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Poly-Condensation of CDTA with Some Diamines

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Abstract

In this research, new condensed polymers (A1-A8) were prepared by poly condensation between 1, 2-cyclohexyl diamine tetraacetic acid CDTA with different diamines such as 1, 6-Diamino hexane, Melamine, 3,3`,5,5`-Tetramethyl benzidine, Benzidine and Cystine. These prepared chelate polymers could be used to remove heavy metals and toxic metal ions in many industrial processes as well as acting as sequestrate for metal ions. The all prepared polymers were characterized by ^{1}H-NMR and FT-IR spectra. The thermal analyses (TGA, DSC) were studied, the intrinsic viscosities were calculated at 30 ˚C using Ostwald viscometer, and all physical properties were measured.

Keywords: Poly Condensation, Chelate polymers, Sequestrate.

Introduction

The use of chelating polymers for remediation of water and soil recently has attracted much attention [1]. Chelating groups are incorporated into the polymeric side chains or backbone. The choice of the type of ligands, ligand density, structure and solubility of the polymer as well as pH govern the metal ion affinity, retention efficiency and selectivity [1-3]. The condensation product of diethylenetriaminepentacetic (DTPA) is dianhydride with diamine [4, 5]. These ligands coordinate lanthanide atoms to form neutral or anionic complexes. Most of them have been found to possess a monomeric or dimeric solid state structure. Condensation reactions between ethylene diaminetetraacetic (EDTA) dianhydride and a diamine give the macrocycles of dioxo polyazacyclo alkanes with different ring sizes. The divalent transition metal coordination chemistry with these ligands has been well studied [6]. Ethylene diamine tetra acetic acid (EDTA), di ethylene triamine penta acetic acid (DTPA) and their derivatives are widely described in the literature [7-9]. Additionally, their complexes abilities are more particularly used in medicine and analytical chemistry [10,11]. Many polymers bearing such groups have been stable complexes with heavy metal ions [12-15].

Experimental

Materials and Instruments

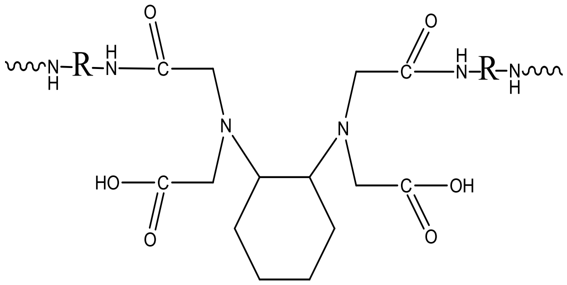
CDTA and all diamines were purchased from Marck and used without any further purification, dimethyIformamide DMF and dioxin distilled before usage. The FTIR spectra were recorded in the range of 4000-400cm^{-1} using a Fourier Transform Shimadzu 7R-40E spectrometer, UV-Vis spectra were recorded by Shimadzu UV-256f.w spectrophotometer, ^{1}H-NMR spectra were carried out on a Brucker AC 500 spectrometer.

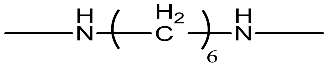
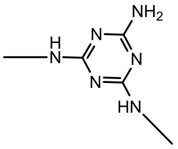
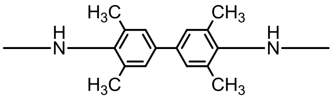
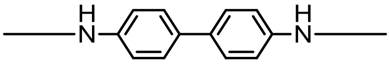
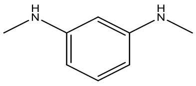
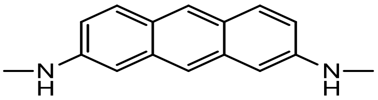
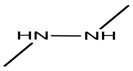
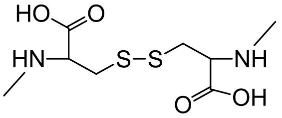
Thermo analyses of polymer and its metal complexes were performed with TGA Curves. Elemental analyses were carried out on elemental system of Germany. Ostwald viscometer was used for measuring viscosities.

Polycondensation of (CDTA) with diamines (A1-A8):

A mixture of (1g, 0.00274 mol) of CDTA was dissolved in 5ml of DMF. A mixture of dissolved 1,6-diaminohexane (0.318 g , 0.00274 mol) in 6ml of Dioxan:DMF mixture (5:1 by vol.) were introduced in a single-neck round-bottom flask equipped with a condenser. The mixture was refluxed and stirred for 1hr. Then the solvent was evaporated and a clear polymer was obtained and washed with diethyl ether. After that the polymer dried under vacuum oven and a constant weight was obtained**.** All prepared polymers (A1-A8) were obtained by the same method of condensed polymerization. Table (1) lists prepared polymers in this method and their properties

