Synthesis of Chelate Polymer Between 2,4 -Diamino-6-Phenyl-1,3,5 Triazine and EDTA As Sequestrant of Metal Ions

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Abstract:

In this research the new condensed polymer was synthesized by poly condensation of EDTA and 2,4-Diamino-6-Phenyl 1,3,5 triazine as a chelating polymer which was complexed with metal ions such as Ti,Co,Cr,Ni,Fe ions. These prepared complexes were characterized by elemental analysis and infrared and Ultraviolet spectroscopies. The physical properties were measured. Intrinsic viscosities were calculated by using Ostwald viscometer.

Introduction :

Chelate – forming polymers are polymers that incorporate chelating (multi dentate) ligands by covalent bonding. Ion- exchange resins represent the most prominent class of chelating polymer and generally contain multifunctional ligands attached at one point or in the network or forming either intra molecular chelating groups [1-3]. The range of chelating ligands of interacting with ion solution is very wide and many have been bonded to polymers. Some of chelates are 8-hydroxyquinoline, hydroxamic acid, oxamines , polyamines acrylic acid type poly vinyl pyridine [4-7] .Approximately five tones of heavy metals from industrial manufacturing are added every year to our nation`s water, which makes clean up a high priority Lead (Pb), mercury (Hg) and cadmium (Cd) in particular are extremely toxic to the majority of living organisms[8] . Recently, the use of chelating polymers for remediation of water and soil has attracted much attention [9]. The pharmacologic effects of EDTA calcium disodium are due to the formation of chelates with divalent and trivalent metals. A stable chelate will form with any metal that has the ability to displace calcium from the molecule [10-11].

Experimental:

Materials and Instruments:

EDTA , DMF, diethyl ether were purchased from BDH and used without further purification ; 2,4-Diamino-6-Phenyl 1,3,5 triazine was obtained from sigma-Aldrich . FT.IR spectra were recorded with Fourier Transform Shimadzu 7R-46G spectrometer in the range of 400-4000cm^{-1}. UV 256 F.W. spectrophotometer .Softening points were measured using Kalen.

Camp.apparatus. Viscosities were measured by using Ostwald viscometer at 30°C in DMF as a solvent.

Polycondensation of EDTA and 2,4-Diamino -6-phenyl 1,3,5 triazineP_1.

(2g,0.02mole) of EDTA was dissolved in 6ml of DMF and (0.6g,0.02mole) of 2,4-Diamino-6-Phenyl 1,3,5 triazine was added in a single –neck round bottom flask equipped with a condenser. The mixture was refluxed and stirred for 2hrs.

The solvent was evaporated; the glassy polymeric product was obtained with 80% yield. The polymer was washed with ether and dried.

Preparation of metal complex polymers:

In a round bottom flask was placed a mixture of dissolved prepared polymer P_1 in DMF and one of the metal ion solution with 1:1 molar ratio. The mixture was heated about 15mins. The solvent was evaporated until the viscose polymer was obtained as colored polymer, washed by ether and dried. Table 1 lists the physical properties of P_1–M (M = Co, Cr , Fe , Ti , Ni) .

Table(1) Physical properties of complex polymer P_1 - M

Complex-Polymer	Color	Yield%	m.p.°C	µindL/g	UV. absorption
P_1-Co	Blue -Violet	80	>300	0.83	380,550
P_1-Cr	Green	75	>300	0.82	400,530
P_1-Fe	Orange	85	>300	0.85	400,600
P_1-Ti	White-Yellow	70	>300	0.84	380,400
P_1-Ni	Green-Yellow	87	>300	0.83	400,530

