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Synthesis and characterization of novel diethyl allyl malonate polymer and its hydroxamic acid derivative

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M.Sc. Thesis

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Synthesis and characterization of novel diethyl allyl malonate polymer and its hydroxamic acid derivative

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Dedication

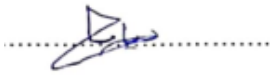
First of all, I thank God who gave me this life and who urged me to find useful knowledge.

There must be a hero in every human's life, a true hero and a role model, and my hero is my father, who has always floded me with his giving. He was always my guide and my strength thanks to my ideal in my life. and my mother Nesreen who encouraged me, strengthened me, and appreciated my ambition. Thanks to my loving husband Hazem who supported me, strengthed me, appreciated my love for education, gave me all the comforts to reach this scientific degree and was always proud for me, I am truly grateful for having me in your life

Thanks my source of strength, she pushed me always to do the best of things and boosted my self-confidence in every moment of weakness I faced, my sister Donia. Thanks to my dear friend Hadeel Abukhaleel who shared the good and bad time in this journey.

Declaration

I certify that this thesis is submitted for the degree of master is my own research, except where otherwise acknowledged, and that this thesis has not been submitted for a higher degree to any other university or institution.



Diana' M. M. Khderat

Date: 10/9/2022

Acknowledgemet

I would like to thank Al-Quds University for giving me the chance to get the M.Sc. degree.

With all respect to my supervisor Dr.Mahmoud Alkhatib and Co- supervisor Dr.Muhannad Qurei. Thanks to Dr.Yassen Qawasmi(Palestine Polytechnic University) who guided me in all stages of work. I would like to express my special thanks to Mr.Ibrahim Ayyad and Mrs Maryam Feraon they helped me whenever I needed in my work.

Warmest thanks to my family, my husband, and my friends.

Abstract

Polymers either soluble, swelable or insoluble in water each have high number of applications, hydroxamic acid polymers are soluble in water and have wide interesting applications in medicine and environment, especially their impressive chelating ability with heavy metals. In this study insoluble linear and cross-linked poly(diethyl allylmalonate) was prepared by emulsion and suspension free radical polymerization using diethyl allylmalonate using different conditions. Polydihydroxamate prepared by two methods, first the reaction of poly(diethyl allylmalonate) with hydroxylamine hydrochloride using potassium hydroxide as a base in methanol and second, preparing of dihydroxamate monomer then polymerized it. All functional groups of the monomers and polymers were detected by FT-IR spectrum. It was also examined by nuclear magnetic resonance(NMR).Thermal properties for polymers determined using Perkin elemer differential scanning calorimeter. Dihydroxamate monomer, linear and cross-linked polydihydroxamate also confirmed by making a magenta complex with Fe^{3+} ions in aqueous solution.

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Abbreviation

AMU: Atomic mass unit

DEAM: Diethyl allylmalonate

DEM: Diethyl malonate

DFO: Deferoxamine

DNA: Deoxyribonucleic acid

DMF: Dimethylformamide

DVB: Divinyl benzene

DVB-MA: Divinyl benzene methacrylate

DVBE: Divinyl benzene ethylene

GDMA: Glycol dimethacrylate

FT-IR: Fourier transform infrared spectroscopy

HA: Hydroxamic acid

HDPE: High density polyethylene

LDPE: Low density polyethylene

PAA: Polyacrylamide

PDEAM: Poly(diethyl allylmalonate)

PMA: Poly(methylacrylate)

PMMA: Poly(methylMethacrylate)

PMA-DVB: Poly (methyl acrylate-divenyl benzene)

PEA: Poly(ethylacrylate)

PHA: Poly(hydroxamic acid)

SAHA: Suberoylanilide hydroxamic acid

UV-VIS : Ultra violet – visible spectrophotometer

Xl: Cross-linked

Chapter one

1. Introduction:

Polymer science is a branch of chemistry that tries to create novel materials for new uses with unique features based on the polymer's nature and average molecular weight[1]. Polymers are macromolecules made up of smaller repeating molecules known as monomers[2],[3]. During the polymerization process, a huge number of low molecular weight monomers come together to form larger molecules with molecular weights in the hundreds of thousands or millions AMU[2],[4].

There are very wide applications for polymers, such as adhesives, coatings, foams, and packaging materials, which also include textile and industrial fibers, composites, electronic, biomedical and optical devices, and precursors for many recently developed high-tech ceramics[1].

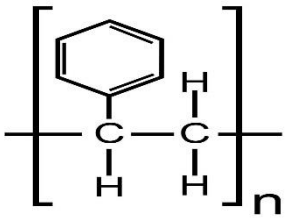
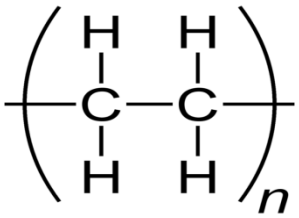
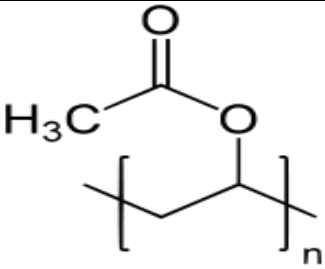
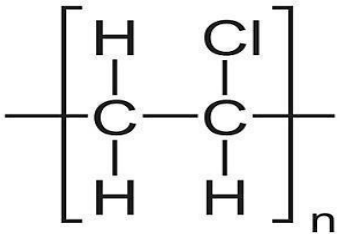
Polymers can be classified according to their structure chains to linear polymers, branched-chain polymers and *Xl*-polymers. A linear polymer is the simplest polymer, with all carbon-carbon bonds arranged in a single straight line, such as HDPE, poly propylene, and others. These polymers have higher strength and difficult to break through. Polymers that have branches in their chain backbone are known as branched polymers, for example LDPE. Cross linking is the production of covalent connections between many polymer chains, resulting in network polymers. *Xl*-polymers have a variety of interesting properties that make them with certain mechanical properties, to insure certain applications. *Xl*-Polymer networks can swell when they absorb water or chemical solvents[1],[3].

Polymer foam, also known as porous polymer material, is a type of polymer that contains a significant number of small foam pores inside its polymer matrix. There are two ways to process polymer foams: foam injection molding and foam extrusion molding.These molding techniques using a supercritical fluid, such as carbon dioxide (CO_2) or nitrogen (N_2), This type of polymers has a number of advantages, including low density, good heat and insulation effects, high specific strength, and corrosion resistance[5].

1.1 Common organic soluble polymers:

Organic soluble polymers are known for their solubility in organic solvent and are not soluble in water. Common examples on this type of polymers are listed in (table 1.1).

Table 1.1 : Common organic soluble polymers.

Polymer	**Polymer structure**	**Solubility**	**Refrances**
Polystyrene		Soluble in benzene, toluene, xylene, chloroform and tetrahydrofuran.	[6]
Polyethylene		Soluble in n-hexane.	[7]
Poly(vinylacetate)		Soluble in different organic solvents.	[8]
Poly(vinylchloride)		Soluble in ketones and esters.	[9]

1.2 Water soluble and water Swellable polymers:

1.2.1 Overview:

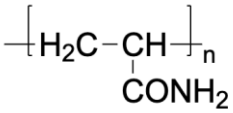
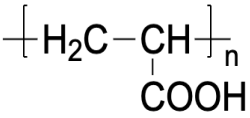
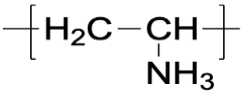
Polymers that may dissolve or swell in water to form a solution or a hydrogel are known as water-soluble or swellable polymers[10].

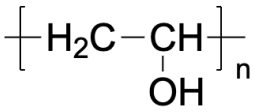
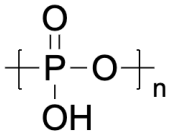
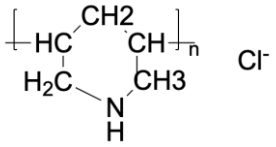
There are different methods using to produe this type of polymers, such as aqueous solution polymerization, inverse suspension polymerization, and inverse emulsion polymerization, and they are all activated by either thermal or redox couple initiators[11]. The presence of hydrophilic groups such as –OH, –CONH–, –$CONH_2$–, and –SO_3H– causes cross linked or hydrogel polymers that they may absorb a huge amount of water[12].

1.2.2 Water-soluble polymer classification according to its source

Polymers may be naturally found in plants and animals (natural polymers) such as proteins, starch, cotton, rubber and silk or may be man-made (synthetic polymers) such nylon-6, 6, poly ethylene and poly(vinyl chloride) also may be semi-synthetic polymers such as cellulose nitrate and cellulose acetate[2],[4],[13].

Table 1.2: Some of synthetic water- soluble polymers[12].

Nonionic water-soluble polymers	**Anionic water-soluble polymers**	**Cationic water-soluble polymers**
		
Poly(acryl amide)	Poly(acrylic acid)	Poly(vinyl amine)

		
Poly(vinyl alcohol)	Poly(phosphoric acid)	Poly(dimethyl diallyl ammonium chloride)

1.2.3 Applications of water soluble polymers:

Water-soluble polymers have numerous applications in pharmaceutical[14], water treatment[15] ,cosmetics, medicine[16], oil recovery[17], pulp and paper manufacture, agriculture,etc[10]. Because of their solution properties and their ability to change the rheology of an aqueous medium and adsorb particles or surface from solution[18]

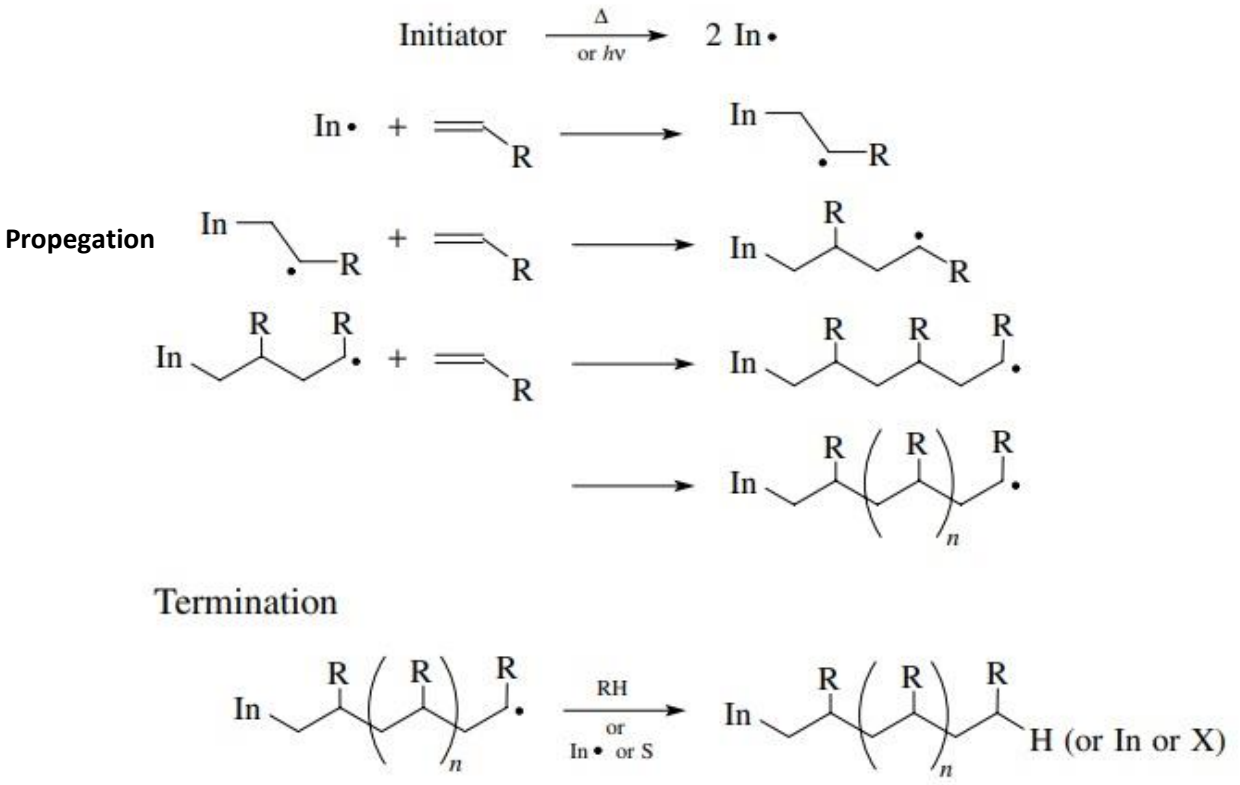
1.3 Chemical synthesis of polymers:

There are different types of polymerization process such as addition polymerization (free radical, cataionic and anionic polymerization) and condensation polymerization[5],[13]. Based on the solubility of monomers the polymerization may be solution polymerization (for water soluble monomers), emulsion and suspension polymerization (for water insoluble monomers or partially soluble)[5].

1.3.1 Free radical polymerization:

As shown in (scheme 1.1) below, there are three steps in free radical polymerization. First is initiation in which free radicals molecules (R•) are created from a free radical initiator (I•), and one of those radicals add to the C=C bond to generate a new radical (RCXY=CXY•) in the presence of an unsaturated monomer (usually of structure CXY=CXY). Second is propegation, in which this radical can react with another monomer, lengthening the chain by one monomer unit and shifting the radical's location to the new chain end. By adding successive units of monomer the polymer chain grows rapidly, while maintaining the active radical site at the end of the propegating or growing chain. A chain radical grow contineously until it loses its active radical site (termination step) either by a termination reaction with

another free radical by a combination or disproportionation reaction with another radical or by a chain transfer reaction with another molecule present in the medium[19],[20].