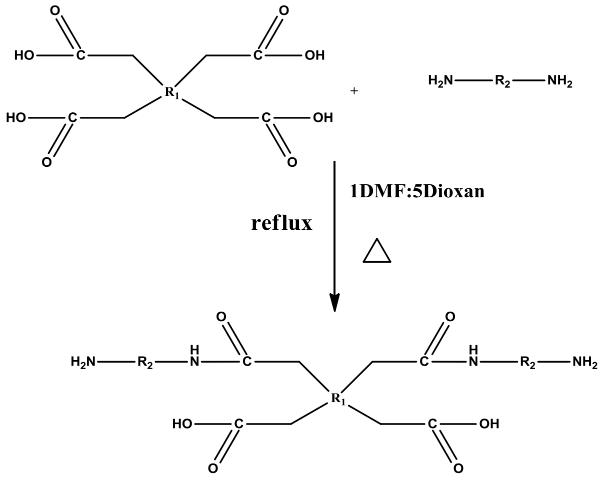
Table (1) Physical properties of prepared polymers [A9-A16].

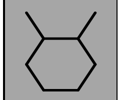
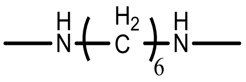
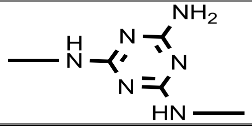
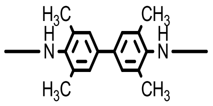
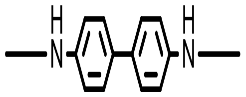
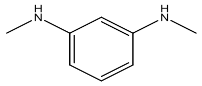
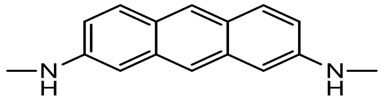
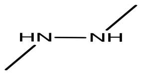
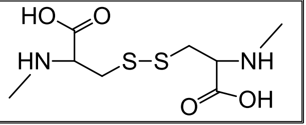


No.	-R-	Color	Melting point °C	Yield %	Intrinsic viscosiy μ_{ln} dl/g
A1		White	240-265	68	0.64
A2		White	220-255	76	0.34
A3		Dark green	190-210	91	0.45
A4		Glassy orange	150-175	89	0.6
A5		Black	130-140	46	0.31
A6		Red	225-240	59	0.44
A7		Yellow orange	Viscose	92	0.56
A8		Yellow brown	170-190	73	0.21

Results and Discussion

CDTA was condensed with different diamines to produce new condensed polymers [A1-A8], as illustrated in equation below.



R_1	R_2			
				
				

These new polymers can behave as ligands for different metal ions. These polymers were characterized by FT-IR spectra figures (1-3) and by ^{1}H-NMR spectra figures(4-6).The thermal analyses were measured as shown in figures(7, 8) which were discussed as illustrated below.

Table (2) Fourier Transform Infrared spectra (FT-IR)

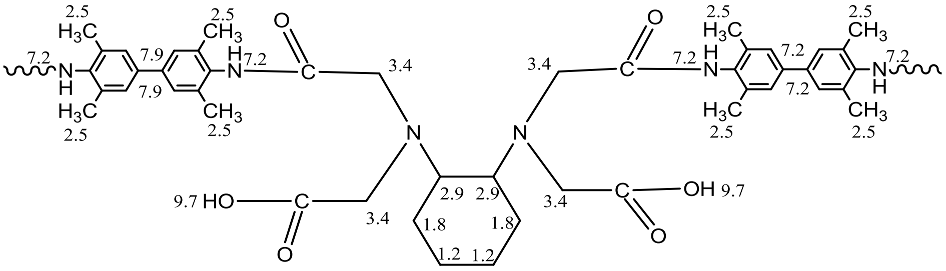
No.	ט(C=O) cm^{-1} amide	ט(C=O) cm^{-1} carboxylic acid	ט(N-H) cm^{-1} amide	ט(C-H) cm^{-1} aliphatic	ט(C-H) cm^{-1} aromatic	ט(C-N) cm^{-1}	ט(O-H) cm^{-1} carboxylic acid
A1	1655	1718	3383	3010-2877	--	1226	3250-2546
A2	1662	1712	3365	3024,2943	--	1220	3410-2800
A3	1685	1734	3377	2937,2864	3020	1112	3441-2846
A4	1670	1691	3300	2866,2937	3034	1176	3421-2725
A5	1662	1728	3394	2941,2868	3014	1170	3417-2646
A6	1660	1734	3348	2870,2941	3016	1217	3140-2756
A7	1660	1712	3290	2934,3083	--	1118	3441-2879
A8	1656	1735	3298	3014,2943	--	1219	3250-2500

Proton Nuclear Magnetic Resonance (1H-NMR)

^{1}H-NMR spectra of some prepared polymers were obtained using DMSO-d6 as a solvent with TMS as internal standard. They were illustrated as shown below.