Measurment of Swelling %

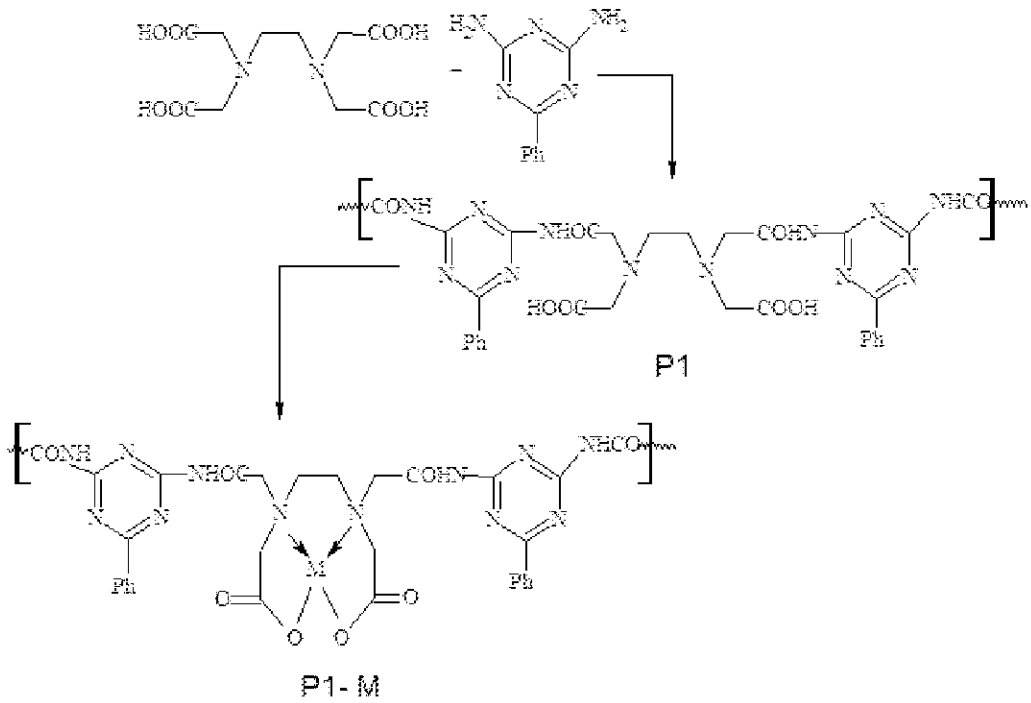
According to the formula [$S\% = \frac{m_1 - m_o}{m_o} \times 100$ %]

Where m_o is the mass of dry polymer m_1 is the mass of swelled polymer.

Swelling curves of prepared complex polymer were shown in fig (7).

Results and Discussion:

The polycondensation of EDTA with diamine was carried out it is possible to condense carboxylic acid with amino group, the polyamide P_1 as a chelate polymer was obtained with high yield 80% as glassy white polymer with µin=0.81 dl/g , the following equation is illustrated the polymerization and its corresponding metal complex polymers .



Scheme (1) Reactions to prepare for P1 and complexes P1-M (M = Co , Cr , Fe , Ti ,Ni)

The FT.IR spectrum of P_1 Fig.(1) shows the NH amide band at 3200cm^{-1} and absorption of C=O amide revealed at 1680cm^{-1}. The –OH absorption appeared at 3450-2900cm^{-1} as a broad band, the C-N absorption was observed at 1350cm^{-1}, the other absorptions were observed at 3100 and 2970cm^{-1} which attributed to CH aromatic and aliphatic respectively. These absorptions such as C=O, OH carboxylic acid were appeared with a shift in peak absorptions due to complex formation with metal ions.

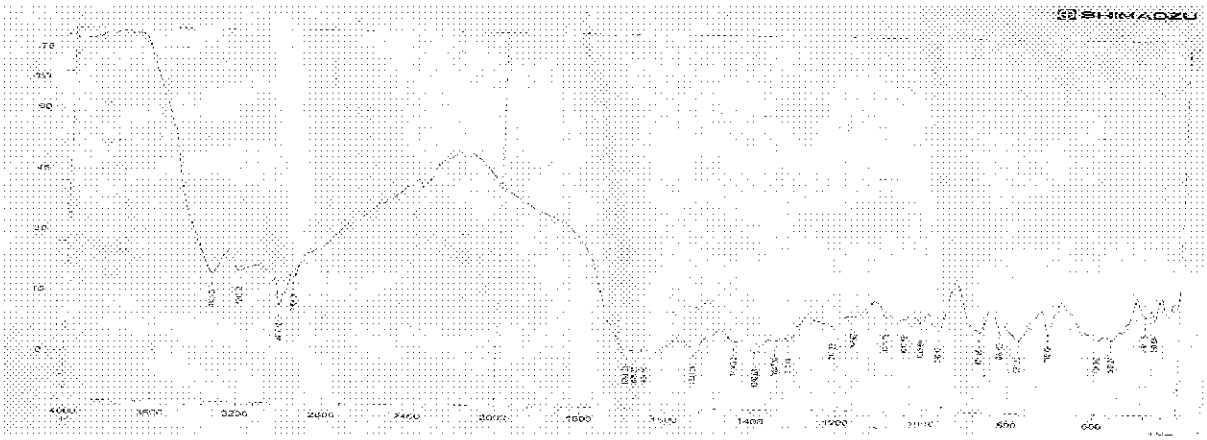


Fig (1) FTIR spectrum of P_1

In the work the new condensed polymer was prepared P_1 containing Phenyl triazin rings through back bone of the polymer chains, which could increase the acting of chelate polymer, which have been suitable complex with many metal ions as indicated in the Fig.(2-6) , and as shown in table(1) with their physical properties and their UV-visible absorption of the prepared complexes polymers.

