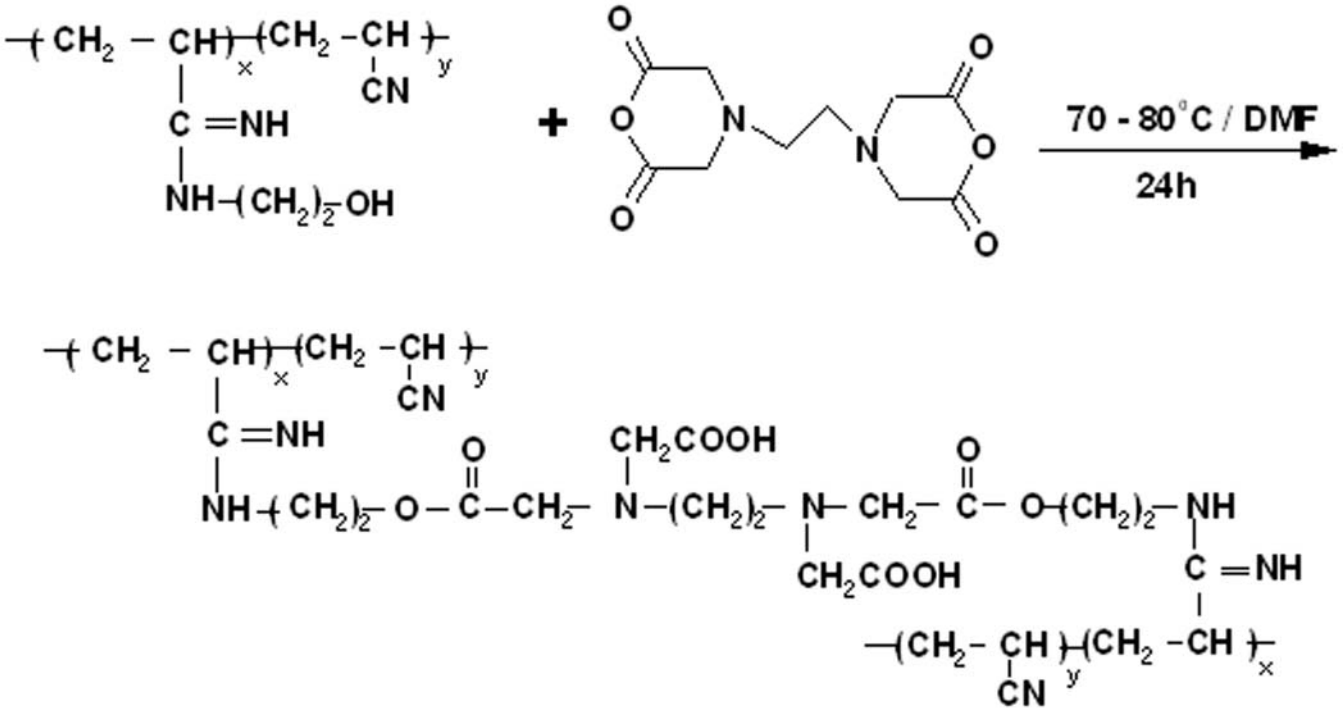
RESULTS AND DISCUSSION

The interaction of amine or hydroxyl functionalized

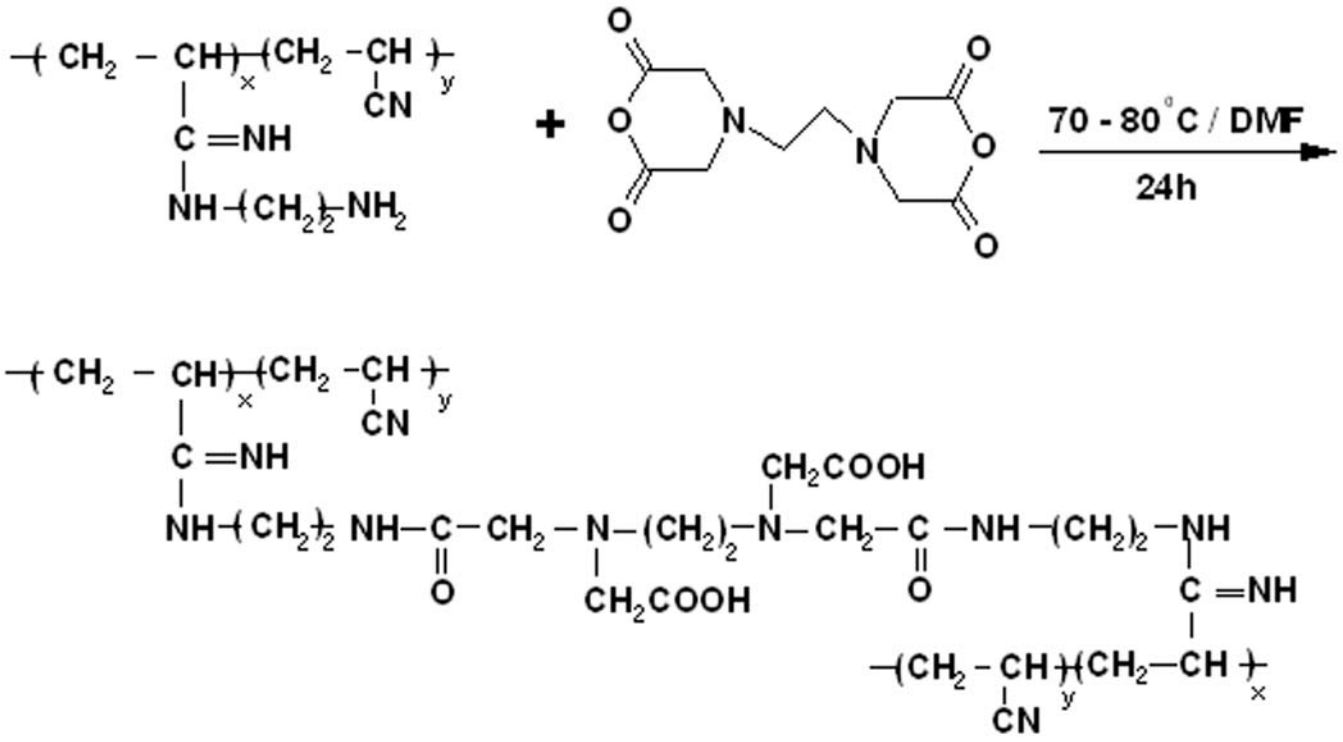
Table 3. Results and experimental conditions for preparation of metal-polymer complexes based on PAN-EDA-EDTA: metal salt (3 mmol) and polymer (100 mg).

Polymer complex	Metal salt (mg)	pH	Metal sorption capacity		Colour
			(mg/g)	(mmol/g)	
L-Cu	$Cu(NO_3)_2.6H_2O$	5	279.4	4.4	Dark blue
	724	3	209.5	3.3	Blue
		1	190.5	3.0	Light blue
L-Ni	$Ni(NO_3)_2.6H_2O$	5	305.2	5.2	Dark green
	973	3	164.4	2.8	Green
		1	123.3	2.1	Light green
L-Co	$Co(NO_3)_2.3H_2O$	5	223.8	3.8	Dark Orange
	974	3	170.8	2.9	Orange
		1	141.4	2.4	Light orange
L-Cr	$Cr(NO_3)_2.3H_2O$	5	260.0	5.0	Black
	1200	3	176.8	3.4	Brown
		1	124.8	2.4	Light brown

L: PAN-EDA-EDTA



PAN-MEA-EDTA



PAN-EDA-EDTA

Scheme I

PAN with A-EDTA and process conditions are illustrated in Scheme I. The new functionalized polymers were insoluble in water and common organic solvents, therefore, the formation of a cross-linking structure was more probable. The EDTA functionality for PAN-EDA-EDTA and PAN-MEA-EDTA were also obtained 3.2 mmol/g and 2.4 mmol/g, respectively.

