Polycondensation of 1,2-Cyclohexyldiaminetetraacetic Acid with Benzidine and Its Chelators with Toxic Metal Ions

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الخلاصه

ادخل السايكلوهكسايل داي امين تترا استك اسد كمركب معقد مناسب ضمن السلسلة البولمرية عند اجراء البلمرة التكاثفية مع البنزدين. حيث شخص البولي أمايد المحضر بواسطة الاشعة فوق البنفسجية والاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي. قيست التحاليل الحرارية.وقيست نسبة الانتفاخ المئوية للبولمر المحضر في الماء وبدرجة حرارة الغرفة. كذلك شخصت المعقدات البوليمرية المحضرة مع بعض ايونات العناصر السامة وقيست اللزوجة الجوهرية بدرجة 30 °م .

ABSTRACT

1,2-Cyclohexyldiaminetetraacetic acid (CDTA) as a suitable complexing compound for toxic metal ions was inserted into the polymer backbone as a condensation reaction with benzidine. The prepared polyamide was characterized by UV.Vis, FTIR and ^{1}H.NMR spectroscopes. Thermal analyses such as TGA, DTA were measured. The swelling % was calculated in water at room temperature. The prepared metal complexes polymer were synthesized and also characterized. Intrinsic viscosities were measured using Ostwald viscometer at 30°C.

INTRODUCTION

Polyaminocarboxylic acid (PACA) chelators such as ethylen diamine tetraaceticacid (EDTA) and diethylenetriaminepentaaceic acid (DTPA), are used for the removal of some metals and radionuclide's that have been incorporated into the body for example, EDTA is used for chelation of lead [1] and Zn-and Ca-salts of DTPA have been used for the chelation of humans exposed to americium and plutonium [2], and curium [3]. (PACA) chelators, such as (EDTA) and (DTPA), require intravenous or subcutaneous administration due to their poor bioavailability can be improved by the addition of differing lengths of alkyl side chains [4].

Some chelators are based on triethylenetriaminohexaaceticacid (TTHA) are rendered partially lipophilic by addition of linear alkyl chains [5-10]. EDTA as a suitable and common complexing compound was inserted into the polymer backbone with poly addition reactions separately between hexamethylenediamine or poly (ethyleneylycol)[11-13].

Aminocarboxylic acid molecules, such as ethylene (EDTA), (DTPA) and their derivatives are widely described in literatures [14-16], and their commplexing abilities are more particularly used in medicine and analytical chemistry [4, 17]. Lead (Pb) presence in soil depending upon the reactant pH, redox potential and other factors surface, it can be remains in the soil with retention time of many centuries, soil- metal

interactions by sorption, precipitation and complexation processes, and differences between plant species in metal uptake efficiency, transport, and susceptibility make a general prediction of soil metal bio availability and risk of plant metal toxicity difficult [18].

Therefore, it was important to improve the chelation effect of many chelating agents such as CDTA by preparing derivative, which was its polymer with Benzidine in this paper and studying the ability of this polymer to make a stable complexes.

MATERIALS AND METHODS

CDTA and benzidine were purchased from Merck and used without any further purification, dimethyIformamide and 1,4-dioxane distilled before use. The FTIR spectra were recorded on fourier transform Shimadzu 7R-40E spectrometer in the range of 4000-400cm^{-1} using KBr disks, UV-Vis spectra were recorded by Shimadzu UV-256f.w spectrophotometer, ^{1}H-NMR spectra were carried out on a Brucker AC 500 spectrometer using DMSo as solvent.

Thermolysis of polymer and its metal complexes were performed with TGA Curves. Ostwald viscometer was used to measure viscosities using DMF as solvent and at 30°C.

Preparation of polyamide (general procedure)

CDTA and benzidine in equivalent mole ratio were introduced in single-neck round –bottom flask containing used solvents (1mlDMF:10ml 1,4-dioxane) and equipped with a condenser, with continuous stirring were refluxed about 1hr., the solvent was evaporated and a orange residue was obtained, washed with diethyl ether, dried under vacuum until a constant weight was obtained.