Scheme 1.1: Steps of free radical polymerization.

1.3.2 Emulsion polymerization:

Aqueous dispersion of polymer particles stabilized by a colloid stabilizer, most commonly a surfactant, is known as emulsion polymerization. Emulsion polymerization has many advantages such as achieve higher rates of polymerization and produce higher molecular weight polymers[19].

The main steps of this emulsion polymerization is emulsifying the monomer (which is normally somewhat insoluble in water) into an aqueous solution of a surfactant then initiating the polymerization by adding a water soluble initiator (e.g. potassium persulfate ($K_2 S_2 O_8$) or an oil-soluble initiator (e.g. 2,2-azobisisobutyronitrile (AIBN)). Typical polymerization monomers involve vinyl monomers of the structure (CH2=CH-)[21]. The free radical polymerization then occure inside the micelles, which are spherical aggregates of typically 50-100 surfactant molecules oriented so that their hydrophobic parts a toward the center of

the micelle while the hydrophilic parts make contact with the aqueous phase, there are formed when the concetration of surfactant is above critical micelle concentration(CMC), as shown in (fig.1.1). By increasing the surfactant concentration, decreasing initiator concentration or lowering reaction temperature, it is possible to achieve high rates of polymerization and produce high molecular weight polymer[19],[21].

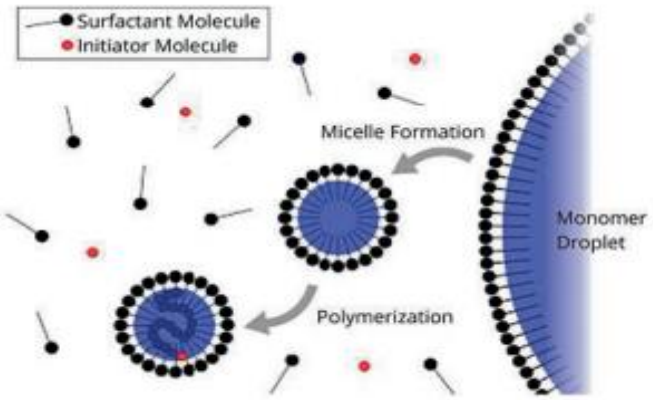


Fig. 1.1: Emulsion polymerization process[21].

1.3.3 Suspension polymerization:

Suspension polymerization is a technique in which monomer(s) that are generally insoluble in water are dispersed as liquid droplets with steric stabilizer and vigorous stirring (which is maintained throughout the polymerization process) to produce polymer particles as a dispersed solid phase(fig. 1.2). While choosing a liquid phase for suspension polymerization, we generally prefer low viscosity, high thermal conductivity. The main aim of suspension polymerization is to achieve as uniform a dispersion of monomer droplets in the aqueous phase as possible, with regulated coalescence of these droplets during the polymerization process[1].

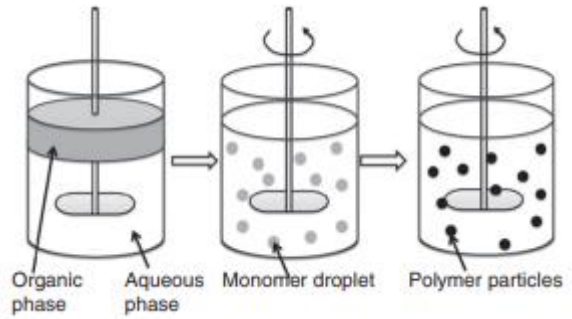
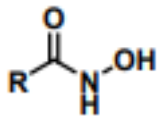


Fig. 1.2 : Suspension polymerization process[22]

1.4 Hydroxamic acid:

1.4.1 Overview:

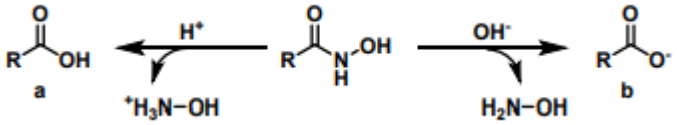
HA also denoted “N-hydroxyamides” or “N-acyl hydroxylamine” was dicovered by Heinrich Lossen in (1869) as a product of hydroxylamine (NH_2OH) and carboxylic acids (RCOOH) reaction (scheme 1.2)[23]. HAs are weak acids, they can be considered diprotic acids[24]. Free hydroxylamine (NH_2OH) is unstable, explosive, and mutagenic[25], So It is commercially available in the form of salts mostly as hydrochloride salt. Free hydroxylamine is generated in situ from hydrochloride salt by treating with base[25]. Unlike common amides, which exhibit high stability, HAs are distinctly reactive, they are smoothly soluble in alkaline solutions due to the stability of the hydroxamate anion[26]. Gupta et al. (2013) described the behavior of hydroxamic acids as quite complicated due to the existence of two tautomeric, keto and enol forms (scheme 1.3)[27].



Scheme 1.2: Chemical structure of the HA moiety.

Scheme 1.3 : Chemical structures of keto and enol form of HA.

Under strongly acidic or basic conditions their chemical behavior is very similar to that of related amides, carboxylic acids, or carboxylates (scheme 1.4)[28].

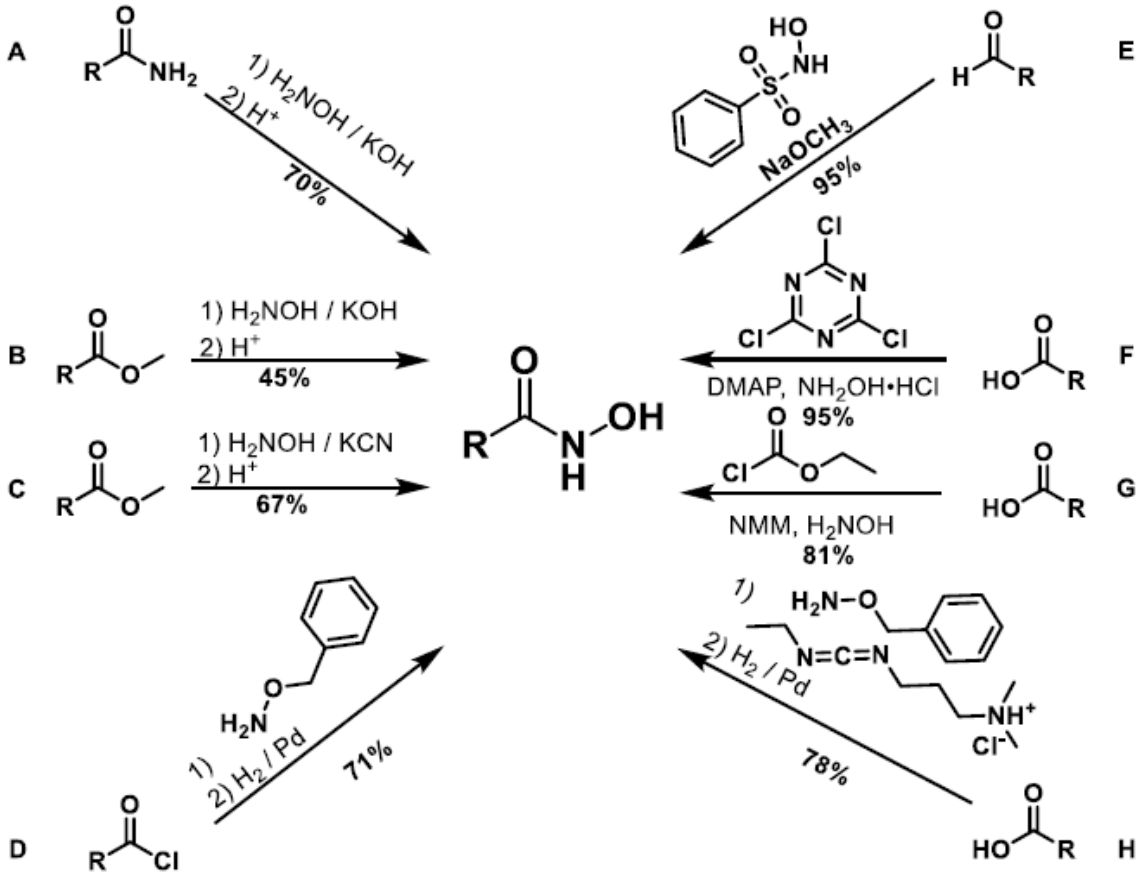


Scheme 1.4 : Reaction pathway of HA under strongly acidic or basic conditions

HAs form bidentate O,O′ complexes with transition metals[29], such as Fe(III)[30], Zn(II),Ni(II)&Cu(II)[31],[32], intensely coloring the metal and HA solutions and has been extensively investigated as a pharmacophoric group of many metalloprotease inhibitors, such as marimastat, a potent broad-spectrum peptidomimetic matrix metalloprotease inhibitor[27]. Hydroxamic acid derivatives are known to show a wide range of biological activities and these molecules are better known for their anticancer properties[25],[33].

1.4.2 Chemical synthesis of hydroxamic acids:

Various HA synthesis methods[25],[26] (Scheme 1.5) was summarized by Keth et al. (2020) [28]. In general, HA are the result of a reaction between hydroxylamine (or one of its derivatives) and a carbonyl compound. Using the ester derivative as starting materials (Scheme 1.5B), a single step preparation can be accomplished. O-acylhydroxylamine is generated initially in this hydroxyl-aminolysis-based pathway, which is then converted to the thermodynamically more stable hydroxamic acid. Alcohols, particularly methanol, are common solvents for this process,the reaction can also be carried out in aqueous solution in the case of water-soluble esters[28], KCN can be added as a suitable catalyst to accelerate the transformation even at neutral pH (Scheme 1.5C)[28],[34]. Amides are another known starting material for the synthesis of hydroxamic acids (Scheme 1.5A)[35]. And Direct reaction of hydroxylamine with acyl chloride(1.5D)[36],[37]. Mixed anhydrides have been employed successfully besides carbodiimidebased coupling methods (Scheme 1.5G, 1.5F)[28]. Angeli in (1896) and Rimini in (1901) were the first to describe the process of creating hydroxamic acids from aldehydes using an oxidizing agent like N-hydroxybenzenesulfonamide to convert aldehydes into hydroxamic acids (1.5E)[28]. Folkers et al. (1995) clarified the preparation of hydroxamic acid by coupling protected hydroxylamines with carboxylic acids under mild codition (Scheme 1.5H)[38].

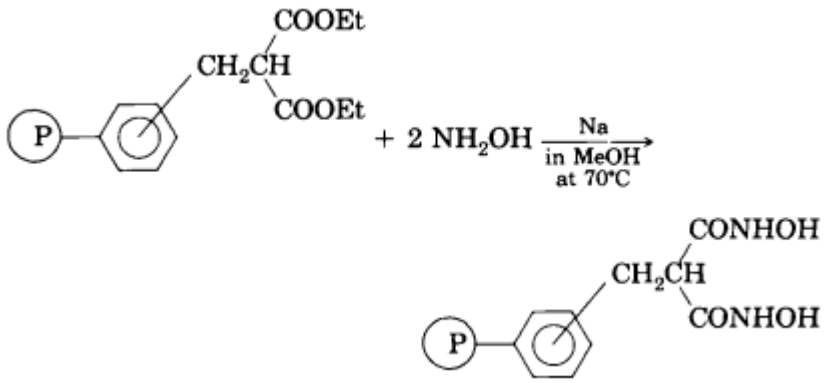


Scheme 1.5 : Various synthetic approaches for the preparation of HA[28].

1.4.3 Preparation of polymers bearing hydroxamic acids:

The first reports on macromolecules containing hydroxamic acids were published in 1942, almost all of the reported methods introduced hydroxamic acids into polymers by modification of polyacryl-derivatives with hydroxylamine via post-polymerization[28].

Takahiro Hirotsu et al. (1986) synthesized chelating polymers having dihydroxamic acid groups through the treatment of polymers having diethyl malonate groups with hydroxylamine (scheme 1.6)[39].



Scheme 1.6: Synthesis of chelating polymers having dihydroxamic acid groups by the treatment of polymers having DEM groups with hydroxylamine.

1.5 Aims of the work:

This work in general aims to produce new polymers that may have midical applications and high potentiality of chelating and removing heavy metal ions from water.

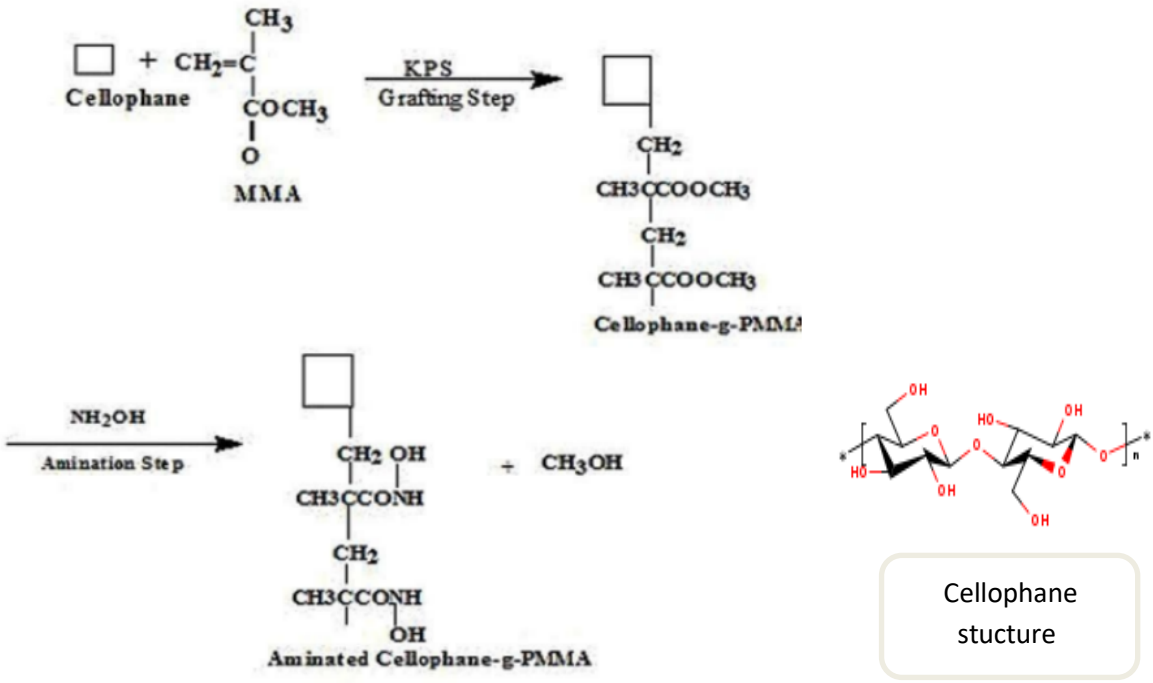
The special aim of this research is to prepare a novel linear and *Xl*-PDEAM and its HA derivative by emulsion and suspension free radical polymerization, then characterize them using different instruments.