The ^{1}H-NMR spectrum of prepared polymer [A3] was shown in figure (4). The signals assignment in the corresponding formula of figure (1) Show the following peaks:-

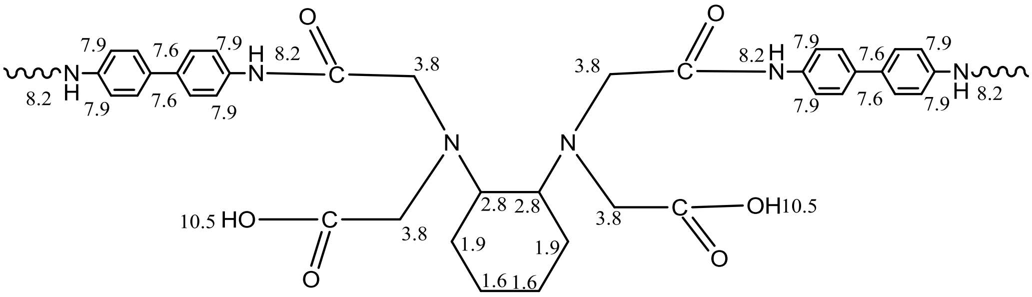
For cyclic hexane signals appeared at δCH_2- 2.9ppm, δCH_2- 1.8,1.2ppm, δCH_2 at 3.9ppm, δ CH=CH aromatic ring at 7.9ppm, δCH_3- 2.5ppm, δ CO-NH- amide 7.2ppm, δ –COOH of 9.7ppm.



Structure A3 with ^{1}H-NMR

The ^{1}H-NMR spectrum of prepared polymer [A4] was shown in figure (5), the signals assignment in the corresponding formula of figure (2) show the following peaks:-

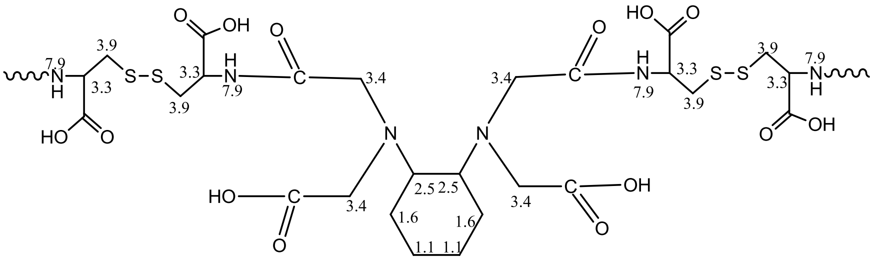
For cyclic hexane signals appeared at δCH_2- 2.8ppm, δCH_2- 1.9,1.6ppm, δCH_2 at 3.8ppm, δ CH=CH aromatic ring at 7.9,7.6ppm, δ CO-NH- amide 8.2ppm, δ –COOH of 10.4ppm.



Structures A4 with ^{1}H-NMR

The ^{1}H-NMR spectrum of prepared polymer [A8] was shown in figure (6), the signals assignment in the corresponding formula of figure (3) Show the following peaks:-

For cyclic hexane signals appeared at δCH_2- 2.5ppm, δCH_2- 1.6,1.1ppm, δCH_2 at 3.4ppm, δCH- 3.9ppm, δCH_2- 3.3ppm, δ CO-NH- amide 7.9ppm, δ –COOH of 8.1ppm.



Structure A8 with ^{1}H-NMR

The thermal stability study

The thermal stability of some selective compounds was investigated by thermo gravimetric analysis (TGA) for [A3, A4] as shown in figures (7, 8). This technique is based on measuring the weight loss as a function of time at constant temperature or as a function of temperature at constant rate of heating. Table (2) below lists the thermal data.

Table (3) thermal analysis.

Codes No.	Temp. ^{0}C	Weight Loss%	Decomposition Temp. ^{0}C		Figure
			T_{endo}	T_{exo}	
A3	350	76	-	-	4.56
	760	90			
A4	330	27	490	605	4.57
	465	55			
	670	92			

We concluded from this research that the new chelate polymers have high thermal resistance. Moreover, this gives an indication of the high molecular weight of e condensed polymers due to containing aromatic rings through the backbone of polymers chins and hydrogen bonding on amide groups. Subsequently, this could enhance some specifications for their uses in different applications.