Table -1:lists the physical properties of the prepared polyamide P1

Color	Conversion %	µlndl/g	Solubility			S.P./ °C
Glassy orange	89	0.41	DMF	H2O	-1,4 dioxane	>300
			+	-	-	

Preparation of metal complex polymer

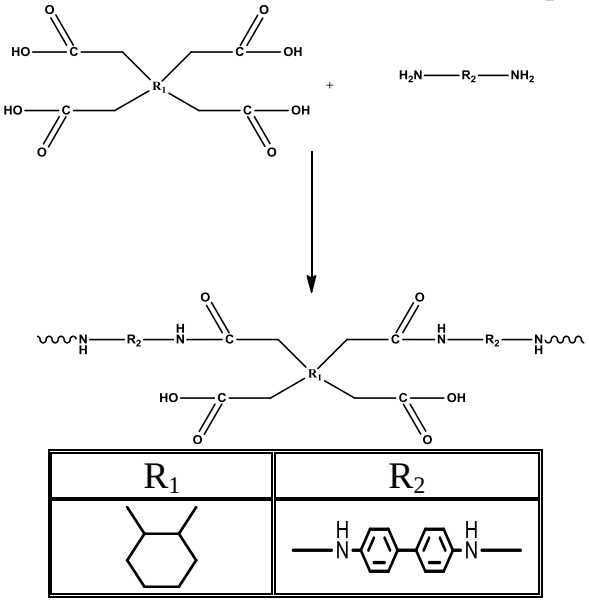
0.01mole of metal nitrate (numbers of mol=Weight$_{(metal\ nitrate)}$/Molecular weight$_{(metal\ nitrate)}$) solution was adjusted to suitable PH values by adding some drops of KOH or HCl aqueous solution, then the polymer (P_1) was added, the metal complex polymer can be prepared at different pHs and purified by ether. Table (2) lists the physical properties of complex polymers.

Table -2: lists the physical properties of complex polymers

No.	Polymers metal	Color	Yield%	μ_{ln}dl/g	UV-Vis λmax
1.	P_1- Ni	Turquoise	70%	0.41	200,400,750
2.	P_1- Cr	Green	60%	0.45	200,512,613
3.	P_1- Pb	White	56%	0.43	190,243,572
4.	P_1-Co	Faint violet	75%	0.46	200,390,655
5.	P_1-Fe	Dark green	80%	0.45	190,250,375,600

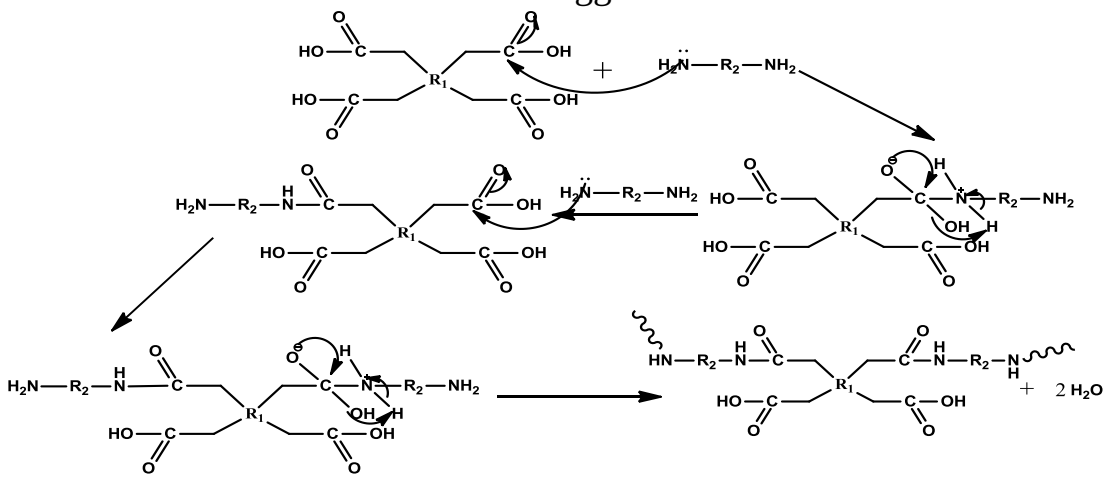
RESULTS AND DISCUSSION

In this research the new amide polymer was prepared from condensation of benzidine with CDTA as chelate polymer containing aromatic rings through back bone of main chain of the polymer , the following equation is illustrated the formation of the polymer .



R_1	R_2

The mechanism of the reaction was suggested as below:



The CDTA acts as a chelate through polymer chain, bearing such groups (carboxyl, amine) making stable complexes with many metal

ions. Table (2) lists the physical properties of polymer complexes, which could used as binding atoms such as toxic metals to form stable complexes with a toxic metal, also it could used as a drug polymer to extract poison metal ions from body, and for water treatment, and soil treatment.

