

Polycondensation of Ethylenediaminetetraacetic Acid with Some Prepared Diamines Derived from Amino Acids or Antibiotic

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Abstract

Many condensed polymers [A1-A7] were prepared via reaction of (Ethylenediaminetetraacetic acid = EDTA), with different prepared imide-diamines by modification [modification of amino acids and antibiotics (B1-B7)]

Imide-diamines were prepared by chlorination of L-amino acids such as

[L-Histidine, L-Alanine, L-Valine, L-Glycine and L-Asparagine] or selected antibiotics such as [Cephalexin monohydrate and Amoxilline] with thionyl chloride at 0°C, then reacted with ammonia to obtain imide-diamines [B1-B7] .

The physical properties of all prepared condensed polymers [A1-A7], new prepared diamines [B1-B7] were studied and characterized by FT -IR spectroscopy to certify the structural formulas.

The thermal analysis (TGA, DTA) were studied, and the intrinsic viscosities were measured at 30°C using Ostwald viscometer.

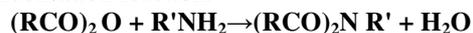
Keywords: polymerization, thermal analysis (TGA, DTA), diamines and Viscosity Measurements

1. Introduction

During the condensation (polymerization) process, the monomers tend to form dimers (two linked monomers) and trimers (three linked monomers) first. Then, these very short chains react with each other and with monomers. The overall result is that, at the beginning of polymerization, there are many relatively short chains. It is only near the end of polymerization that very long chains are formed. [1-4].

In organic chemistry, an imide is a function group consisting of two carbonyl groups bound to nitrogen. These compounds are structurally related to acid anhydrides .The relationship between esters and amide and between imides and anhydrides are analogous; the amine-derived groups are less reactive. In terms of commercial application, imides are best known as components of high strength polymers. [5].

Most common imides are prepared by heating dicarboxylic acids or their anhydrides and ammonia or primary amines. The result is a condensation reaction:



These reactions proceed via the intermediacy of amides. The intra-molecular reactions of carboxylic acids with amides are far faster than the intra-molecular reaction, which is rarely observed [6].The Ethylenediaminetetraacetic acid (EDTA)= (C₁₀H₁₆N₂O₈) molecule has six potential sites for bonding metal ions: the four carboxyl groups (-COO⁻) and the two amino groups (-NH₂), each of the latter with unshared pair of electrons. Thus, EDTA is a hexadentate ligand [7], See figure (1). It is used to treat acute and chronic lead poisoning by pulling toxins (including heavy metals such as lead, cadmium, and mercury) from the bloodstream. The word "chelate" comes from the Greek root *chele*, which means "to claw." EDTA has a claw-like molecular structure that binds to heavy metals and other toxins.[8]

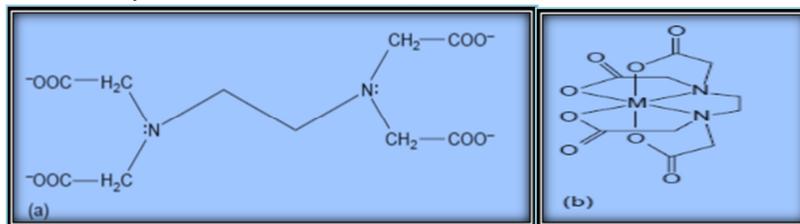


Figure 1: EDTA structure(a) and its cheater form (b)

2. Experimental

2.1 Materials

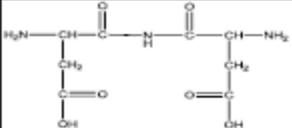
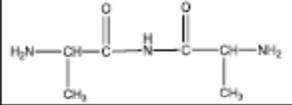
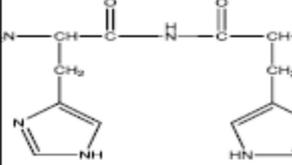
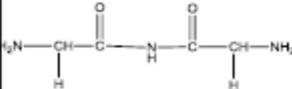
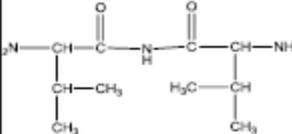
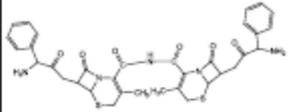
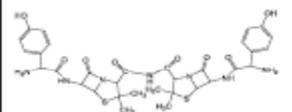
Most of the chemicals used were of Analytical Grade. The drug (antibiotics) were obtained from (the state Enterprise for the drugs Industries ,and Medical Appliances) in Samarra- Iraq (SDI)., EDTA, L-amino acids and solvents were purchased from (B.D.H) and Merck and used without any further purification, dimethylformamide and dioxan distilled before use. The FTIR spectra were recorded in the 4000-400cm⁻¹ range from a fourier transform Shimadzu 7R-40E spectrometer, Thermalizes of polymers were performed with TGA Curves. Ostwald viscometer was used for measured of viscosities.