Elemental analysis of the resulting polymers were listed in Table 2. The calculated elemental analysis values based on obtained mass increased in the final product and showed non-reacted amines and hydroxyls present in polymers obtained.

EDTA functionalized polyacrylonitriles were mixed with aqueous solutions of metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} in pH values of 1, 3, and 5. The metal sorption capacities of functionalized poly-

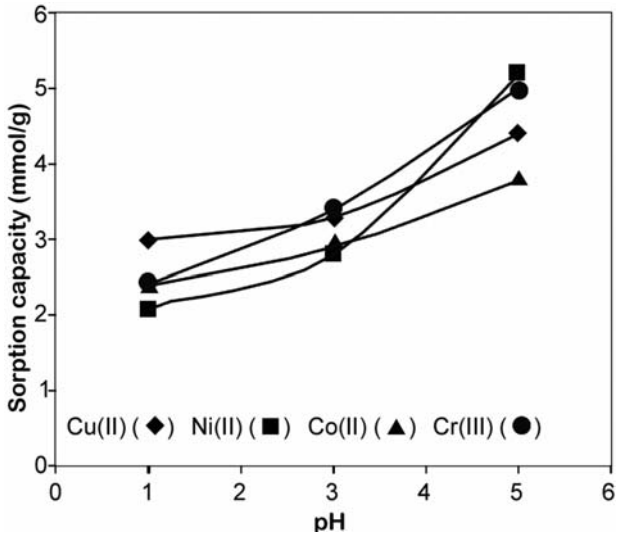


Figure 1. Metal sorption capacity (mmol/g) of PAN-EDA-EDTA versus pH for various metal ions.

Table 4. Results and experimental conditions for preparation of metal-polymer complexes based on L PAN-MEA-EDTA: metal salts (2 mmol) and polymer (100 mg).

Polymer complex	Metal salt (mg)	pH	Metal sorption capacity		Colour
			(mg/g)	(mmol/g)	
L´-Cu	$Cu(NO_3)_2.6H_2O$	5	203.2	3.2	Dark blue
	(460)	3	133.4	2.1	Blue
L´-Ni	$Ni(NO_3)_2.6H_2O$	5	105.7	1.8	Dark green
	(570)	3	88.1	1.5	Light green
L´-Co	$Co(NO_3)_2.3H_2O$	5	88.4	1.5	Dark orange
	(590)	3	94.2	1.6	Light orange
L´-Cr	$Cr(NO_3)_2.3H_2O$	5	135.2	2.6	Black
	(760)	3	119.6	2.3	Brown

L′ = PAN-MEA-EDTA

Table 5. FTIR Absorption signals (cm^{-1}) for PAN-MEA-EDTA, PAN-EDA-EDTA, and its metal complexes.

Assignment	PAN-MEA-EDTA	PAN-EDA-EDTA	L-Cu	L-Co	L-Ni	L-Cr
O-H, N-H	3508	3448	3462	3531	3447	3462
C-H	2930	2933	2945	2931	2948	2930
CN(nitrile)	2250 vw	2251	2251	2251	2251	2251
C=O ester,amide, imine,	1749	1680 b	1690	1688	1688	1690
carboxylic acid	1657	-	1618	1616	1616	1626
C-O	1179	-	1325	1294	1358	1294
C-N	1055	1140	1135	1125	1125	1125
N-H out-of-plane	-	864 vw	831	815	831	828

L= PAN-EDA-EDTA, vw= very weak , b= broad.

Table 6. TGA Results for PAN-EDA-EDTA and its copper complex (PAN-EDA-EDTA-Cu, prepared at pH 5).

Temperature (°C)	PAN remained (wt%)	PAN-EDA remained (wt%)	PAN-EDA-EDTA remained (wt%)	PAN-EDA-EDTA-Cu remained (wt%)
50	100	99	98	99
100	100	97	93	95
150	99	96	91	93
200	99	91	90	92
250	99	71	81	87
300	98	27	73	81
350	88	26	70	73
400	80	25	66	59
450	72	24	62	50
500	67	23	57	48
550	65	22	39	47
600	62	21	23	46
650	60	20	9	45
700	56	20	5	38

acrylonitriles were measured by gravimetery analysis, UV-Vis spectroscopy and atomic absorption techniques. Some results and preparation conditions of metal-polymer complexes are presented in Tables 3 and 4.