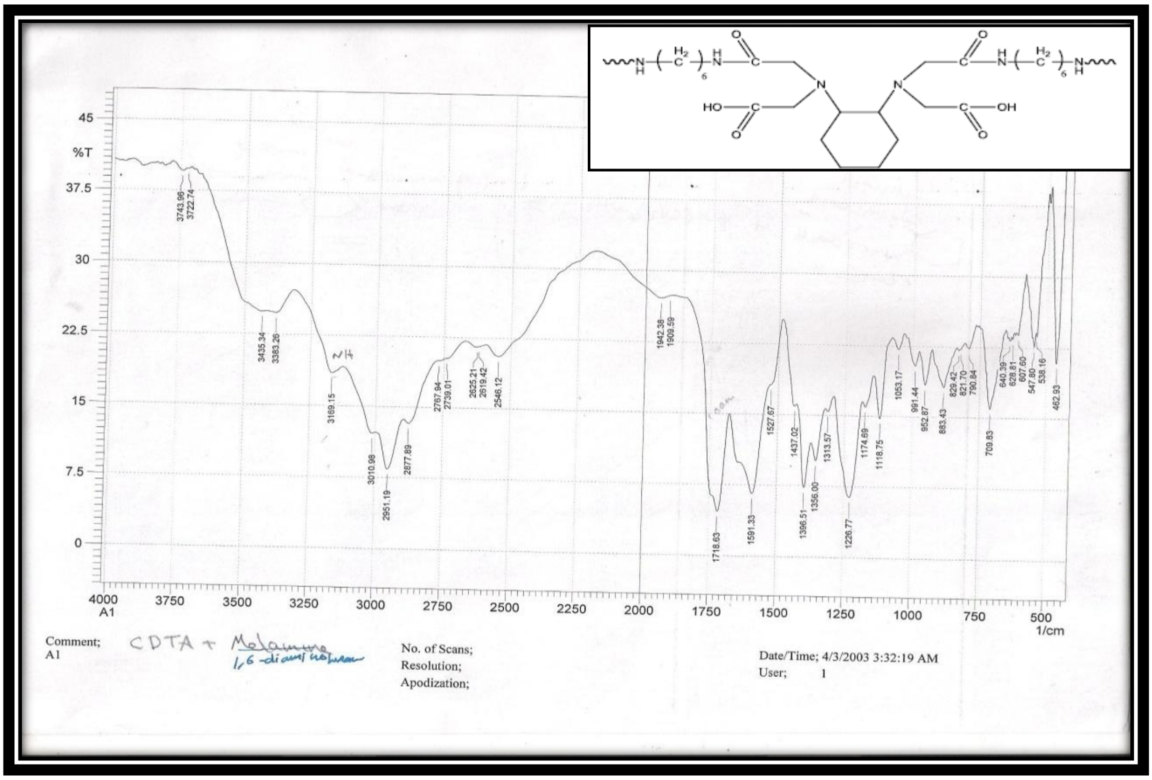


Fig.(1) FT-IR spectrum for polymer A1.