Modification of L- amino acids and antibiotics (B1-B7):

A thionyl chloride (5 ml, 0.04 mol) was add gradually to a mixture of (0.04 mol) of dissolved amino acids or antibiotics in (10 ml) of DMF, the mixture was stirred using ice bath and the yellow product was collected and washed with ether.

The corresponding imide derivatives were prepared using dissolved (2gm.of urea) which added to a dissolved of amino acid chlorides or antibiotic acid chlorides. After stirring for 2hrs, the solvent was evaporated; the product was recrystallized from ethanol. Table (1) shows the physical properties of prepared compounds.

Table (1) Formula and physical properties of prepared compounds [B1-B7]

No.	Formula	Color	Melting point °C	Yield %
B1		Dark orange	230-235	50
B2		Brown	Viscose	45
B3		Gray	260-262	55
B4		Yellow	120-125	62
		brown	190-195	64a
B6		Red orange	200-203	56
B7		Faint red	125-130	59

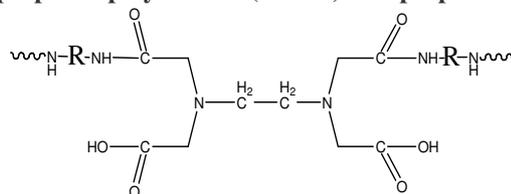
Polycondensation of (EDTA) with prepared imide-diamines (A1-A7):

(1gm. 0.00342 mol) of EDTA was dissolved in 5ml of DMF , then the (0.938 gm , 0.00342 mol) of dissolved B1 in 6ml of Dioxan : DMF mixture (5:1 by vol.) were introduced in a single-neck round-bottom flask which was equipped with a condenser , the mixture was refluxed and stirred with magnetic bar for 1hr., then the solvent was evaporated and clear polymer, was obtained , washed with diethyl ether. Finally, it was dried under vacuum oven, a constant weight was obtained. All prepared polymers (A1-A7) were obtained by the same method of condensation polymerization. See Table -2 .

Table (2) lists the physical properties of prepared polymers.

No.	-R-	Color	Softening point °C	Conversion %	$\mu\text{ln dl/g}$
A1		Red brown	230-240	65	0.52
A2		Black	Viscose	53	0.23
A3		Dark brown	Viscose	58	0.35
A4		Dark green	Viscose	68	0.42
A5		Faint brown	210-225	75	0.75
A6		Brown	215-230	82	0.47
A7		Dark yellow	200-210	86	0.72

(2) Physical properties of prepared polymers of (EDTA) with prepared imide-diamines (A1-A7)



Viscosity Measurements [9,10]

Ostwald, capillary viscometer was used to determine viscosities of the prepared polymers in dioxane at 300C. DMF was also used as the solvent for some of the prepared polymers. Four types of viscosities of the polymers were calculated μ_{rel} , μ_{sp} , μ_{red} and μ_{in} , the last type which is the intrinsic viscosities was estimated by extra-piloting the curve in Fig. (1). the results of intrinsic viscosities are listed in Table (2).

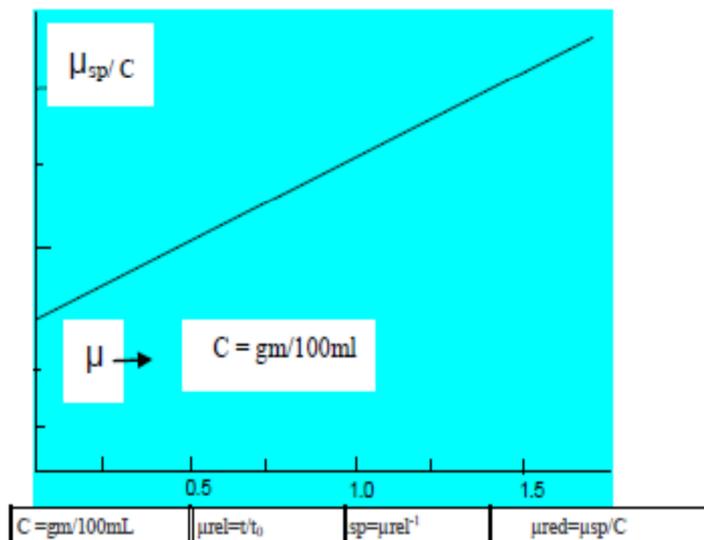


figure 2 : Curve of μ in to concentration

Where t = time of flow rate of polymer solution
 t_0 = time of flow rate of the solvent only