Chapter two

2-Litereature review:

2.1 Preperation of HAs polymers:

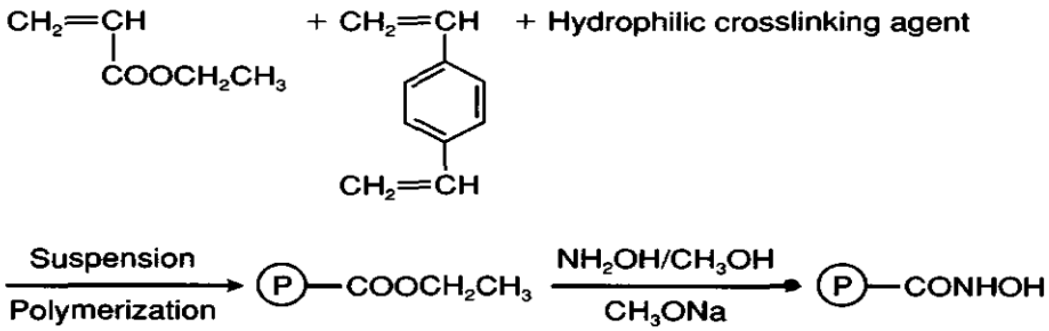
Fawal et al. (2021) used a new method to make poly(hydroxamic acid)(PHA) from poly(methyl methacrylate)(PMMA). PMMA was first grafted onto cellophane membranes under controlled conditions. Second, at 40°C, hydroxylamine was combined with PMMA to functionalize the polymer with HA. The reaction possible mechanism was proposed in (scheme 2.1) [40].



Scheme 2.1: Schematic diagram of the amination process of the cellophane-g-PMMA membranes.

Rahman et al. (2016) created a PHA ligand from polymer grafted corn-cob cellulose (which obtained from Khaya plant), by adding methyl acrylate to the surface of cellulose and then converting it into HA ligand by free radical polymerization, the grafted cellulose reacted with hydroxylamine hydrochloride in basic solution at 70°C for 6 hours after preparation of cellulose grafted with poly(methylacrylate)(PMA), the appearance of the HA group in the IR spectrum verified the conversion of PMA groups into PHA groups[41].

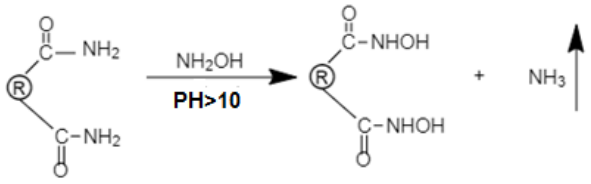
Lee et al. (1995) created PHA from PEA as a starting material by suspension polymerization. DVBE and GDMA were used to made *Xl*-PEA. (scheme 2.2) covers all chemical steps to prepare PHA from PEA[42].



Scheme 2.2: Reaction steps of preparation PHA from *Xl*-PEA with DVB and hydrophilic *Xl*-agent[42].

Haron et al. (1994) prepared PHA from PMA hydrogel by in one step. PMA starting material was converted to resin. PMA-DVB was prepared by using suspension polymerization of DVB-MA solutions, then the product reacted with hydroxyl ammonium chloride to produce HA under basic medium in the presence of potassium hydroxide (KOH) at 45C° for 24 hours[43].

Domb et al. (1988) described a technique for synthesizing PHA from PAA as a starting material, in which PAA interacted with hydroxylamines at 26 °C using a base, the description of the method is shown below (scheme 2.3)[44].



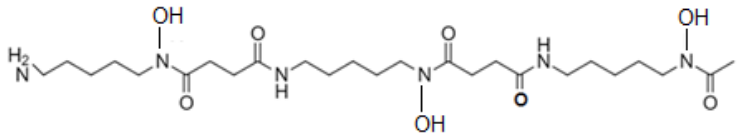
Where R is backbone of polymer

Scheme 2.3: Reaction of PAA and hydroxylamine to produce PHA.

2.2 Applications of HAs:

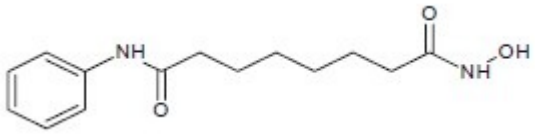
Mzinyane et al. (2020) prepared PHA ligand and it was used for removal of Cu (II) and Fe (II) ions from aqueous solution. The optimum conditions for adsorption were 2 hours agitation time, solution pH of 6 and adsorbent dosage of 1g. The maximum removal efficiency was 90% for Cu (II) and 99.3% for Fe (II)[45].

Keth et al. (2011) discussed the use of HA to treat iron overload due to its high chelating properties with iron ions[28]. Deferoxamine(DFO) (scheme 2.4) is well known for its high stability constant for iron complex preventing iron accumulation due to its strong chelating capability [28],[46].



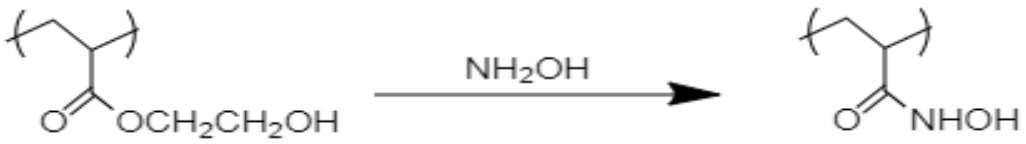
Scheme 2.4: Chemical structure of DFO

Histone is necessary for the cell cycle, and its absence may result in cancer.Histone deacetylase is an enzyme that removes the acetyl group from histone proteins. The DNA will be less accessible to the transcription factor as a result of this removal. Marks et al. (2007) investigated the effects of SAHA on various histone deacetylase classes. SAHA(scheme 2.5) can inhibited histone deacetylase effectively, according to the findings[25],[28],[47], ,[48]&[49].



Scheme 2.5: SAHA structure.

Polomoscanik et al. (2005) synthesized poly functionalized HA gel that can be swell in water and uptack iron ions effectively. (scheme 2.6) representing the synthesis reaction of PHA from Poly(2-hydroxyethyl) acrylate[50].



Crosslinked gel

Scheme 2.6: Synthesis of PHA from Poly(2-hydroxyethylacrylate)

Hydroxamic acid can be used in medicine as an enzymes inhibitor if this enzymes contain a heavy metal. Browner et al. (1995) showed the reaction of hydroxamat with zinc containing enzyme (matrilysin)[51].

Chapter three

3-Methodology:

3.1 Chemicals:

DEAM monomer 99% (Sigma-Aldrich), potassium persulfate 99% (Sigma- Aldrich), sodium lauryl sulfate 99% (Sigma- Aldrich), sodium metabisulfite (Riedel-de Haen), paradivinyl benzen, hydroxylamine hydrochloride, potassium hydroxide, $FeCl_3$ and hydrochloric acid.

Solvent: Degassing distilled water and methanol

3.2 Instruments:

FT-IR BRUKER-Tensor II, UV- 1601 SHIMADZU and Perkin Elemer Differential Scanning Calorimeter in Abu-Dies/Al-Quds University, NMR BRUKER(500MHz) in The Hebrew University.

3.3 Experiments:

3.3.1 Free radical Polymerization of diethyl allyl malonate:

PDEAM $\xrightarrow{\text{Polymerization}}$ linear or cross-linked PDEAM

3.3.1.1 Emulsion polymerization"linear polymer":

- At 60-80 °C

0.024g (0.000083 mole) of Sodium lauryl sulfate as surfactant was transferred to a 100 ml RBF, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 1g (0.0049 mole) of DEAM monomer was added as well using micropipette. 0.593g (0.0021 mole) of potassium persulfate ($K_2S_2O_8$) as free radical initiator was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reflux reaction was carried out at (60-80 °C) with stirring for

6 hours. After that, the linear polymer was put in glass petri desh to dried at room temperature**.**

- At room temperature:

0.024g (0.000083 mole) of sodium lauryl sulfate as surfactant was transferred to a 100 ml round bottom flask, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 1g of DEAM monomer (0.00499mole) was added as well using micopipette. 0.593g (0.00210 mole) of potassium persulfate ($K_2S_2O_8$) as free radical initiator and 0.033g (0.000174 mole) of sodium metabisulfite ($Na_2S_2O_5$) as catalyst to fee radical initiator was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reaction was carried out at room temperature with stirring for 24hours. After that, the linear polymer was put in glass petri desh to dried at room temperature**.**

3.3.1.2 Suspension polymeriztion:

3.3.1.2.1 linear polymerization:

- At 60-80 °C

1g (0.00499 mole) of DEAM monomer was transferred to a 100 ml round bottom flask using micopipette, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 0.593g (0.00210 mole) of potassium persulfate ($K_2S_2O_8$) as free radical initiator was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reflux reaction was carried out at (60-80 °C) with for 6 hours. After that, the linear polymer was put in glass petri desh to dried at room temperature.

- At room temperature:

1g of DEAM monomer (0.00499mole) was transferred to a 100 ml round bottom flask using micopipette, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 0.593g (0.00210 mole) of potassium persulfate ($K_2S_2O_8$) as free radiacal inititor and 0.033g (0.000174 mole) of sodium metabisulfite ($Na_2S_2O_5$) as catalyst to free radical initiaor was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reaction was carried out at room temperature

with stirring for 24hours. After that, the linear polymer was put in glass petri desh to dried at room temperature**.**

3.3.1.2.2 Cross-linked suspension polymerization

Using (1% and 0.5% for moles of monomer) paradivinyl benzene as cross linking agent

- At 60-80 °C

1g(0.00499 mole) of DEAM monomer was transferred to a 100 ml round bottom flask using micopipette, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 0.593g (0.00210 mole) of potassium persulfate ($K_2S_2O_8$) as free radical initiator and (1% , 0.5%) para divenyl benzene as cross linking agent was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reflux reaction was carried out at (60-80 °C) with stirring for 6 hours. After that, the cross-linked polymer was put in glass petri desh to dried at room temperature**.**

- At room temperature:

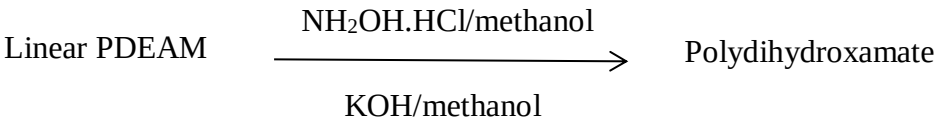
1g (0.00499 mole) of DEAM monomer was transferred to a 100 ml round bottom flask using micopipette, 50ml of degassed distilled water was added to the round bottom flask and was immediately closed with the septum. 0.593g (0.00210 mole) of potassium persulfate ($K_2S_2O_8$) as free radical initiator, 0.033g (0.000174 mole) of sodium metabisulfite ($Na_2S_2O_5$) as catalyst to free radical initiaor and (1% ,0.5%) para divenyl benzene as cross linking agent was dissolved in 15 ml degassed distilled water. Syringe was used to transfer this solution to the reaction. The reaction was carried out at room temperature with stirring for 24hours. After that, the cross-linked polymer was put in glass petri desh to dried at room temperature**.**

3.3.2 Preparing of dihydroxamate polymer:

Fieser et al. (1967) procedure for the general synthesis of hydroxamic acid was used in this research to synthesize dihydroxamate polymer [52].

3.3.2.1 Preparing of diydroxamate polymer using poly(diethyl allylmalonate) as starting material:

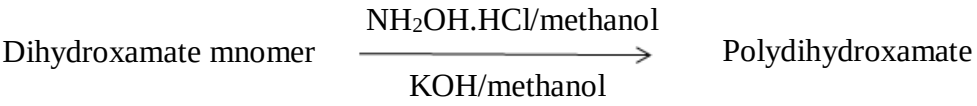
The reaction is observed in the following equation:



46.7g of hydroxylamine hydrochloride (0.672039 mole) was transferred to a beaker then dissolved in 240 ml of methanol. In another beaker, 56g of potassium hydroxide (0.998118 mole)was prepared in 140 ml of methanol and boiled.The two solutions was cooled to 30-40 ℃, and the second solution was added to the first. After cooling in ice to ensure complete separation of potassium chloride, then the solution was filtered quickly and stored in the fridge , 8.5 ml of this solution was added to PDEAM and was kept in sonicator for 24hours. After that, polydihydroxamate was put in glass petri desh to dried at room temperature.