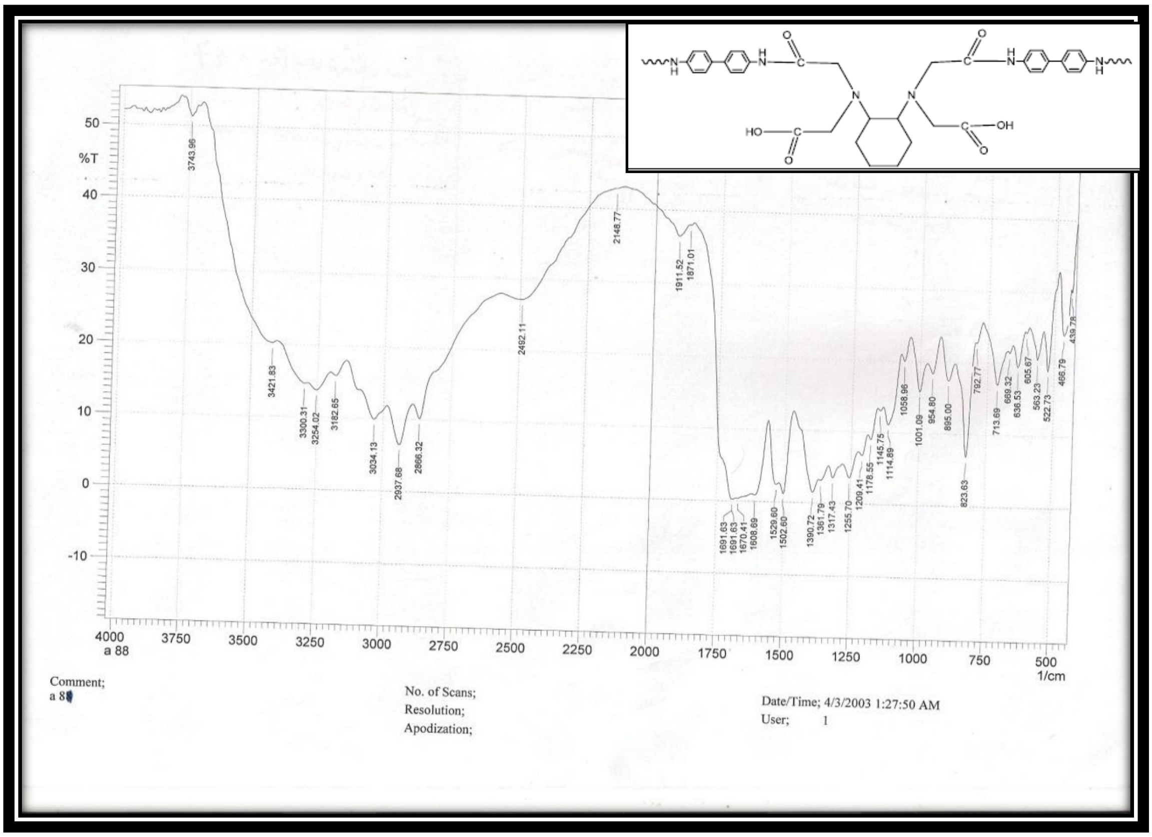


Fig.(2) FT-IR spectrum for polymer A4.

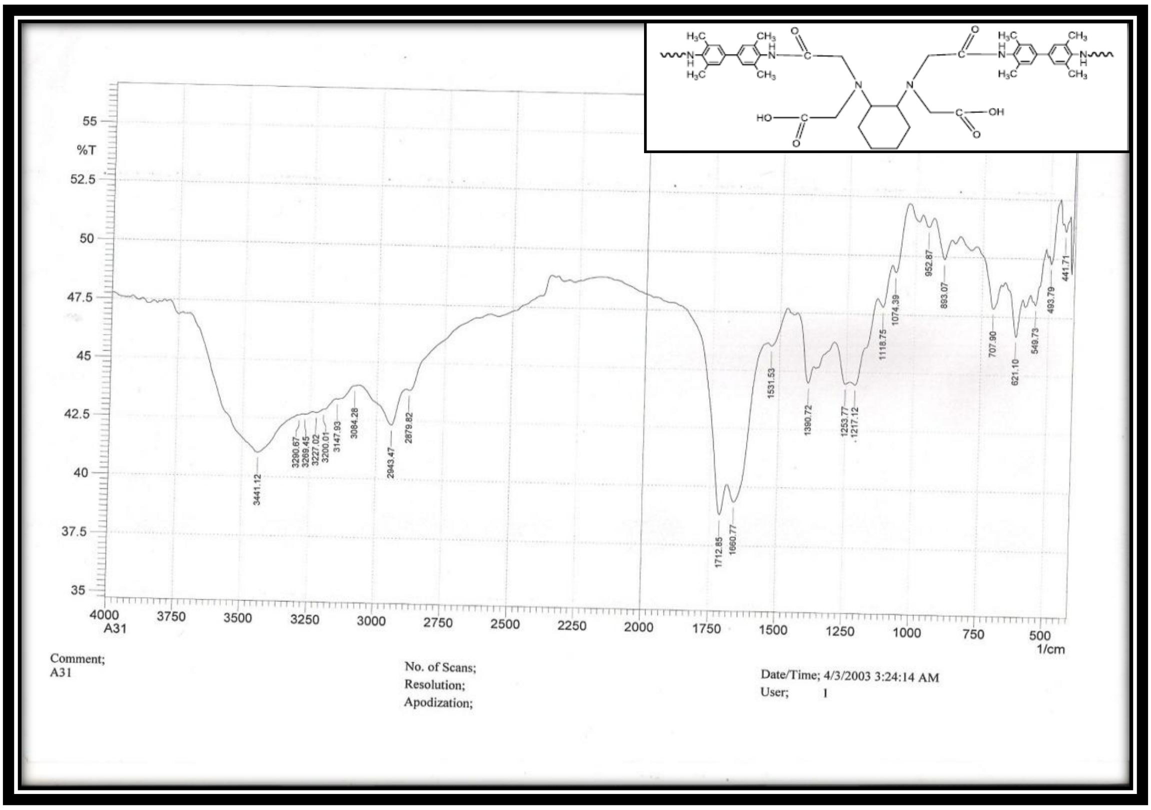


Fig. (3) FT-IR spectrum for polymer A7.