Results and Discussion

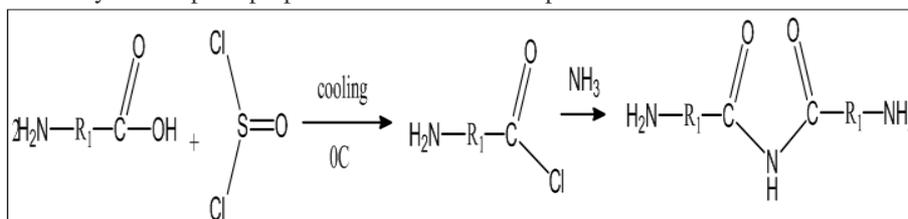
$$C = \text{gm}/100\text{ml}$$

The mechanism of modification of (B1-B7):

L-amino acid and antibiotics

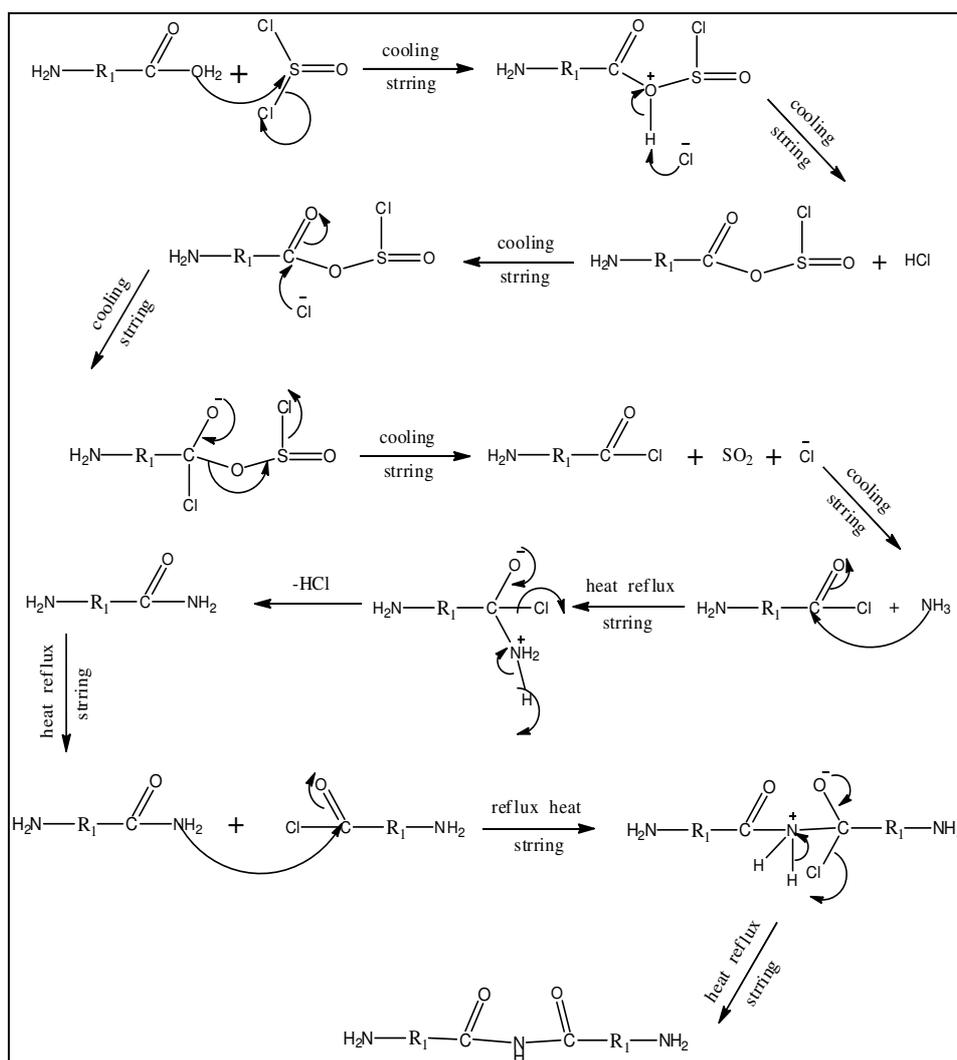
The modification of amino acids and antibiotics done by reacting them with thionyl chloride [11,12], at 0°C to prevent the polymerization between amino acid chlorides and then immediately adding urea to release ammonia (NH_3).