The highest and lowest metal sorption obtained for Ni^{2+} in pH 5 and Co^{2+} in pH 1, which was proximately 5.2 mmol/g and 1.5 mmol/g, respectively. The change of the sorption capacity (mmol/g) of PAN-EDA-EDTA for various metal ions over a range of pH (1-5) is shown in Figure 1. All the metal-polymer complexes are intensely coloured solids.

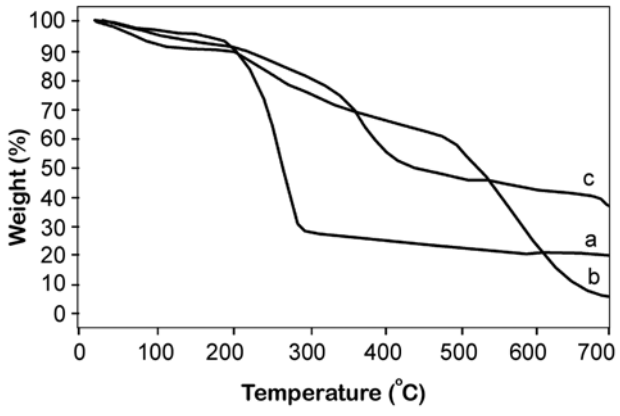
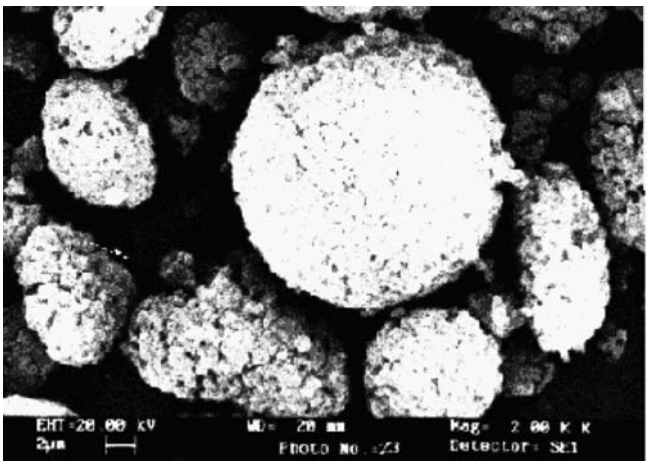


Figure 2. TGA curves for PAN-EDA (a), PAN-EDA-EDTA (b) and PAN-EDA-EDTA-Cu (c), prepared at pH 5.

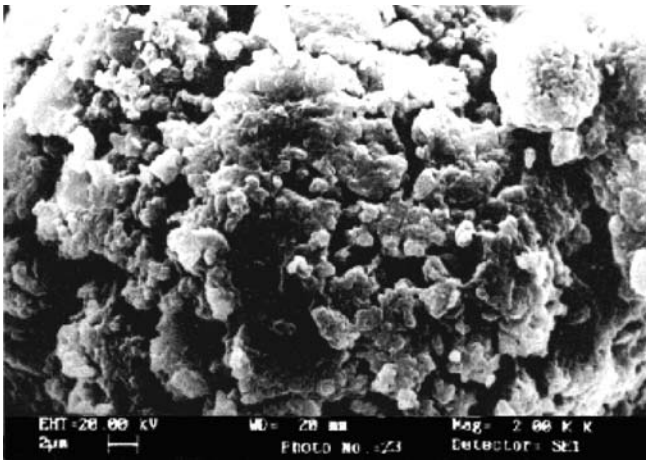
The FTIR spectra data of the complexed PAN-EDA-EDTA in comparison with those of the non-complexed gave some information about the bonding site of the polymer-metal ions (Table 5).