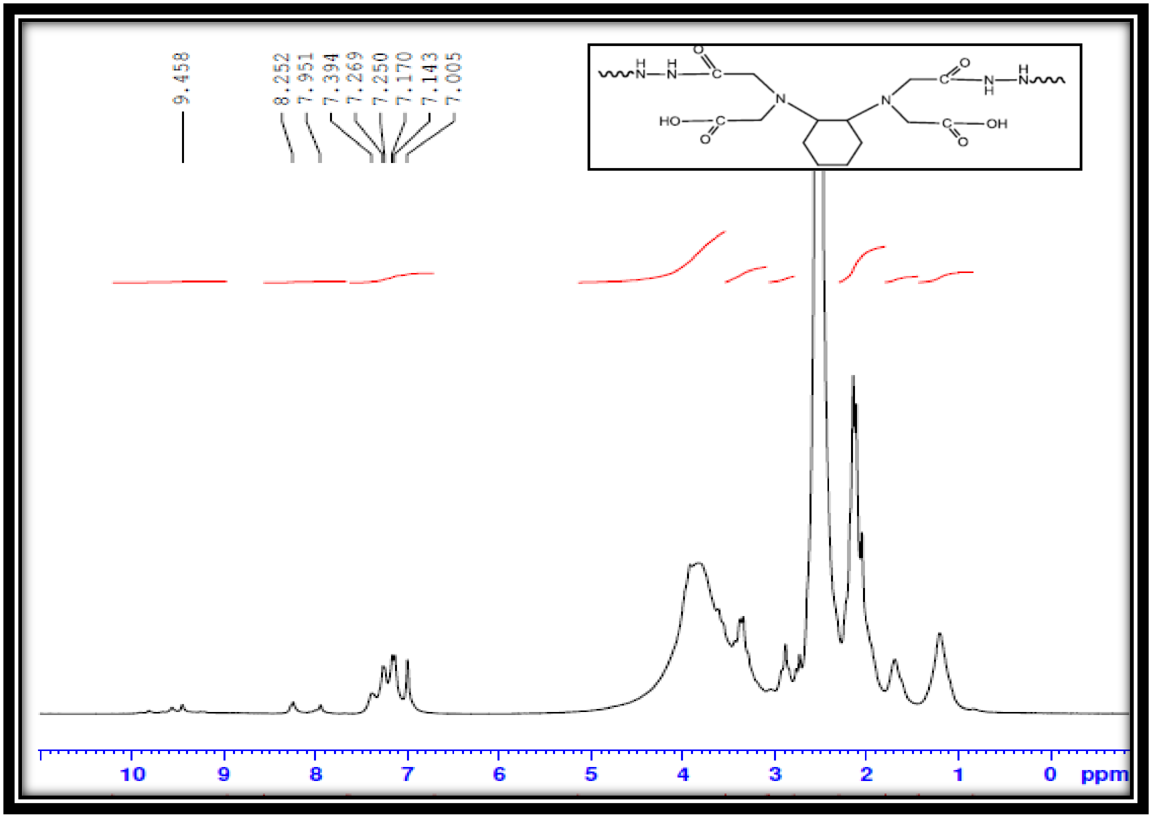


Fig. (4) ^{1}H-NMR spectrum for prepared polymer A3.

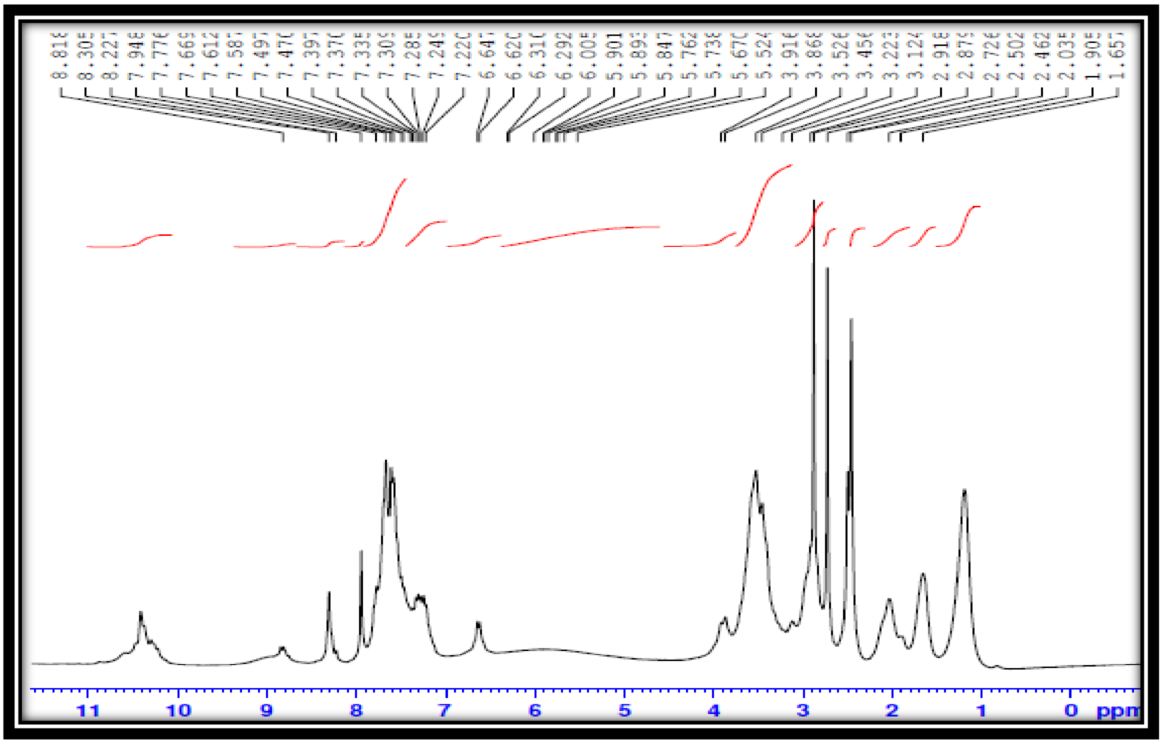


Fig.(5) ^{1}H-NMR spectrum for prepared polymer A4.