So the reaction done by two steps to prepare imide-diamine compounds as shown in scheme 1



Scheme 1 General reaction for the modification of L-amino acids and antibiotics

The mechanism goes as shown in scheme 2:



Scheme 2 : General mechanism for prepared imide-diamines

Fourier Transform Infrared spectra (FT-IR)

The relevant vibration bands of the free ligands and the complexes are in the region 400–4000 cm^{-1} [13].

The FT-IR spectra assignment off Modification of L- amino acids and antibiotics (B1-B7)were summarized in (Table 3) ,

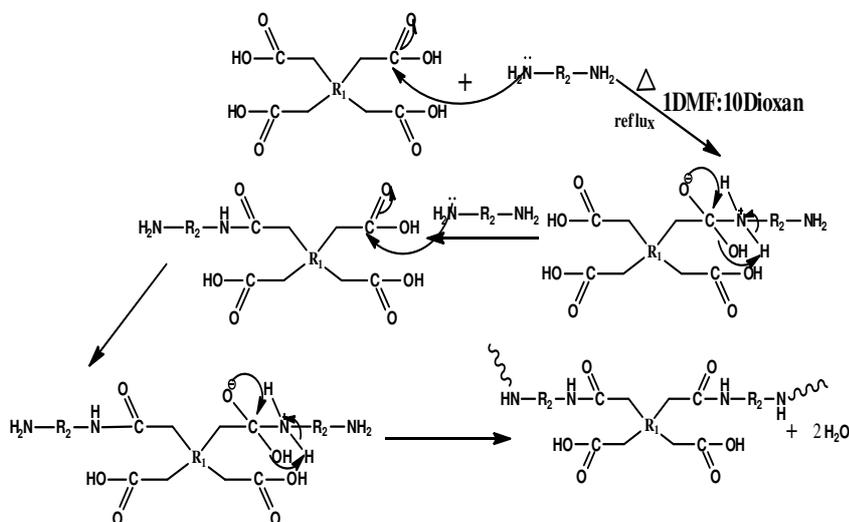
Table (3): Selected FT-IR bands for Modification of L- amino acids and antibiotics (B1-B7)

No.	$\nu(\text{C}=\text{O})$ cm-1 imide	$\nu(\text{N}-\text{H})$ cm-1	$\nu(\text{NH}_2)$ cm-1	$\nu(\text{C}-\text{N})$ cm-1	$\nu(\text{C}-\text{H})$ cm-1 aliphatic	$\nu(\text{C}-\text{H})$ cm-1 aromatic
B1	1790	3315	385,3443	1201	2966	--
B2	1738	3300	300,3188	1112	2907	--
B3	1741	3416	163,3136	1226	2887	3020
B4	1800	3371	269,3178	1111	2970	--
B5	1790	3370	324,3207	1055	2912	3034
B6	1784	3383	279,3178	1215	2990	3097
B7	1790	3450	320,3207	1111	2965	3028

Polycondensation of (EDTA) with prepared imide-diamine compounds (A1-A7):

In this research the new amide polymer was prepared from condensation of prepared imide-diamines with EDTA as chelate polymer containing amino acids and antibiotics through back bone of main chain of the

polymer ,the following equation is illustrated the formation of the polymer .
 The mechanism of the reaction was suggested as below:



Fourier Transform Infrared spectra (FT-IR) Fourier Transform Infrared spectra (FT-IR)

The relevant vibration bands of the compounds were recorded in KBr disc in the region 400–4000 cm^{-1} . The assignment of the characteristic bands (FT-IR) spectrum of the (A3), figure (4), and (A5), Figure (5) are summarized in Table (4).

FTIR- spectrum, Fig (4) of polymer (A₃) exhibits the characteristic absorption bond at 1656 cm^{-1} due to the C=O stretching vibration of the carboxylic groups. The absorption at 1667 cm^{-1} was attributed to the formation ester groups.

Table (4) : Poly condensation of (EDTA) with prepared imide-diamine compounds (A1-A7)

No.	$\nu(\text{C=O})$ cm^{-1} amide	$\nu(\text{N-H})$ cm^{-1} amide	$\nu(\text{C-H})$ cm^{-1} aliphatic	$\nu(\text{C-H})$ cm^{-1} aromatic	$\nu(\text{C-N})$ cm^{-1}
A1	1675	3375	2955	--	1228
A2	1653	3240	2950	--	1242
A3	1656	3398	2998	3014	1211
A4	1689	3398	2997	--	1223
A5	1691	3325	2951	--	1232
A6	1691	3350	2955	3076	1213
A7	1693	3375	2956	3035	1138

The thermal stability study

Fig .(6) Showed TGA and DTA of prepared polymers [A1] (B1 with EDTA) which indicate the high thermal resistance, and showed three steps of weight loss-temperature, the first is ranged at 255C° with 33.704 % weight loss % , the second at 540 C° with 41.9% weight loss % and the third at 785C° with 97.4% weight loss % . This high thermal resistance is indicating the high molecular weight of the polymer, and presence of amide and imide groups through the backbone of the polymer chain.