3.3.2.2 Preparing of dihydroxamate polymer using dihydroxamate monomer as starting material:

The reaction is observed in the following equation:



8.5 ml of hydroxylamine solution that was prepared in (section 3.3.2.1) was added to 1g(0.00499mol) of DEAM monomer and stirring for 24hours. After that, dihydroxamate monomer was dried, then polymerized as shown in (section 3.3.1.2.1 at room temperature).

3.3.3 % HA on the polymers ($FeCl_3$ Test):

In this work, an estimation of the hydroxamic acid functionality was made by forming a complex between the hydroxamic groups and Fe^{+3} and monitoring the UV absorbance of the complex[53] at λ_{max} 461nm.

1-Preperation of solution (100ppm) from dihydroxamic acid monomer.

0.01g of dihydroxamate monomer was put in 100ml volumetric flask and it was dissolved in few amount of distilled water, the solution medium was converted to acidic using hydrochloric acid and the volume was completed with distelled water up to the mark of the flask. The same steps were applied for each dihydroxamate polymers.

2-Preperation of $FeCl_3$ solution.

4.866 g of $FeCl_3$ was dissolved using small amount of distilled water in 100ml volumetric flask then the flask was completed with distilled water up to the mark to prepare 0.300 molar $FeCl_3$ solution, 1ml of this solution was trasferred using pipette to 100 ml volumetric flask and completed with distelled water up to the mark (cocentration of $FeCl_3$ was 0.003molar (486.600 ppm)).

3-Preperation of calibration curve.

Five volumetric flasks (50ml) were used, 2ml of monomer solution was put in each flask using pipette, 5ml of $FeCl_3$ solution (486.600ppm) was put in the first flask using pipette, 10ml was put in the second, 15 ml was put in the third and 20ml was put in the last one, the volume of each flask was completed with distelled water up to the mark, the concentration of the monomer become(4ppm) in each flask and $FeCl_3$(48.600ppm, 97.00ppm, 146.00ppm and 194.600ppm respectively).

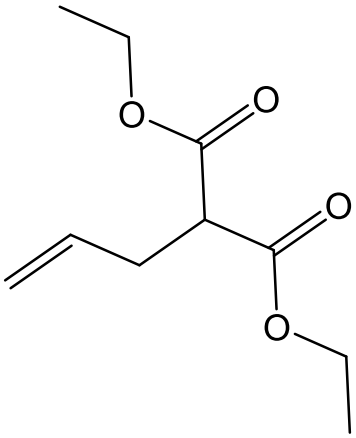
The absorbance of each solution was measured using UV-Vis spectrometer at λ_{max}=461nm and the calibration curve was drawn(Absorbances Vs Concentrations of $FeCl_3$).The same steps were applied for each dihydroxamate polymers(PHA).

% HA on polymer = (Absorbance for $FeCl_3$ in PHA solution / Absorbance for $FeCl_3$ in dihydroxamate monomer solution) * 100%

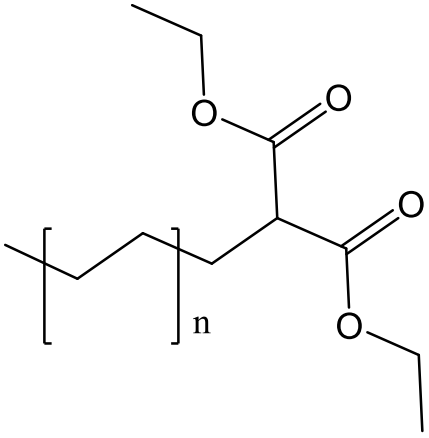
Chapter four

4.Results and discussion:

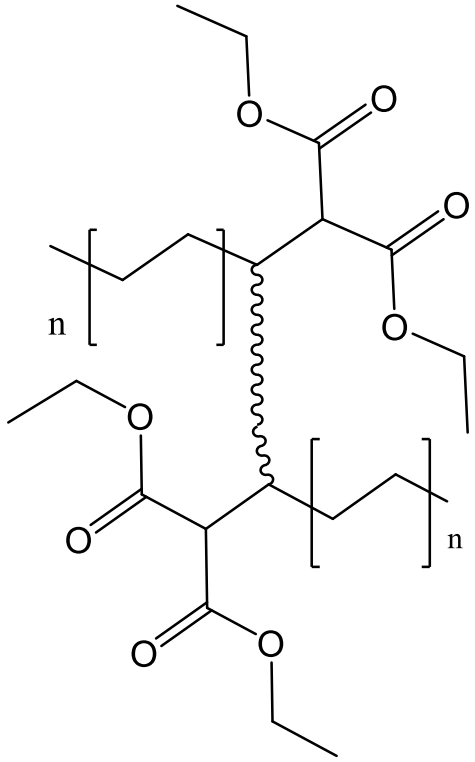
In this research, linear (scheme 4.2) and *Xl*-PDEAM (scheme 4.3) was prepared by emulsion and suspention free radical polymerization of DEAM monomer $C_{10}H_{16}O_4$ (scheme 4.1) (molecular weight 200.23 g/mol, Boiling Point 222.0°C to 223.0°C) also dihydroxamate monomer (scheme 4.4), linear polydihydroxamate (scheme 4.5) and *Xl*-polydihydroxamate (scheme 4.6) were prepared.



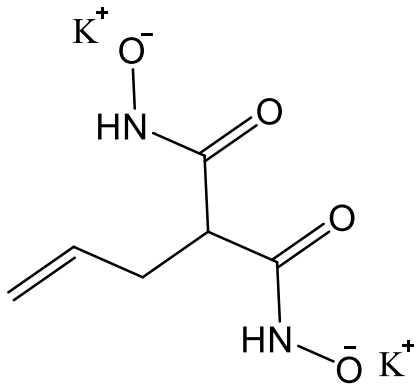
Scheme 4.1: Structure of DEAM monomer.



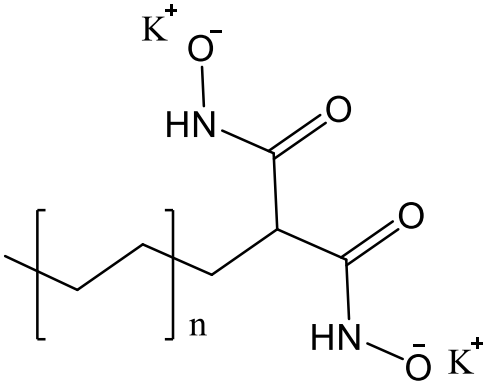
Scheme 4.2: Structure of linear PDEAM.



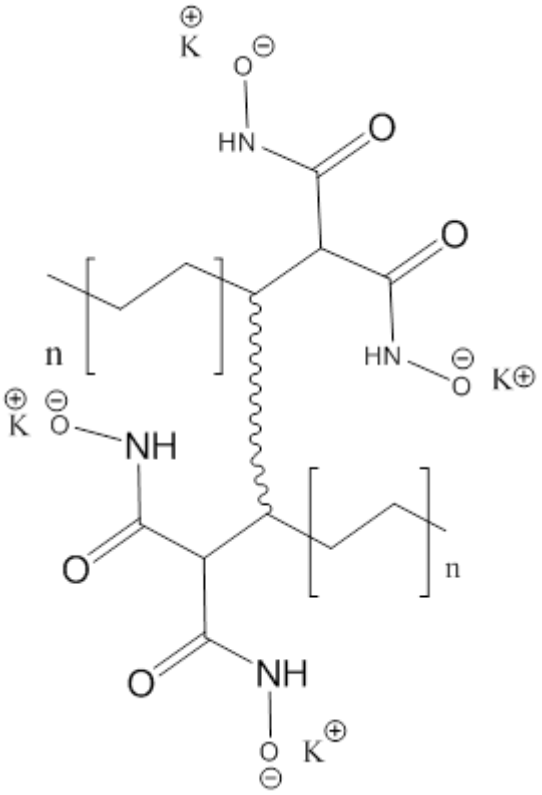
Scheme 4.3: Structure of *XI*-PDEAM.



Scheme 4.4: Structure of dihydroxamate monomer.



Scheme 4.5: Structure of linear polydihydroxamate.



Scheme 4.6: Structure of *XI*-polydihydroxamate.

Dihydroxamate monomer was appeared as a viscus fine particles that dissolved in water, linear polydihydroxamate as pale-yellow to wight particles also soluble in water and *Xl*-polydihydroxamate as partialy gel particles were insolule in water. Linear and *Xl*-PDEAM also insoluble in water. Dihydroxamate monomer, linear and *Xl*-polydihydroxamate were confirmed by making a magenta complex with Fe^{3+} ions in aqueous solution. While the starting material DEAM monomer and PDEAM gave negative result with Fe^{3+}(fig.4.1).

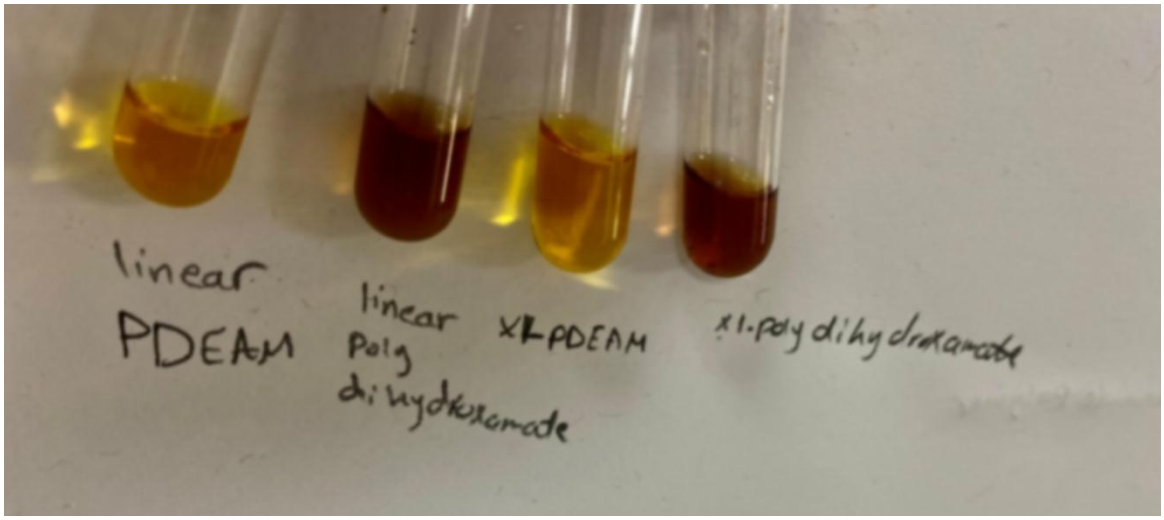


Fig. 4.1: Reactions of linear PDEAM, linear polydihydroxamate, *Xl*-PDEAM and *Xl*-polydihydroxamate with $FeCl_3$ solution.

The percentage of emulsion polymerization for linear PDEAM and *Xl*-PDEAM was about 75% and 69% respectively when the heating was used in polymerization and 70%, 65% respectively when the polymerzation was done at room temperature, it was concluded that heat helps to form a stable emulsion by increase the kinatic energy of particles and its become more contact to each other this was increased the rate of polymerization. In suspension polymerization the percentage was lower than emulsion under same conditions this gave an indication that micelles helped to acheaved high rate of polymerization, for linear PDEAM and *XI*-PDEAM was nearly 69%, 65% respectively when heat was used and 64%, 62% respectively when heat was not used. And for polydihydroxamate that prepared from dihydroxamate monomer was 74%.

4.1 Fourier Transform Infrared (FT-IR) spectrum:

Table 4.1 shows frequencies observed from the corresponding functional groups of DEAM monomer (fig.4.2)

Functional groups	**Frequency(cm^{-1})**
C=O	1730.12
C=C	1643.83
C=C-H	3081.68
C-C-H	2982.95
C-O	1234.02

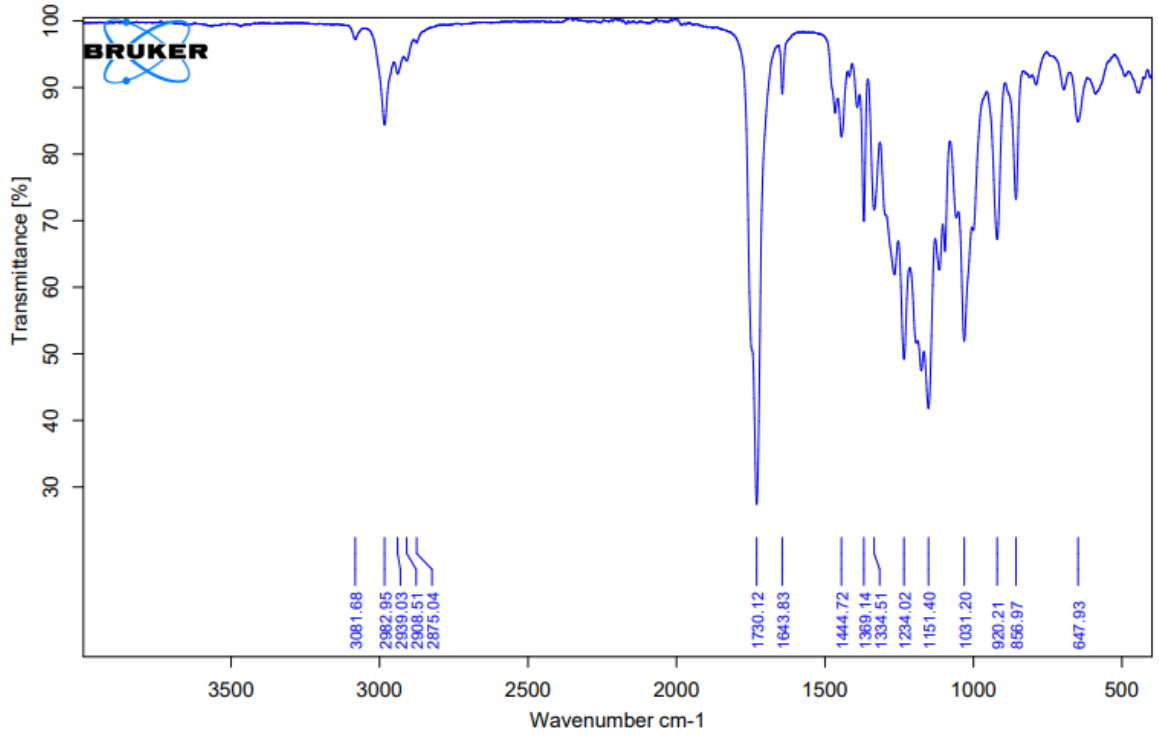


Fig 4.2: FT-IR spectrum for DEAM monomer

-For linear PDEAM:

Linear PDEAM which prepared by emulsion and suspension free radical polymerization in differrent coditions showed difference in the FT-IR bands that appeared in spectrum of DEAM monomer shown in (fig.4.2), where as the stretching bands of C=C and C=C-H nearly disappeared (fig.4.3, fig.4.4, fig.4.5, fig.4.6). This indicates that the polymerization process on the C=C has been successful.