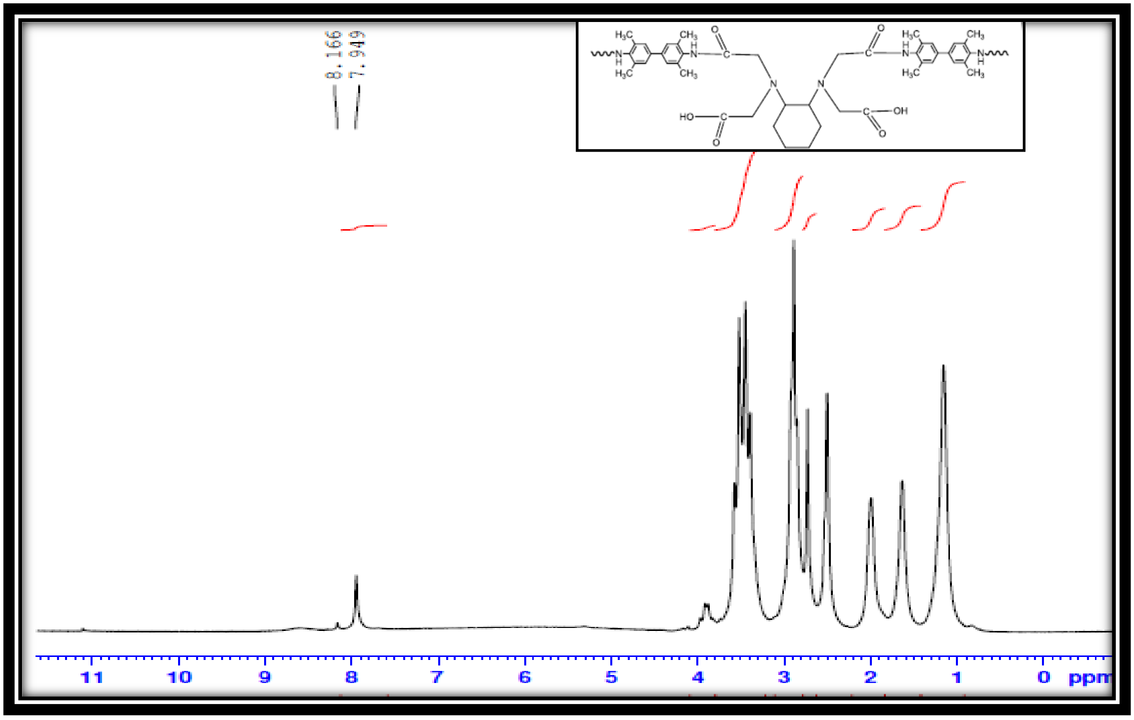
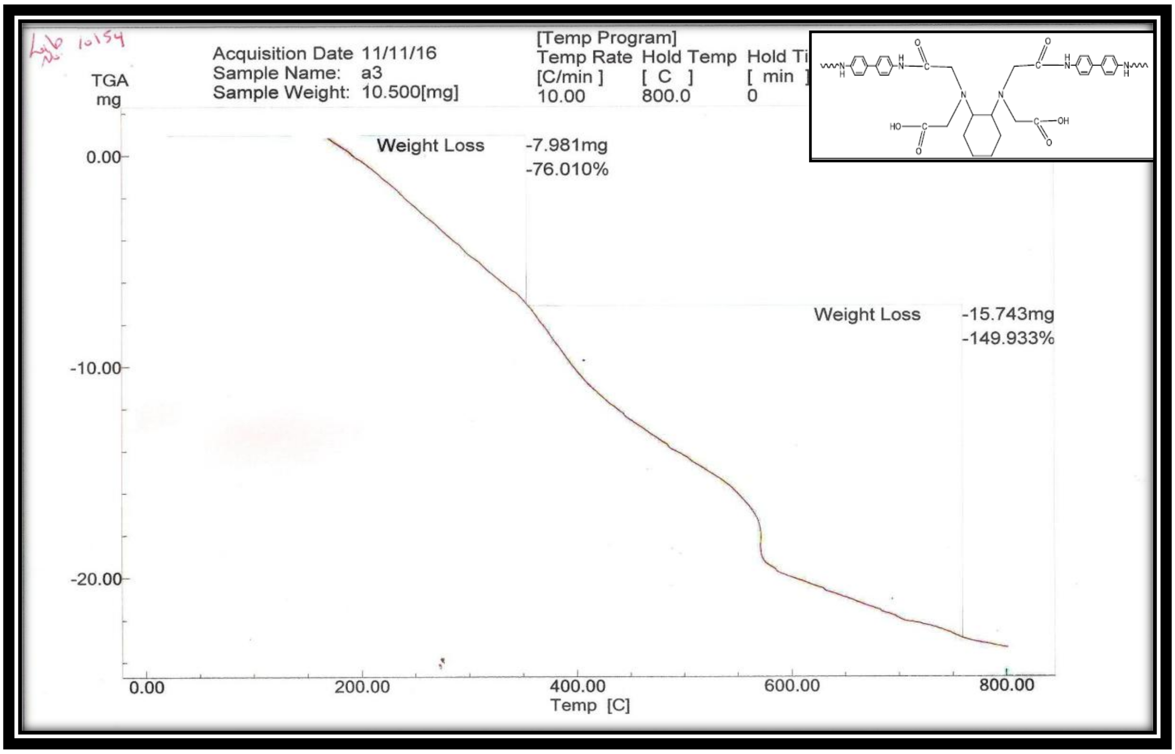