Thermal gravimetry analysis (TGA) of PAN-EDA, PAN-EDA-EDTA and its copper complex (prepared at pH 5) are shown in Figure 2. It was observed that PAN-EDA over 200°C has very strong mass decrease in comparison with PAN-EDA-EDTA and its copper complex. The weight loss pattern of PAN-EDA-EDTA and its complex up to about 360°C was aproximately the same, but between 360°C and 560°C metal-polymer complex decomposed stronger than the non-complex polymer. There remained mass of PAN-EDA-EDTA-Cu (45-50 wt%) at 700°C corresponds to the formation of cupper oxide. Also, the TGA results of PAN, PAN-EDA, PAN-EDA-EDTA and its copper complex (PAN-EDA-EDTA-Cu) are presented in Table 6.

The scanning electron micrographs of the PAN, PAN-EDA, PAN-EDA-EDTA and its copper complexes (prepared in pH 3 and pH 5) show that there is a strong change in morphology of polymer surface from PAN-EDA to PAN-EDA-EDTA. PAN-EDA-EDTA beads in comparison with its copper complexes (PAN-



(a)



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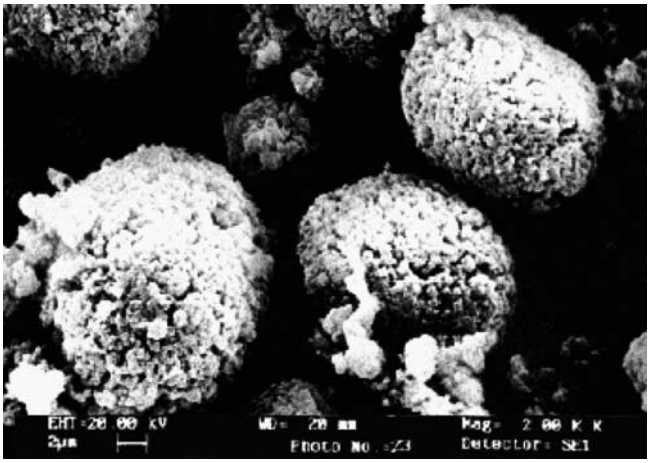
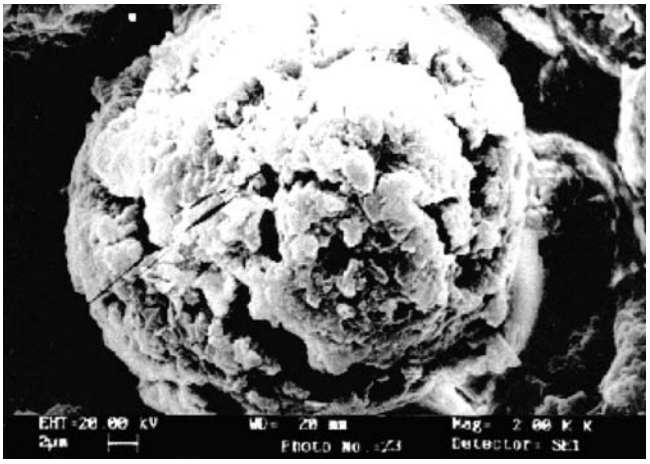
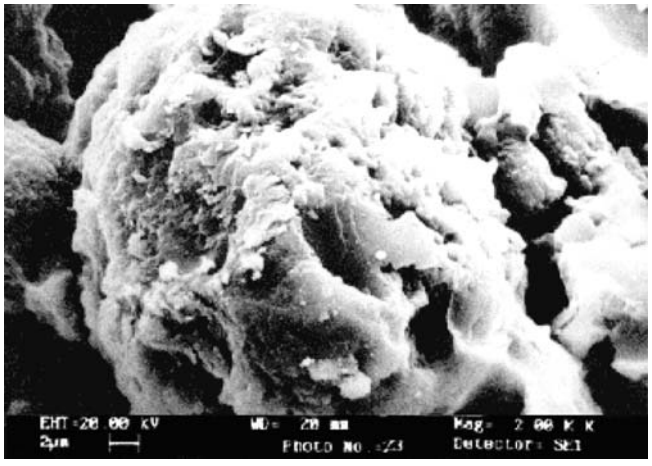


(b)



(d)



(e)

Figure 3. SEM Images of PAN (a), PAN-EDA (b), PAN-EDA-EDTA (c), and PAN-EDA-EDTA-Cu prepared at pH 3 (d) and pH 5 (e).