The best polymerization condition for preparing of PDEAM as concluded from FT-IR for emulsion & suspension free radical polymerization is (at 60-80 ℃), this indicated by clearly increased of the intensity of C-C H stretching bands that appeared between 2900cm-1 and 2981cm^{-1}.

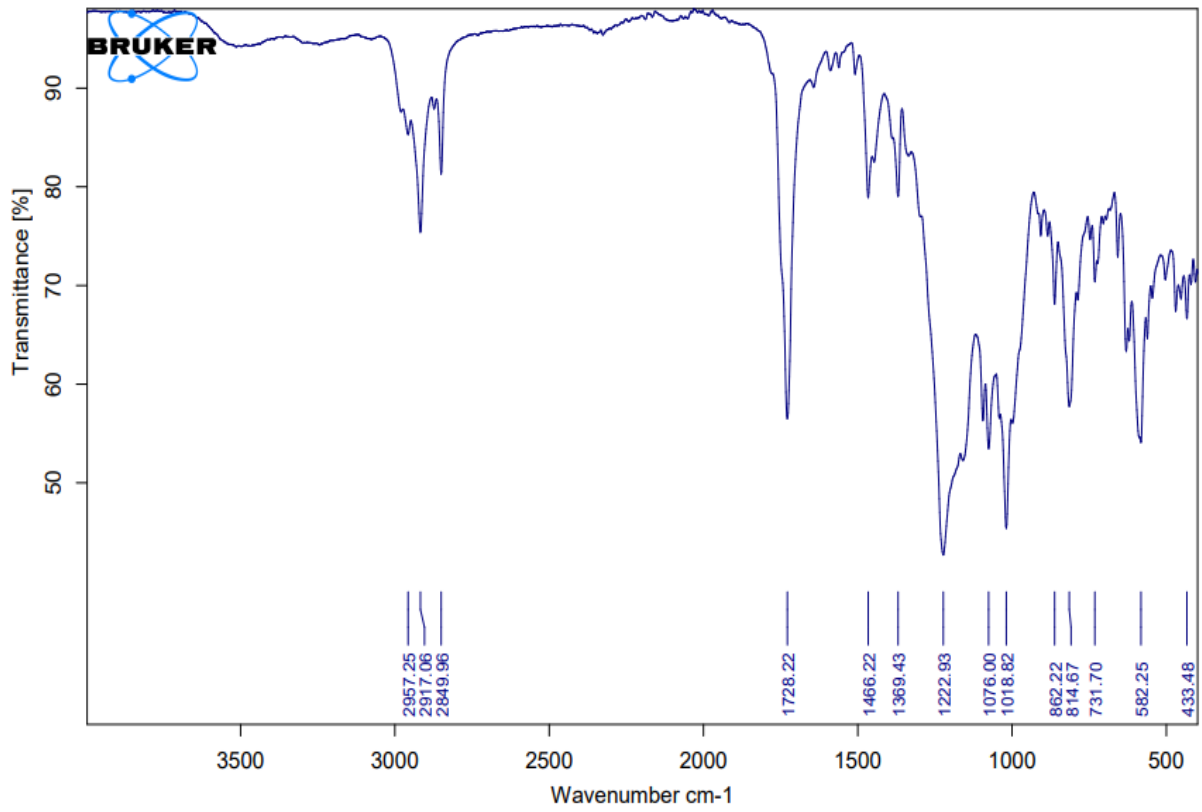


Fig 4.3: FT-IR spectrum for linear PDEAM prepared by emulsion free radical polymerization(at 60-80℃).

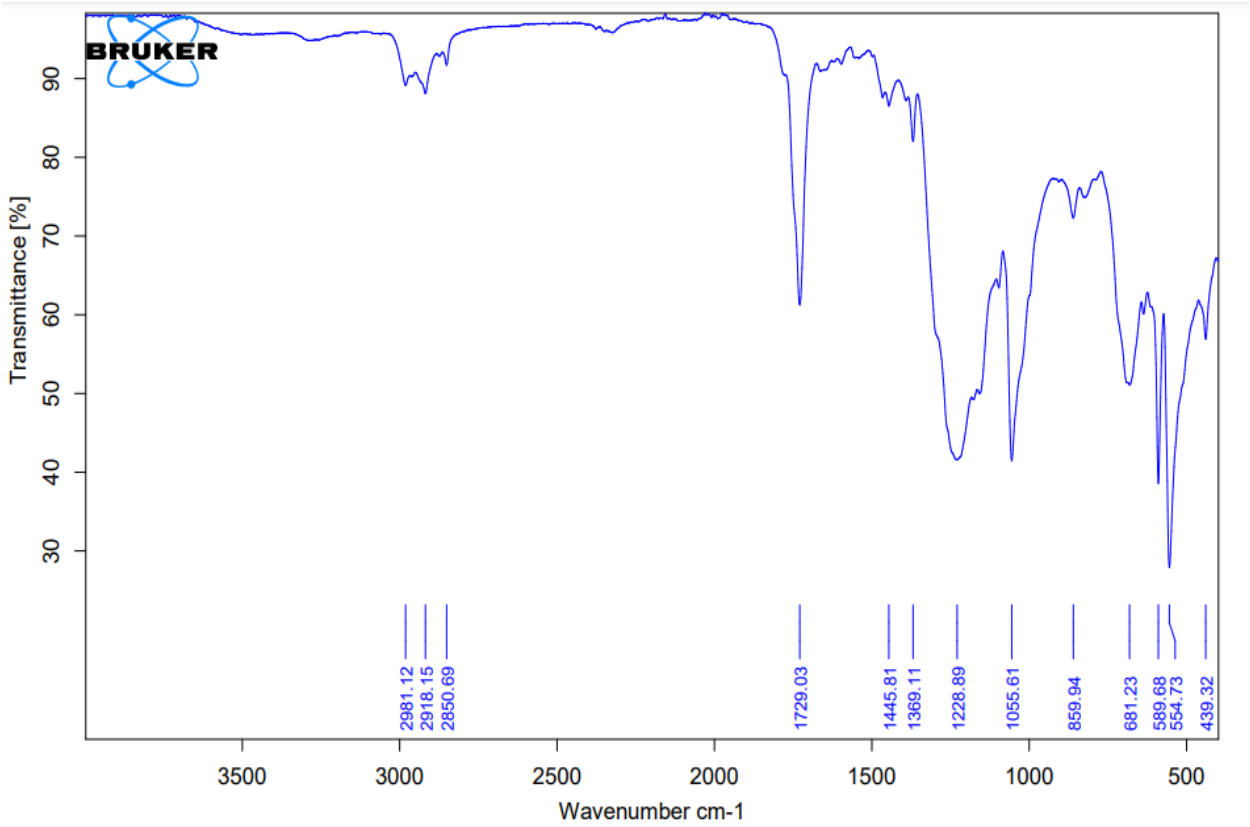


Fig 4.4: FT-IR spectrum for linear PDEAM prepared by emulsion free radical polymerization(at RT).

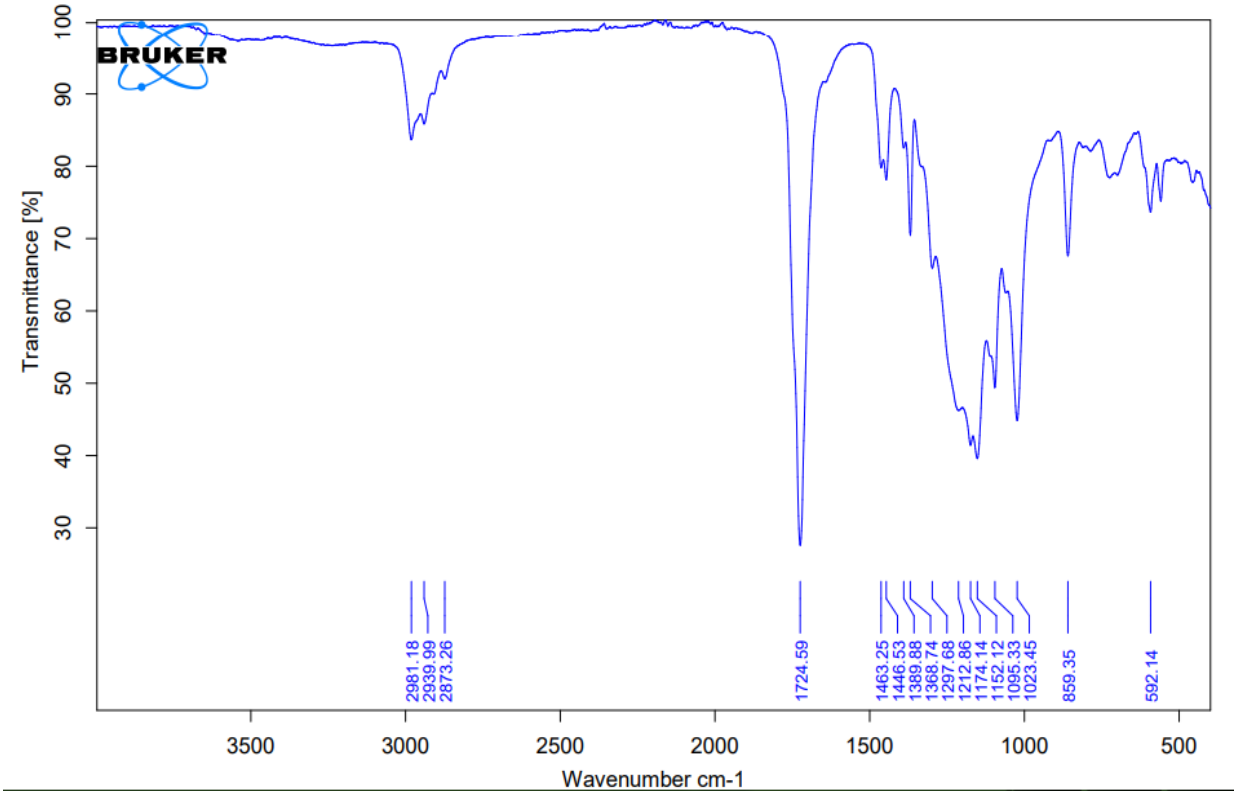


Fig 4.5: FT-IR spectrum for linear PDEAM prepared by suspension free radical polymerization(at 60-80℃).

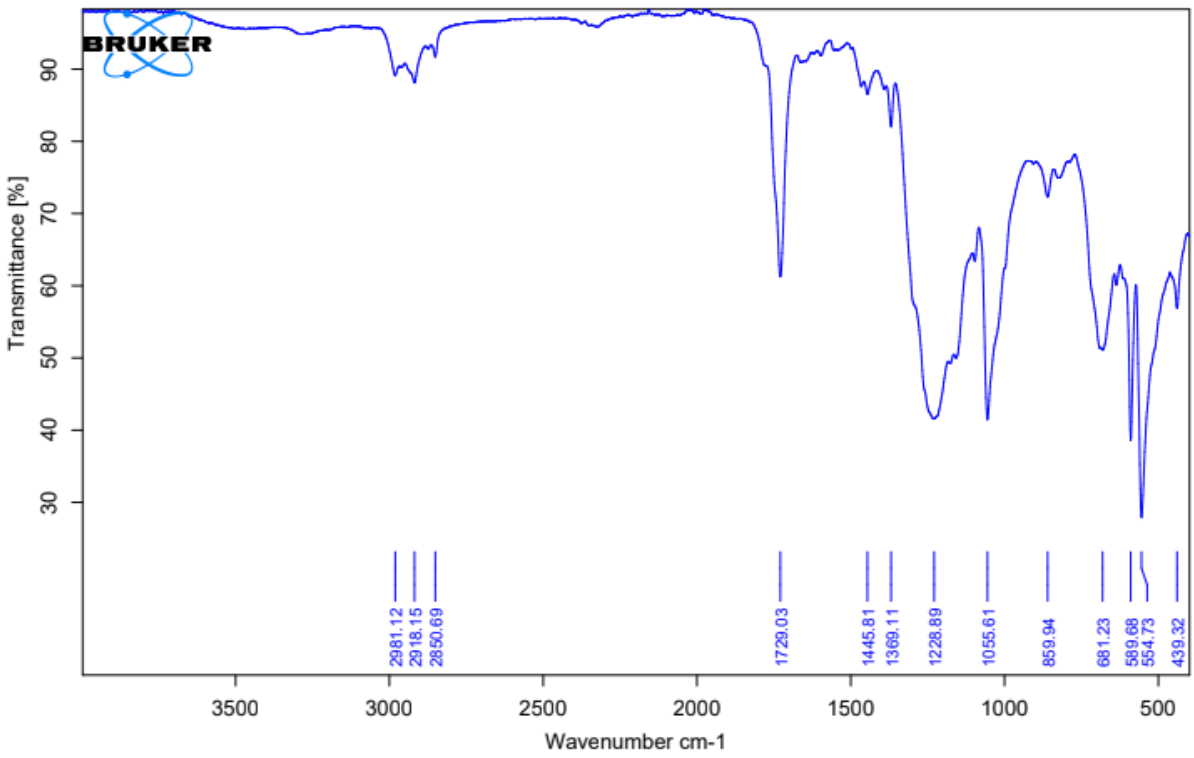


Fig 4.6: FT-IR spectrum for linear PDEAM prepared by suspension free radical polymerization(at RT).