FT-IR spectra Fig. (1) shows peaks at 3224 cm^{-1} assigned to -NH- and at 3421-2725cm^{-1} broad band assigned to characteristic absorption of O–H carboxylic acid for CDTA and the absorption appeared at 1670cm^{-1} assigned to C=O stretching of amide, 1691cm^{-1} assigned to C=O stretching of carboxylic acid, peak at 2937-2866cm^{-1} assigned to cyclic C-H stretching of CDTA, peak at 3034cm^{-1} was attributed to C-H stretching of aromatic ring and at 1176 cm^{-1} assigned to C-N.

^{1}H-NMR spectra Fig.(2) shows signals as illustrated in the structure of the prepared polymer

For cyclic hexane signals appeared at δCH- 2.8ppm(q), δCH_2- 1.9, 1.6ppm(m), δCH_2-CO at 3.5, 3.8ppm(s), δCH=CH aromatic ring at 7.2-8.3ppm(m), δ CO-NH amide at 8.8ppm(s), δCOOH at 10.4ppm(s).

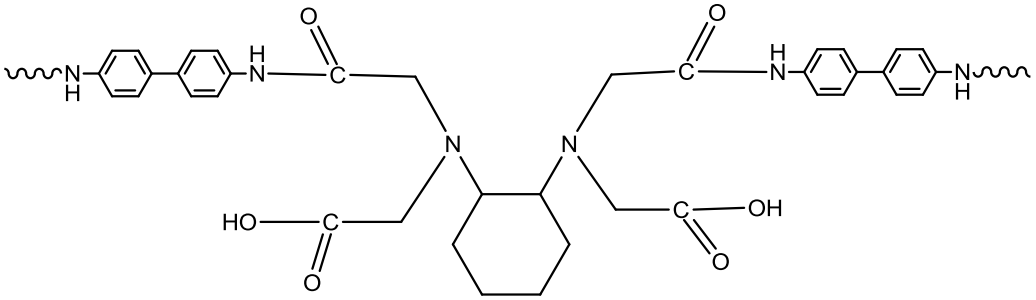
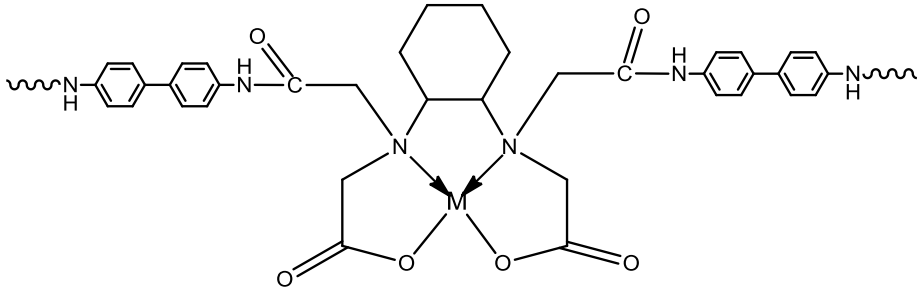


Fig. (3) Showed TGA and DTA of prepared polymer P_1 (Benzidine with CDTA) which indicate the high thermal resistance, and showed three steps of weight loss-temperature, the first is ranged at 320 °C with 27.233 % weight loss, and the second at 450 °C with 28.500% weight loss, and the third at 673.7°C 41.273% weight loss. This high thermal resistance indicated the high interaction between amide hydrogen bonding and the high molecular weight of the polymer containing aromatic rings through back bone of its structure.

Table (2) above shows the change in color of metal-polymer complexes due to electron transition in UV-Vis λ_{max} which are listed, and their (suggested) corresponding metal-polymer structure is described below:



Intrinsic viscosity was measured by capillary viscometer type Ostwald viscometer at 30°C using DMF as a solvent. The intrinsic viscosity of the material, measured in deciliters per gram (dl/g) is dependent upon its polymer chains. The longer the polymer chain the more entanglement between chains and therefore the higher the viscosity.
Swelling % was determined in water according to the following relationship

$$\mathbf{S\ \%=(M_1-M_0)/M_0}$$

Where M_0 is the mass of the dried polymer, M_1 is the mass of swollen polymer in time $t_{/day}$.
The swelling% data was listed in table (3) and illustrated in Fig.4.

Table -3:Swelling% of the Polymer P_1

Swelling%	Time/day
1.2	1
1.7	2
2	3
2.2	4

The low swelling % indicated the high stability of polymer in water.

CONCLUSION

The CDTA-Benzidine condensed polymer could form stable complexes with some metal ions, for removing the toxic metal ions of water, to remove the toxic environmental pollution.