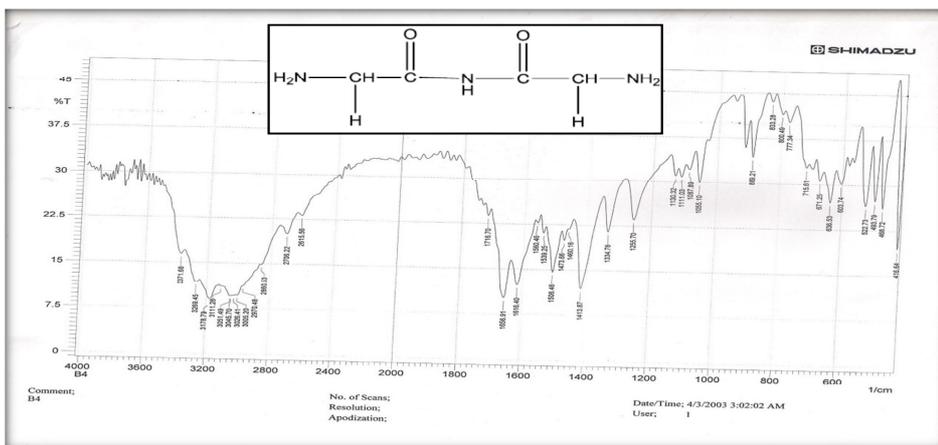


Figure.3 FT-IR spectrum for compound B4

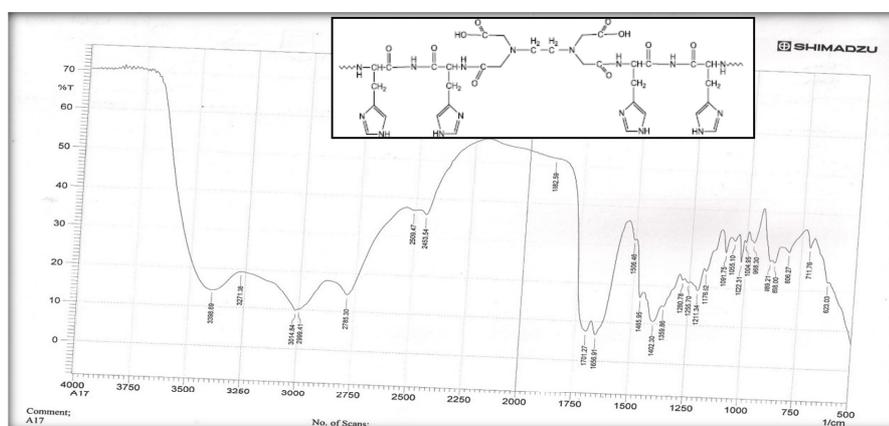


Figure.4 FT-IR spectrum for polymer A3

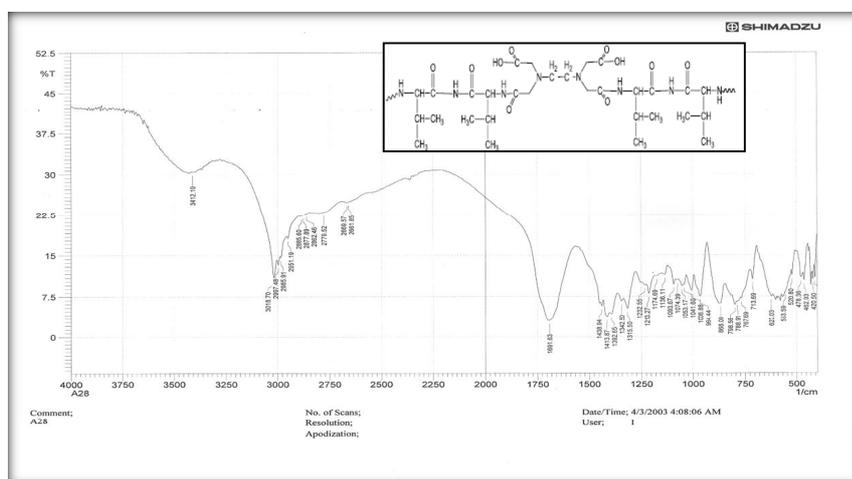


Figure.5 FT-IR spectrum for polymer A5

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