-For *Xl*-PDEAM:

Cross-linked polymer can be inferred by the apperance of cross-linking agent bands, for *Xl*-PDEAM the main band for cross-linking agent is C-H stretching band for benzene ring for paradivinyl benzene after 3000cm^{-1}, this was appeared when polymerization occurred at RT using both 0.5% paradiviyl benzene (on 3225.15cm^{-1}) (fig.4.7) and 1% (on 3254.42cm^{-1}) (fig.4.8). When polymerization occurred (at 60-80 ℃) the C-H stretching band for benzene ring didn't apperared clearly (fig.4.9)&(fig.4.10)..

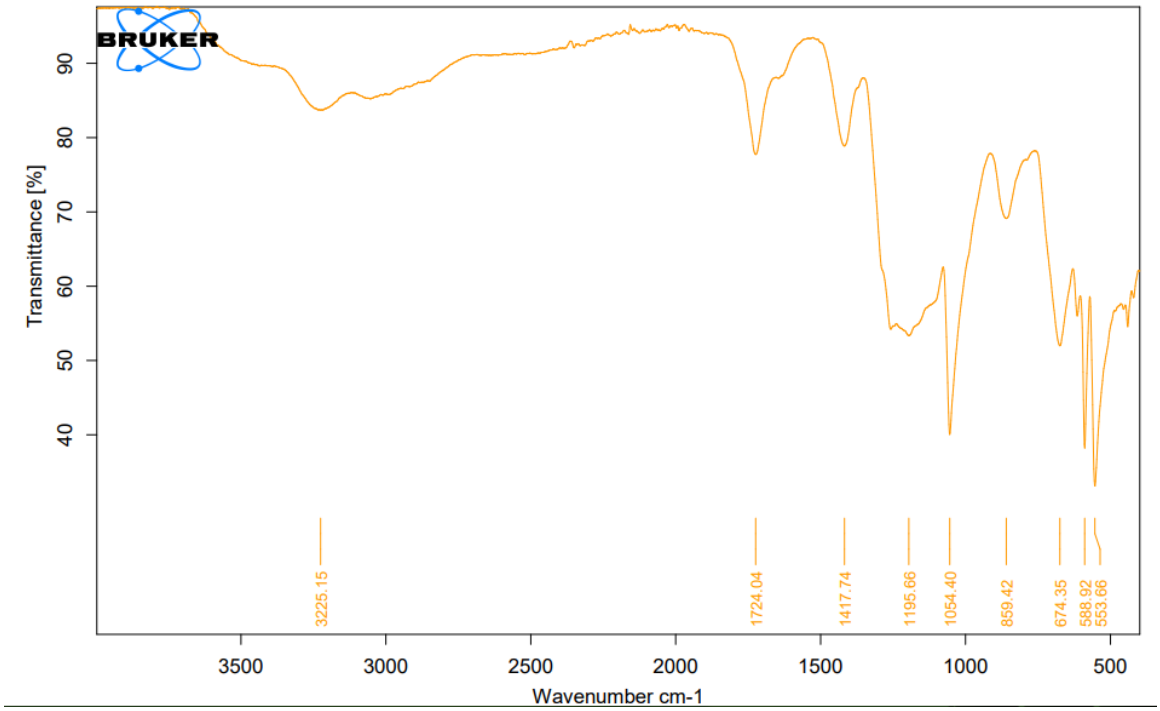


Fig 4.7: FT-IR spectrum for *Xl*- PDEAM prepared by suspension polymerization(at RT using 0.5% paradivinyl benzene).

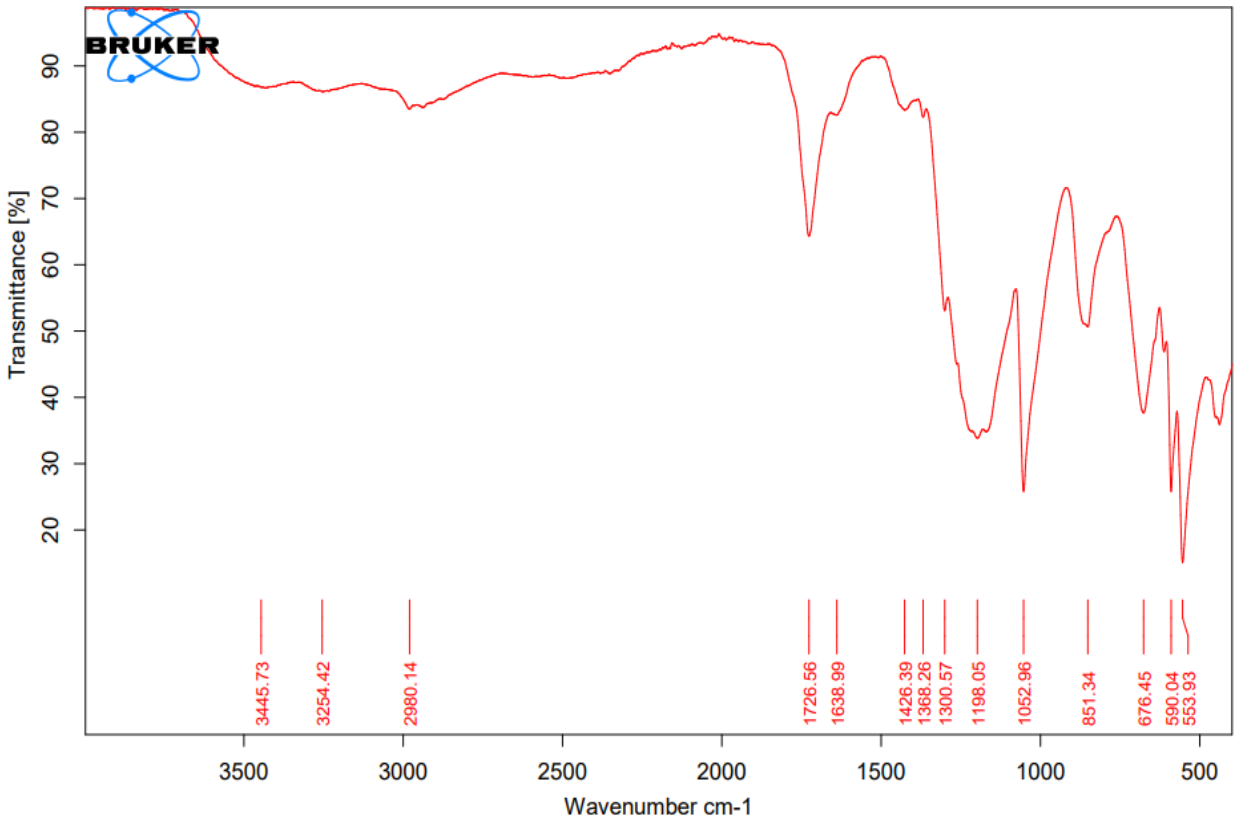


Fig 4.8: FT-IR spectrum for *Xl*-PDEAM prepared by suspension polymerization(at RT using 1% paradivinyl benzene).

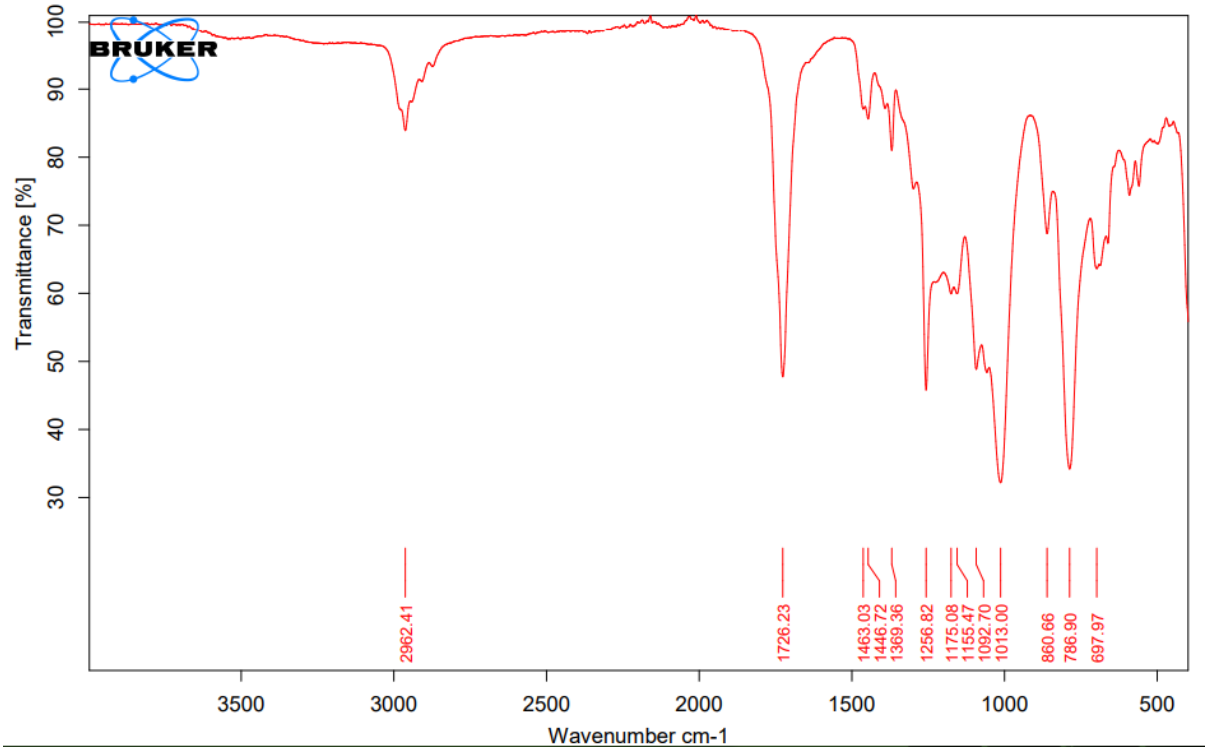


Fig 4.9: FT-IR spectrum for *Xl*- PDEAM prepared by suspension free radical polymerization(at 60-80℃ using 0.5% paradivinyl benzene).

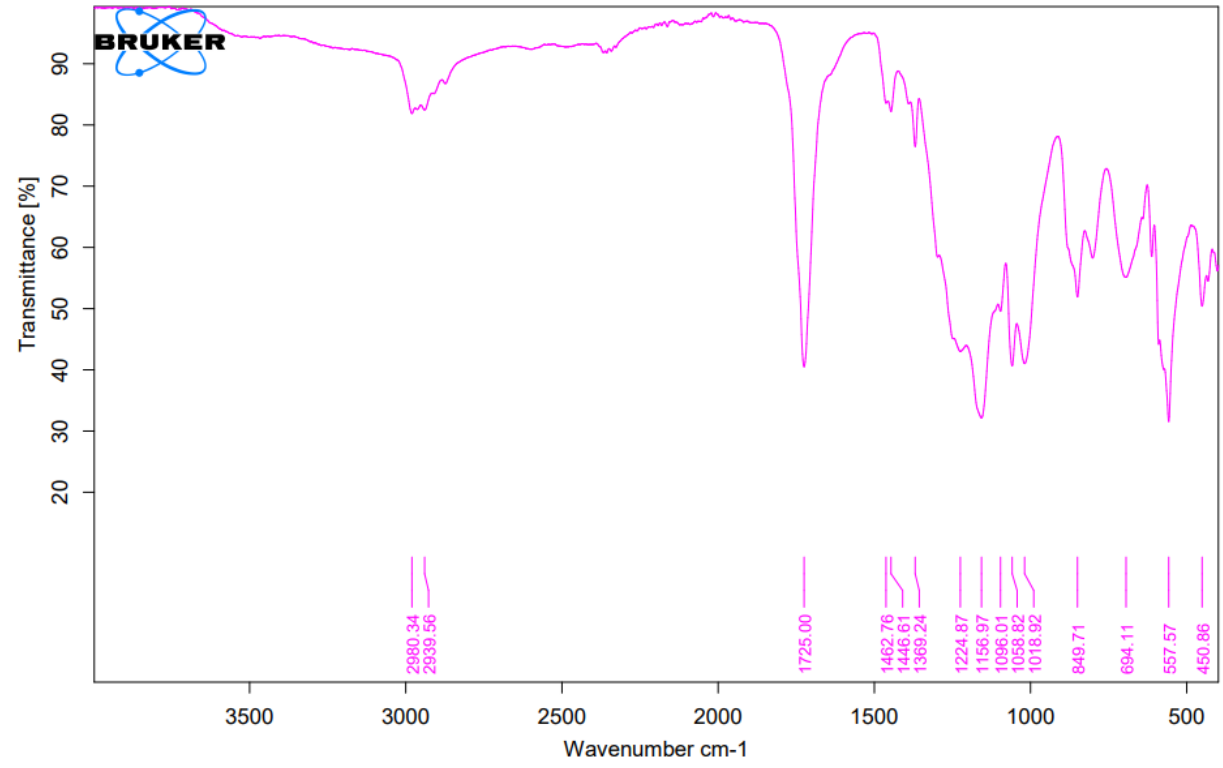


Fig 4.10: FT-IR spectrum for *Xl*- PDEAM prepared by suspension polymerization(at 60-80℃ using 1% paradivinyl benzene).