In this search, the use of CDTA as chelating agent with Benzidine to make condensed polymer, the produced polymer acts as chelating polymer and act as a sequestrant of poison metal ions from soil and water. The presence of Benzidine gave the polymer high thermal stability at 573.7°C with 97% weight loss.

Finally, we recommended that the future work could be extended inorganic studies for prepared polymer P_1 and their polymer complexes could be used them in many applications.

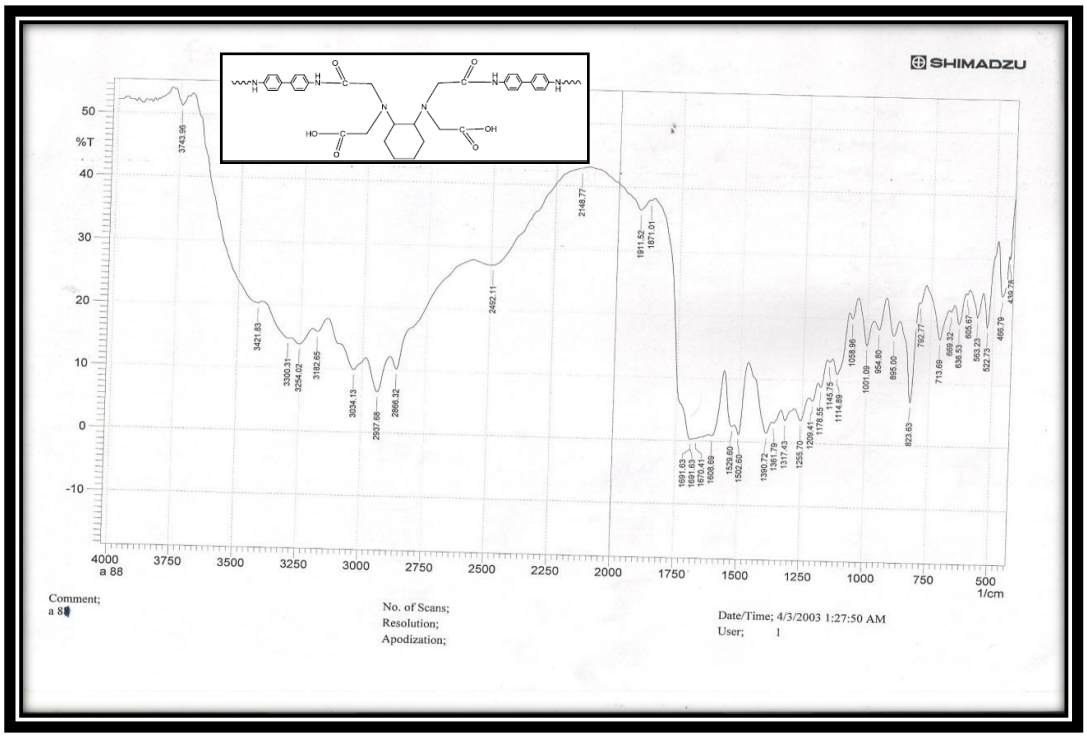


Fig.-1: FT-IR spectrum for prepared polymer

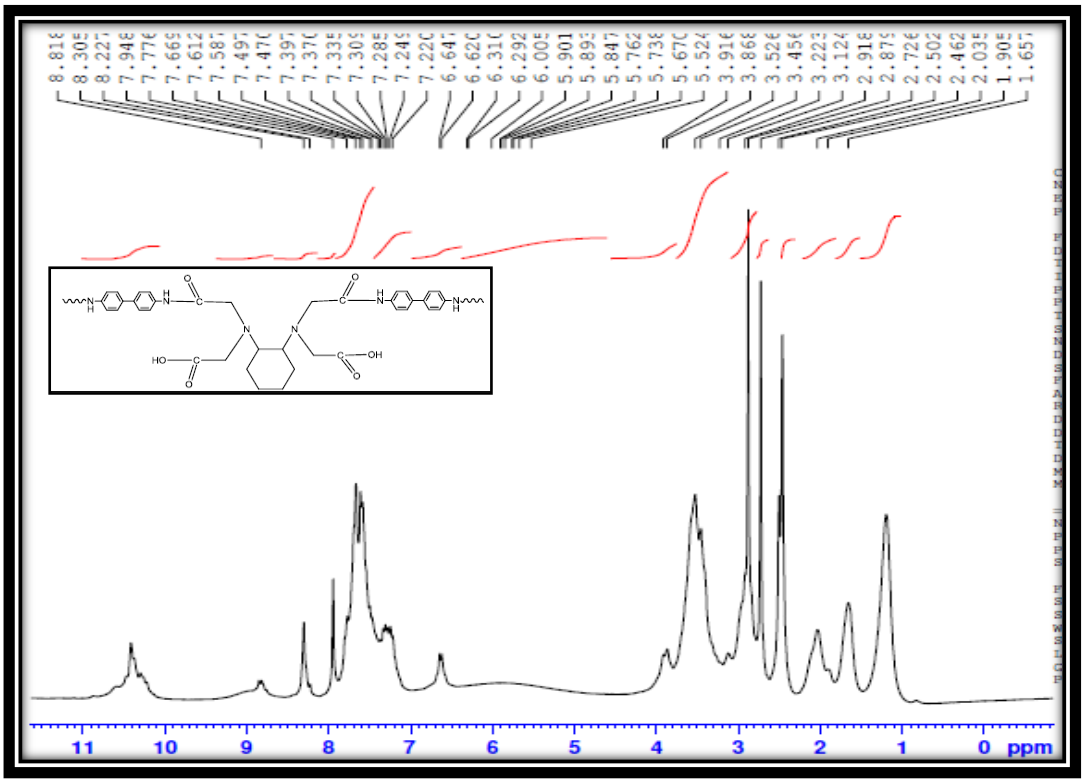


Fig.-2 ^{1}H.NMR spectrum for prepared polymer

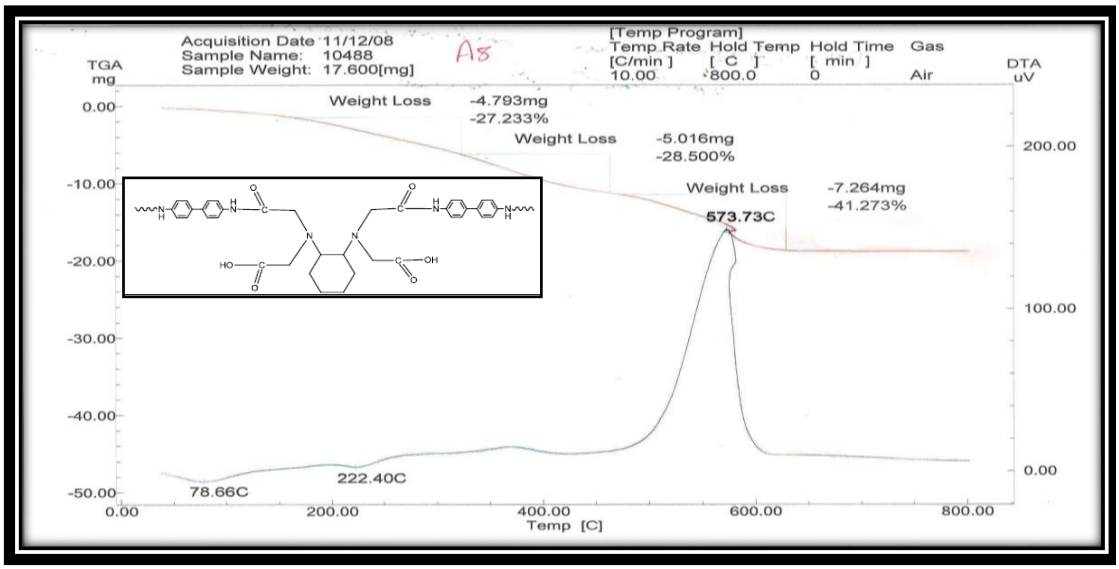


Fig.-3 TGA and DTA chart for prepared polymer

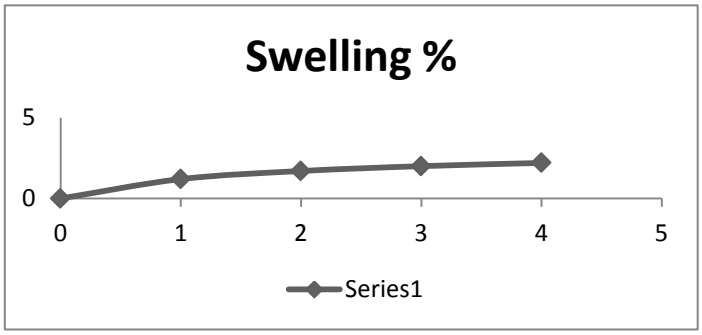


Fig. -4: swelling % of prepared polymer

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