EDA-EDTA-Cu) had rougher surface and it was observed that the presence of more copper ions in the polymer causes the surface smoother (Figure 3).

CONCLUSION

Two novel EDTA-containing polymers based on polyacrylonitrile (PAN) were prepared by reaction of EDTA-dianhydride with ethylenediamine containing PAN or monoethanolamine containing PAN.

Functionalized polyacrylonitriles by EDTA formed complexes with Cu^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+}. All the complexes showed a change of the chemical shift in FTIR spectra due to the metal ion complexing with the EDTA-containing polymer.

Thermal gravimetry study on copper-polymer complex showed the presence of metal in final polymer and SEM images possessed a smooth surface for copper polymer complex in comparison to the non-complexed polymer. EDTA containing polymer showed excellent sorption for various metal ions.

REFERENCES

1. Sahni S.K., Reedijk J., Coordination chemistry of chelating resins and ion exchangers, *J. Coord. Chem. Rev.*, **59**, 1-139 (1984).
2. Warshawsky A., Polymeric ligands in hydrometallurgy. In: *Syntheses and Separations using Functional Polymers*, Sherington D.C. and Hodge P. (Eds.), John Wiley, Chichester, 325-332 (1988).
3. Geckeler K.E., Metal Complexation Polymers. In: *The Polymeric Materials Encyclopedia*, Salamon J.C. (Ed.), CRC, Boca Raton, **6**, 4101 (1996).
4. Beauvais R.A., Alexandratos S.D., Polymer-supported reagents for the selective complexation of metal ions: An overview, *React. Func. Polym.*, **36**, 113-123 (1998).
5. Kahovec J., Matejka Z., Stamberg J., EDTA ester of bead cellulose a fast-kinetics chelating sorbent, *Polym. Bull.*, **3**, 13-17 (1980).
6. Maeda S., Tsurusaki Y., Tachiyama Y., Naka K., Ohki A., Ohgushi T., Takeshita T., Synthesis and properties of superconductors prepared from ethylenediaminetetraacetic acid (EDTA)-ethylenediamine (ED) polyamide YBC chelate, *J. Polym. Sci. Part A: Polym. Chem.*, **32**, 1729-1738 (1994).
7. Montembault V., Soutif J.-C., Brosse J.-C., Synthesis of chelating molecules as agents for magnetic resonance imaging, 3. Polycondensation of diethylenetriaminepentaacetic acid bisanhydride with diols and diamines, *React. Func. Polym.*, **29**, 29-39 (1996).
8. Tuelue M., Geckeler K.E., Synthesis and properties of hydrophilic polymers (Part 7)-Preparation, characterization and metal complexation of carboxy-functional polyesters based on poly(ethylene glycol), *Polym. Int.*, **48**, 909-914 (1999).
9. Geckeler, K.E., Choi, S.-J., A novel biodegradable carboxy-functional lactose copolymer, *Macromol. Rapid Commun.*, **22**, 855-858 (2001).
10. Arsalani N., Mousavi S.Z., Synthesis and characterization of water soluble and carboxy-functional polyester and polyamide based on ethylenediaminetetraacetic acid and their metal complexes, *Iran. Polym. J.*, **12**, 291-296 (2003).
11. Todorov N.G., Valkov E.N., Stoyanova M.G., Chemical modification of polyacrylonitrile with amines, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 863-866 (1996).
12. Todorov N.G., Stoyanova M.G., Tosheva S., Water-soluble polymer carriers ionically bonded substances with physiological activity, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 1933-1938 (1997).