-For poly dihydroxamate:

Addtion of HA group to linear PDEAM was well done, this observed throgh the apperance of new bands indicated to hydroxamate group include the band on 1099.01cm^{-1} was refered to C-N stretching band, 1585.82cm^{-1} for N-O stretching and on 3222.12cm^{-1} is overlapping for O-H and N-H stretching band. The symetrical and asymetrical bands of C=O appeared on 1724.08cm^{-1} and 1667.23cm^{-1} (fig. 4.11).

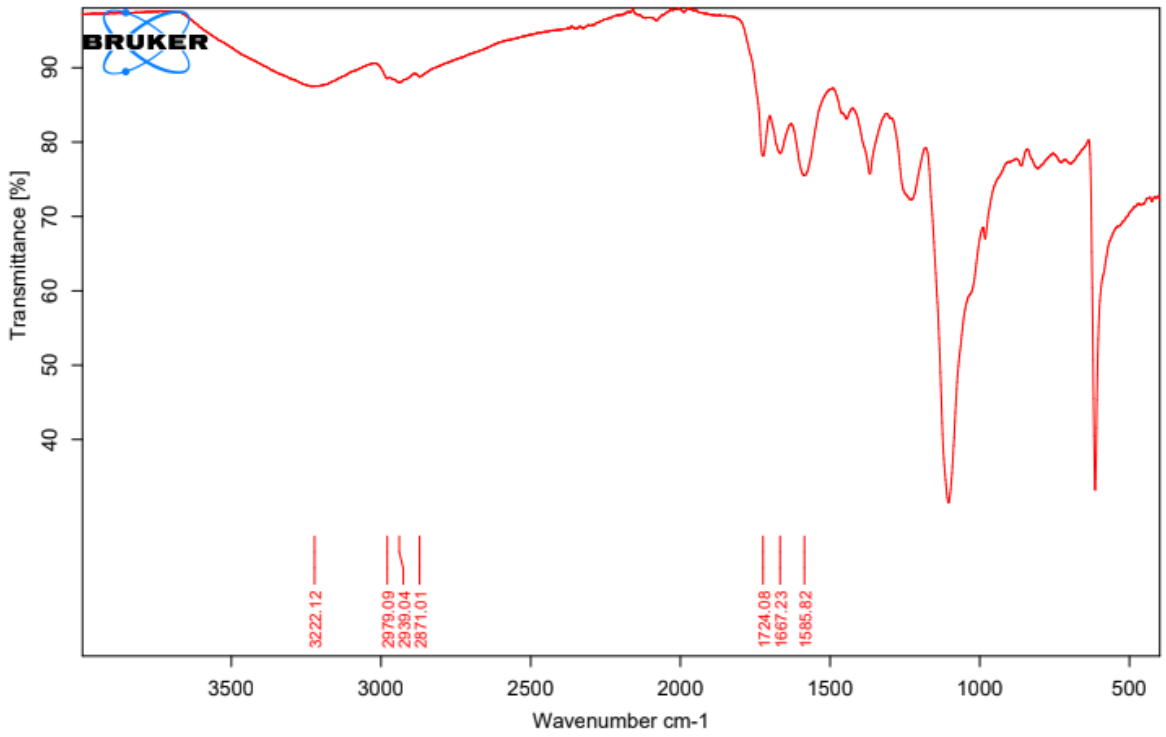


Fig 4.11: FTIR spectrum for linear polydihydroxamate prepared by addition of HA groups to PDEAM

Table 4.2 frequencies observed from the corresponding functional groups of dihydroxamate monomer.

Functional groups	**Frequency(cm^{-1})**
Symmetrical & asymmetrical C=O	1630.5 and 1732.9
C=C	1543.96
C-N	1058.9
N-H	3299.19
O-H	3100.00
C=C-H	3053.93

The FT-IR spectrum of the monomer confirmed the presence of hydroxamate functional group.(fig. 4.12)

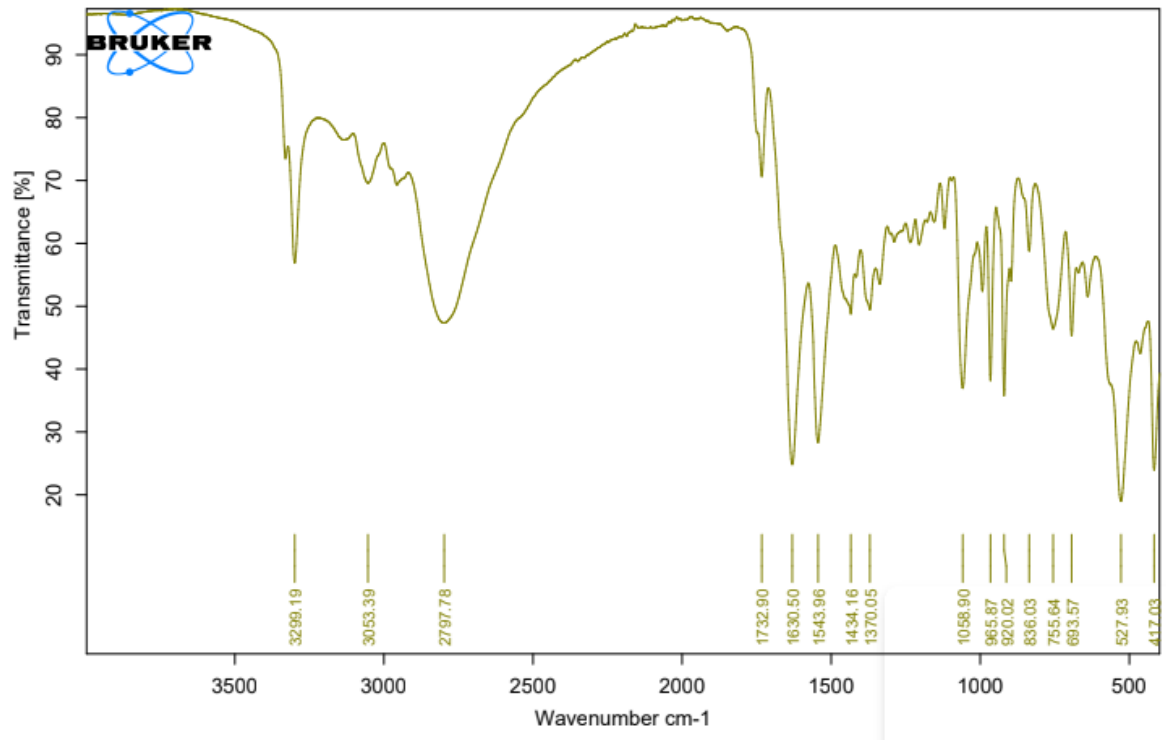


Fig 4.12: FT-IR spectrum for dihydroxamate monomer.

Polydihydroxamate prepared successfully by polymerization of dihydroxamate monomer, C=O stretching band was appeared on 1632.30cm^{-1}, the band intensity of C=C on 1547.25 cm^{-1} and C=C-H on 3054.19cm^{-1} were decreased but didn't disappeared, this indicates that

the polymerization process did not occur completely, perhaps it needed more time. The band on 1054.42cm^{-1} refered to C-N stretching band, stretching band for N-H on 3298.92cm^{-1} and O-H on 3196.10cm^{-1}.(fig. 4.13)

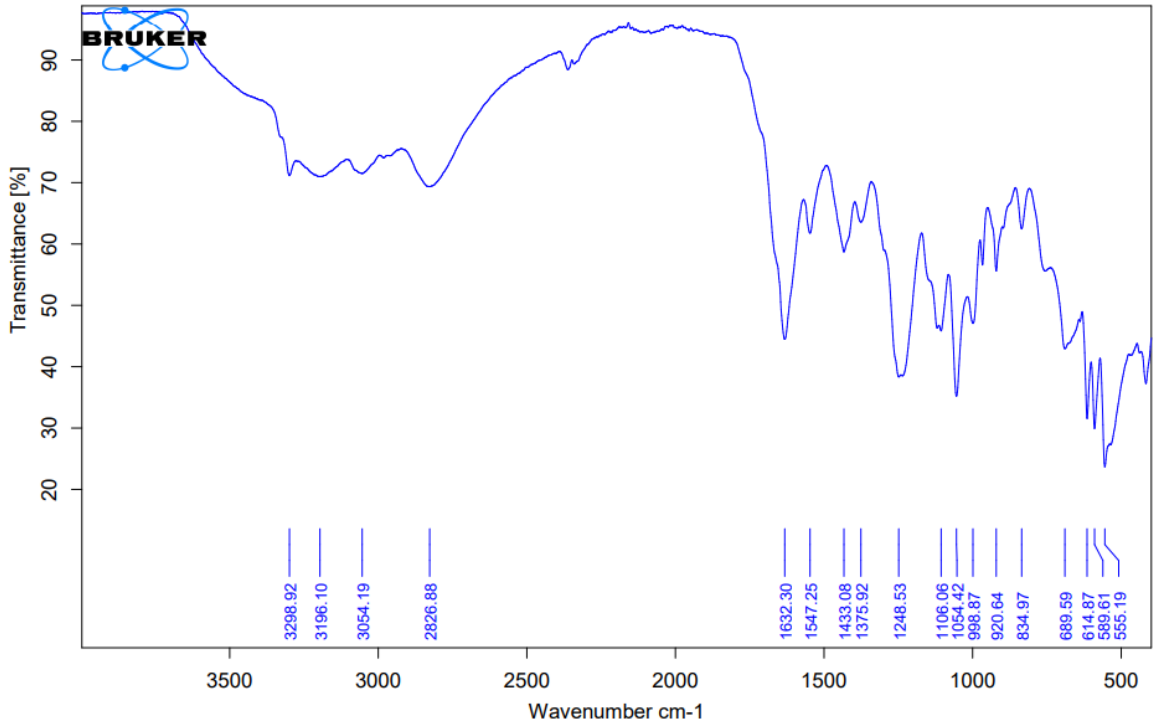


Fig 4.13: FT-IR spectrum for polydihydroxamate prepared by polymerization of dihydroxamate monomer.

4.2 Differential scanning calorimetry (DSC) data:

The melting point of polymers were determined using Perkin elemer differential scanning calorimeter. The used temperature range was from room temperature to 450°C with a heating rate of 10°C/min.

There are two modes for analysis, heating and cooling, in the cooling mode(upper curve) there are no transition peaks appeared. In the heating mode(lower curve), linear PDEAM (fig.4.14) was stable at all temperature between 22.63°C and 120°C, crystallization was occurred in the range (120°C -240°C) and melting was in the range (300°C -380°C), melting point was 333.20°C.

Linear polydihydroxamte, first case, when the hydroxamic acid groups added to PDEAM(fig.4.15), the polymer was stable from 22.63°C to 110°C, between 110°C and 149°C glass transition was occred, the crystallization occurred in the range (149°C -220°C) and melting was in the range (240°C -360°C), melting point was 319.20°C. The difference in crystallzation and melting for PDEAM and polydihydroxamte was due to difference in the functional groups on the two polymes (ester groups on PDEAM and hydroxamate groups on polydihydroxamate). Second case, when hydroxamic acid groups added to DEAM monomer and then polymerized(fig.4.16) the stable state of polymer was between 22.63°C and 90°C, there are three peaks appeared in the ranges (120°C-165°C, 165°C-195°C and 195°C-225°C) this indicated that there are more than one degradation step or may due to presence of impurities, the melting was occurred in the range (225°C-350°C), melting point was 304.69°C.

Cross-linked polymers do not melt and finally decompose when they are heated[54]. There are different peaks appeared in DSC analysis for *Xl*-PDEAM and *Xl*-polydihydroxamate indicated different functional groups, *Xl*-PDEAM (that was prepared using 0.5% cross-linking agent at room temperature) was stable from 22.63°C to 150°C, crystallization was in the range(150°C -245°C) and degradation between 300°C and 460°C (fig.4.17). When *Xl*-PDEAM was used to prepare *Xl*-polydihydroxamate, the product was stable from 22.63°C to 100°C, glass transition occurred in the range(100°C -120°C) this indicated that cross-linking did not existing may be the hydroxamate group affect on it, crystallization in the range(140°C -220°C) and melting occurred in the range(245°C -400°C).