Fig. (6) ^{1}H-NMR spectrum for prepared polymer A8.


Lab No. 10154

Acquisition Date 11/11/16
Sample Name: a3
Sample Weight: 10.500[mg]

[Temp Program]
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Hold Temp [C] 800.0
Hold Ti [min] 0

Fig. (7) TGA for prepared polymer A3

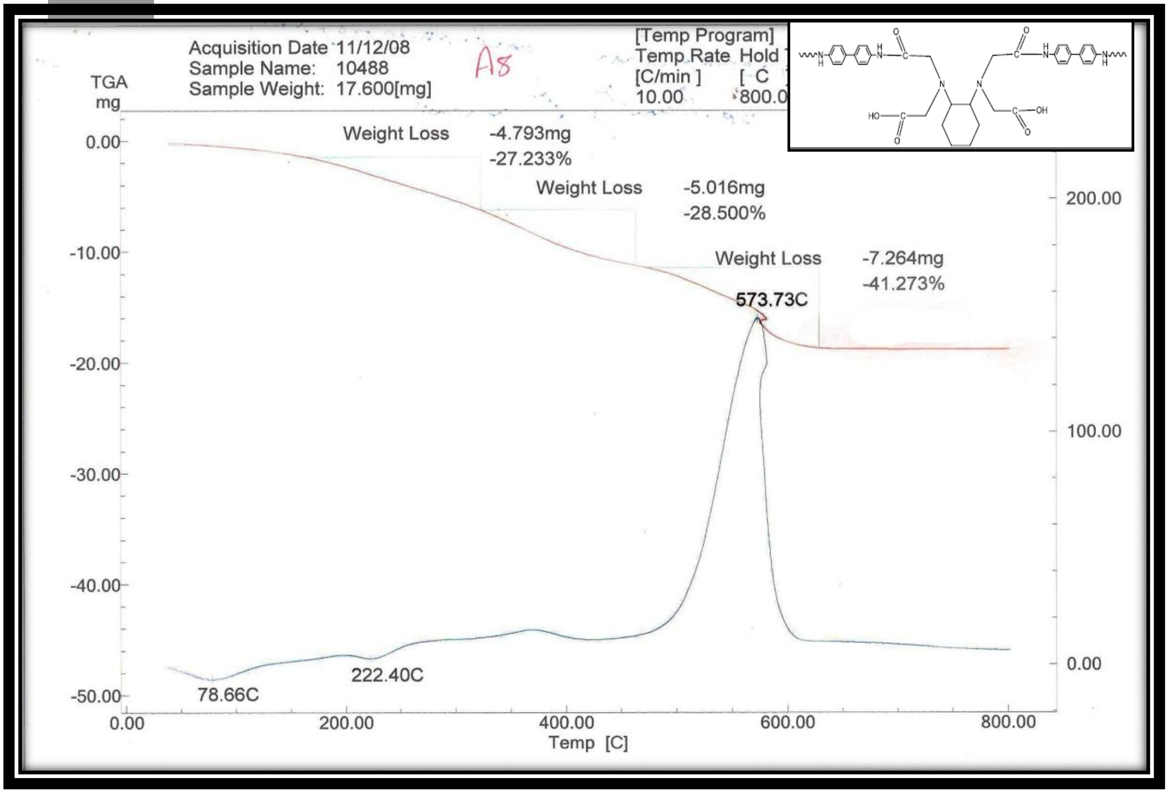

Fig. (8) TGA and DTA for prepared polymer A4

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