The high softening points indicated high thermal stabilities for all prepared polymers (P_1-M), which attributed to incorporation the triazin rings and hydrogen bonding amide groups through the polymer chains.

Table (1) shows the characteristic colors and $\lambda_{max}$of metal – polymer complexes due different electron transitions as shown in table 1. The experimental results of element analysis were quiet suitable with the theoretical results.

We concluded from these results that the prepared polymer (P_1) could be used as sequestrate polymer for toxic metal ions which could used in different application uses.

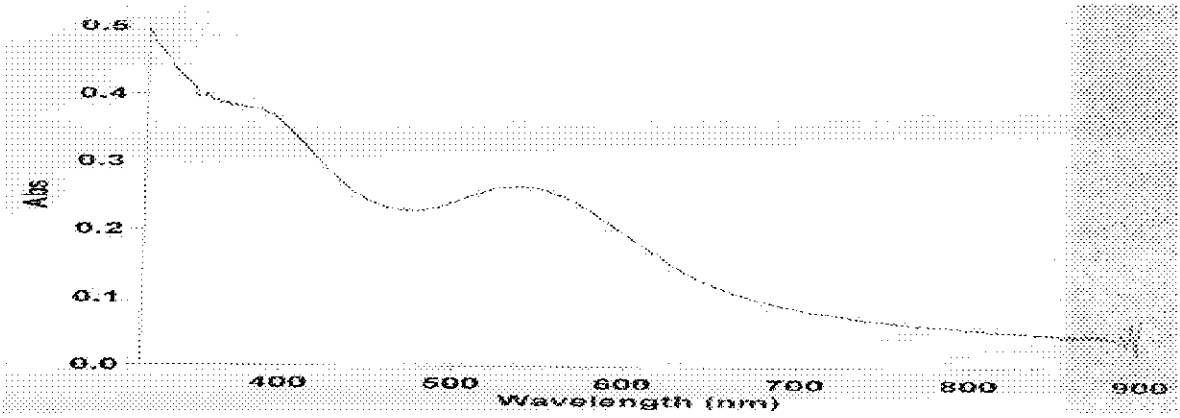


Fig (2) UV.Vis spectrum of P_1- Cr

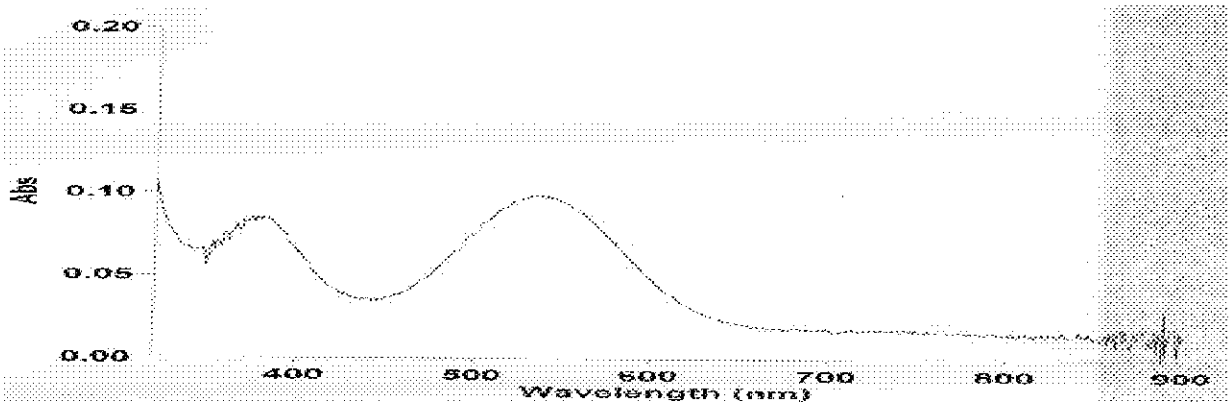


Fig (3) UV.Vis spectrum of P_1 - Co

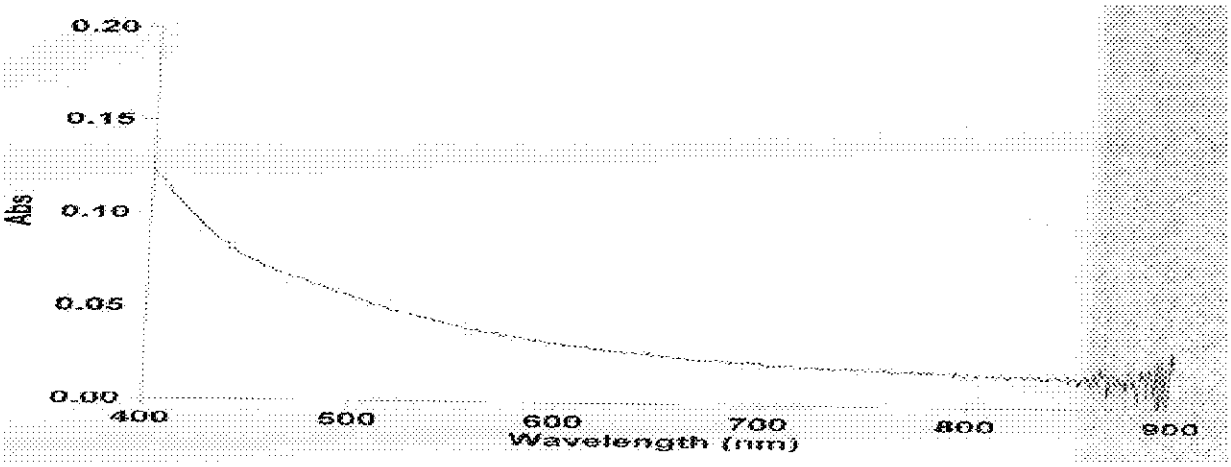


Fig (4) UV.Vis spectrum of P_1 - Ti

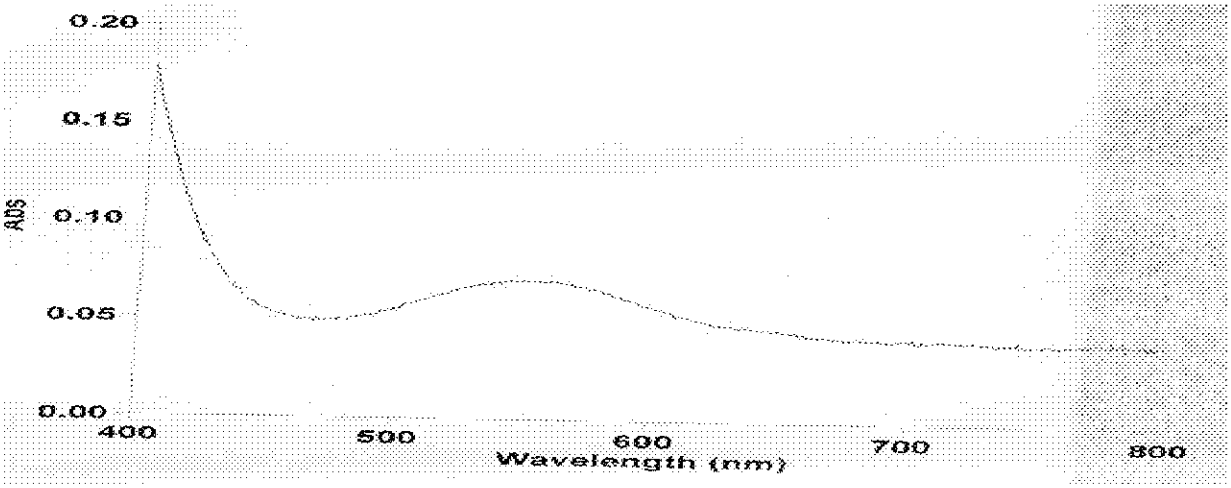


Fig (5) UV.Vis spectrum of P_1 - Fe

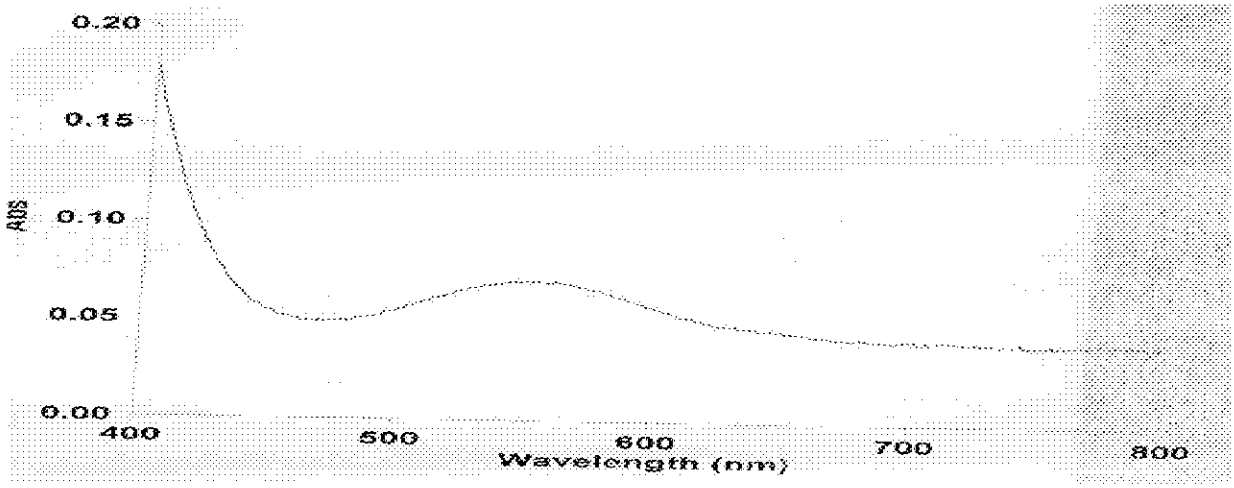


Fig (6) UV.Vis spectrum of P_1 - Ni

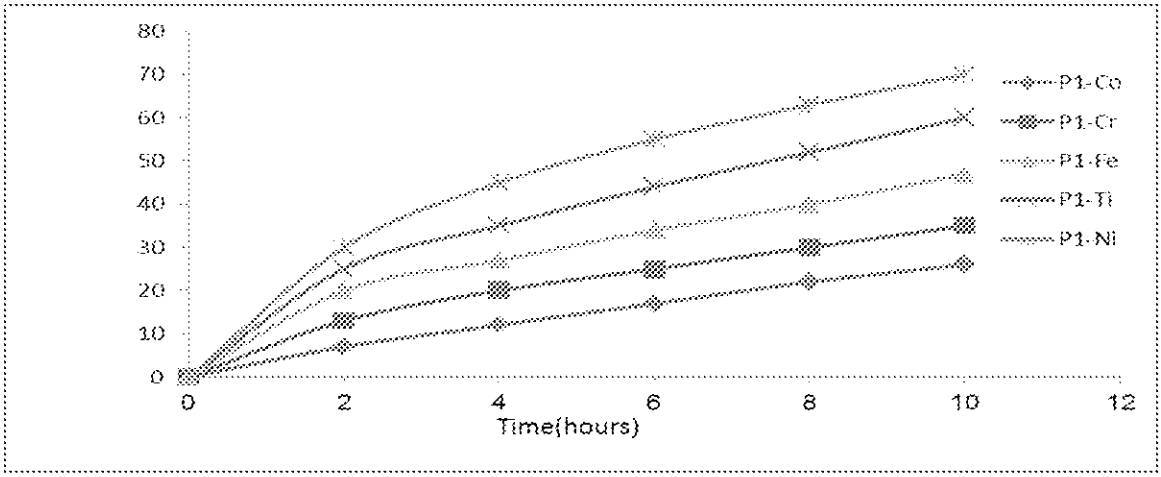


Fig (7) Swelling % of prepared complex polymers in PH 1.1

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تحضير بوليمر مخلبي من 2، 4 – ثنائي أمينو – 6 – فنيل – 1، 3، 5 – ثلاثي أزين و الأثلين ثنائي الأمين رباعي حامض ألخليك لسحب الايونات الفلزية .

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الخلاصة:

حضر في هذا البحث بوليمر تكاثفي جديد من البلمرة التكاثفية بين الاثلين ثنائي الأمين رباعي حامض ألخليك مع (2، 4- ثنائي أمينو-6– فنيل- 1، 3 ، 5 – ثلاثي أزين) الذي استعمل كبوليمر مخلبي لتكوين معقدات مع أيونات العناصر الكوبالت والتيتانيوم والرصاص والنيكل والحديد ، وشخصت المعقدات المحضرة بواسطة التحليل الدقيق للعناصر وبواسطة طيف الأشعة تحت الحمراء ومطياف الأشعة فوق البنفسجية ، وقيست اللزوجة الجوهرية باستخدام الاوستوالد فيسكوميتر ودرست الصفات الفيزيائية للبوليمرات المحضرة .