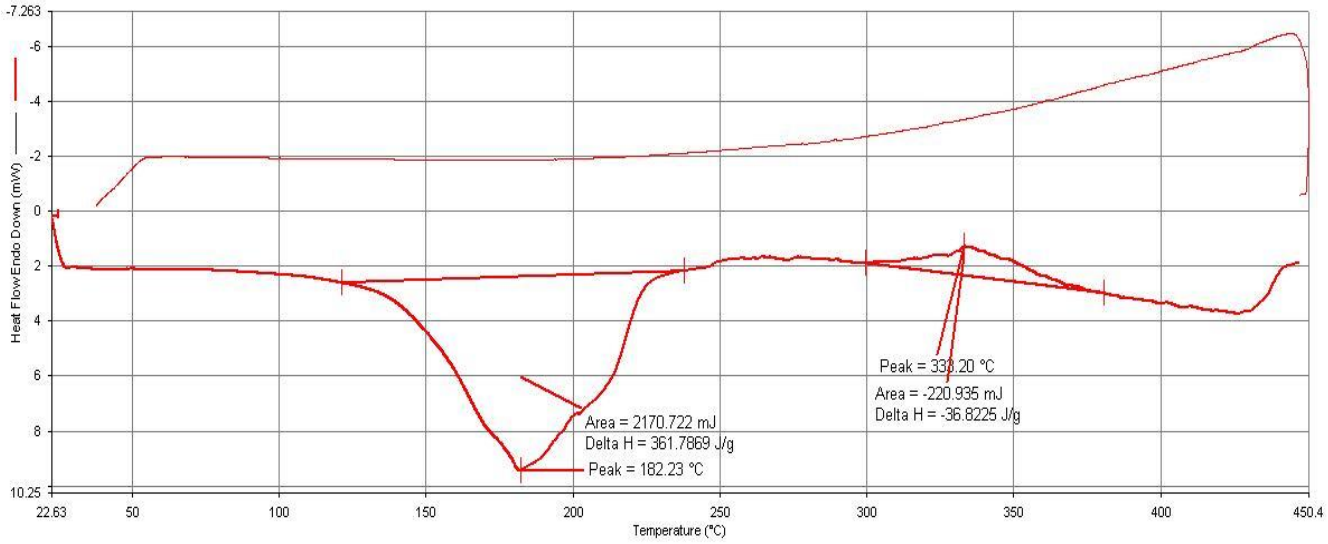


Fig.4.14: DSC for linear PDEAM.

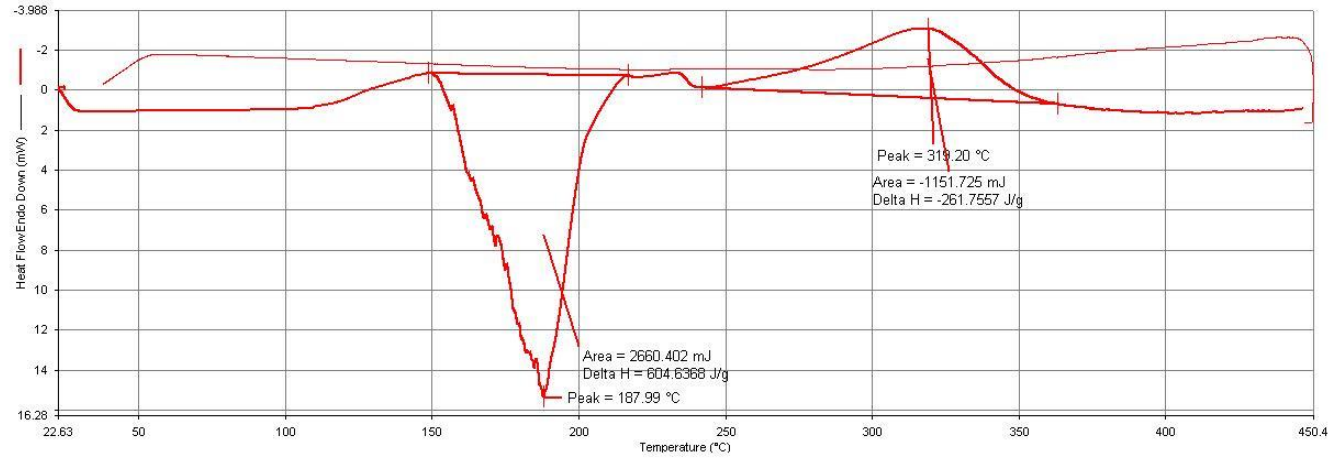


Fig.4.15: DSC for linear polydihydroxamate prepared by adding of hydroxamic acid groups to linear PDEAM.

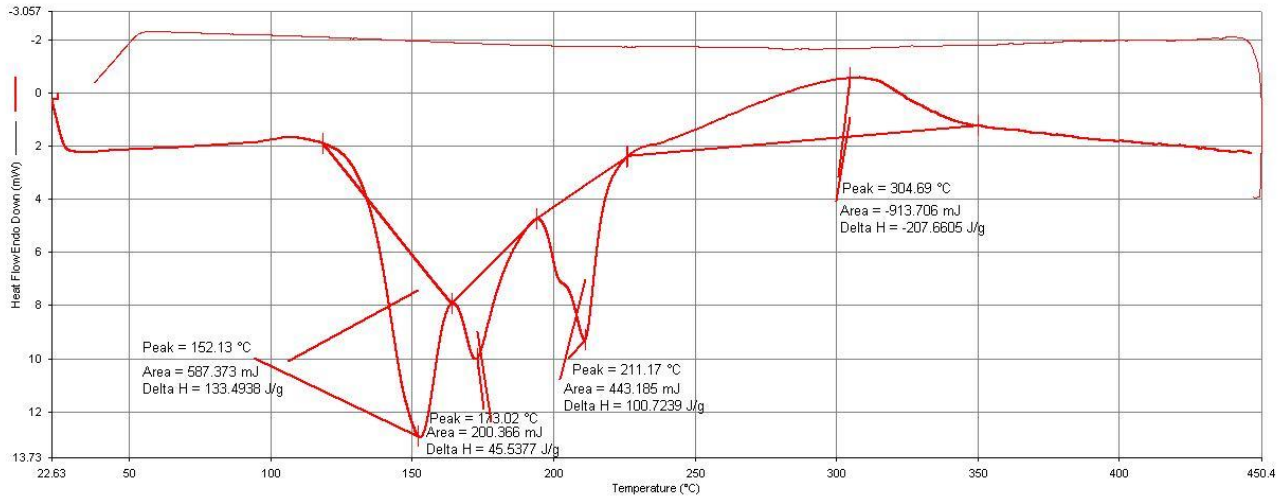


Fig.4.16: DSC for linear polydihydroxamate prepared by polymerization of dihydroxamate monomer.

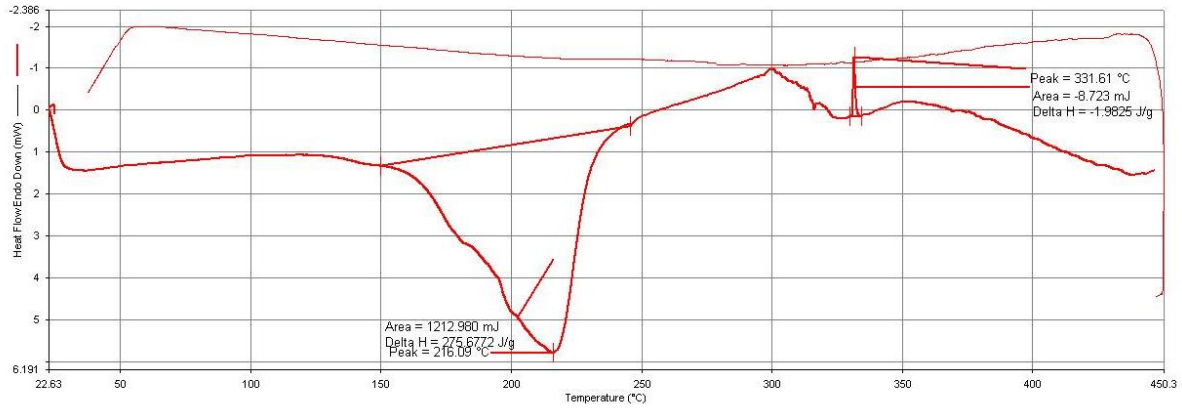


Fig.4.17: DSC for *Xl*-PDEAM(0.5% paradivinyl benzene at room temperature)

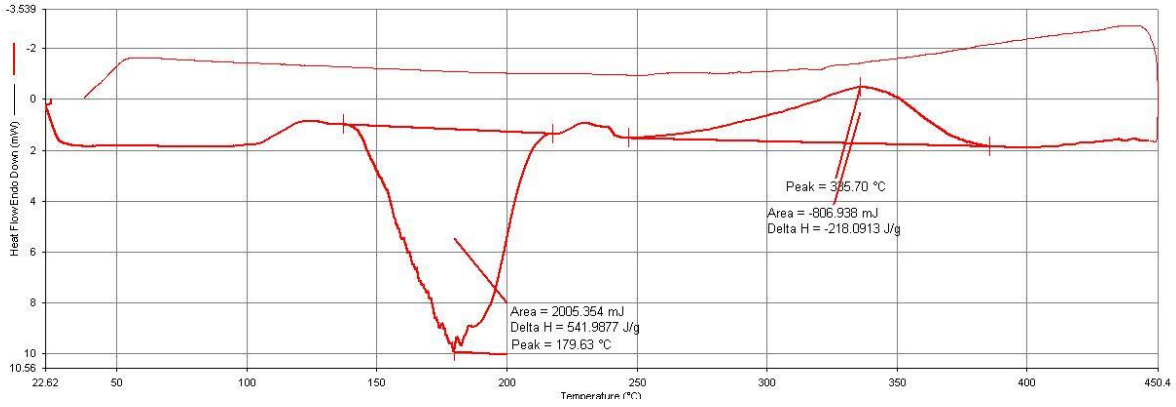


Fig.4.18:DSC for product of *Xl*-PDEAM(0.5% paradivinyl benzene at room temperature) and hydroxamic acid.

4.3 Nuclear Magnetic Resonance (NMR) spectroscopy:

(Fig.4.19) show the ^{1}H NMR spectrum for the DEAM monomer[55].

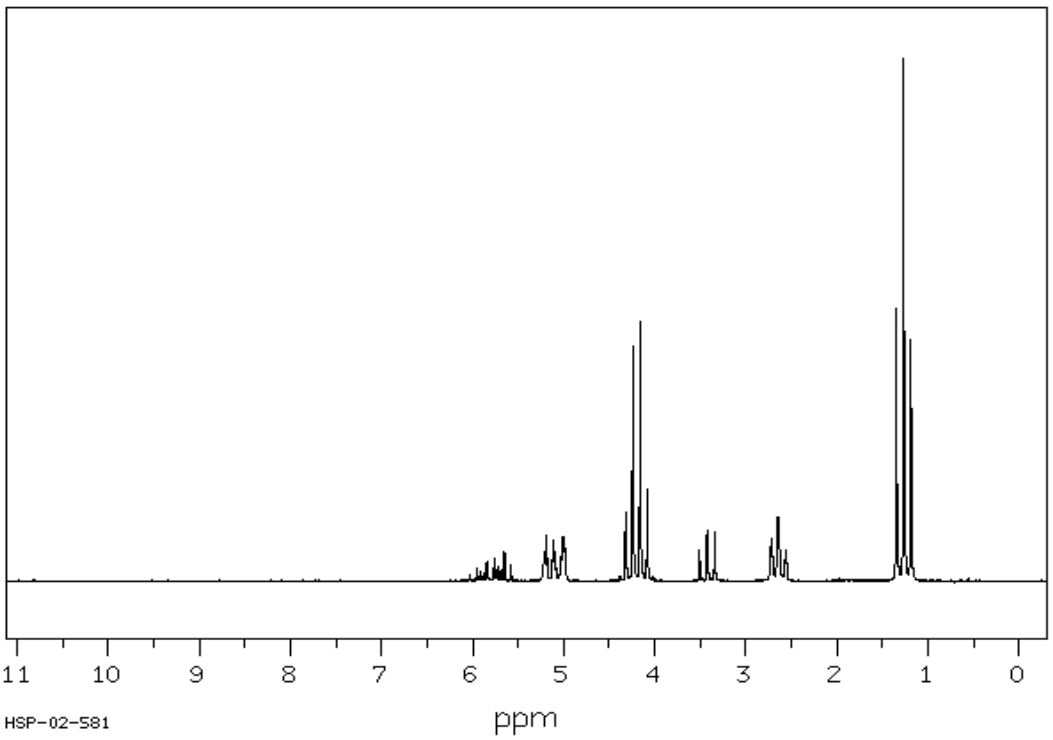
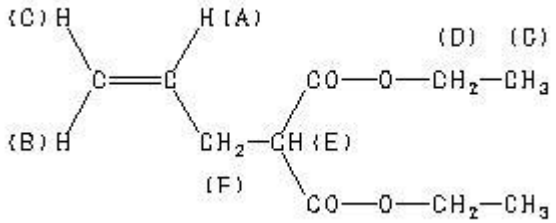


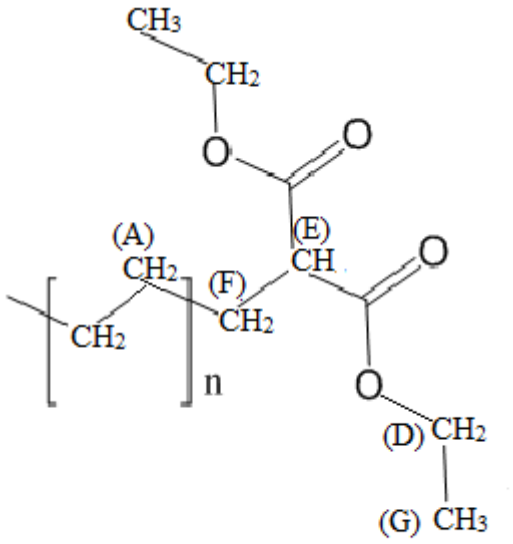
Fig.4.19: $^{1}HNMR$(0.04ml : 0.5 ml $CDCl_3$, 89.56MHz)for DEAM monomer.

The signals that appeared in fig.4.19 interpreted as follows:



Assign.	Shift(ppm)
A	5.77
B	5.10
C	5.04
D	4.192
E	3.412
F	2.644
G	1.266

The peak for A(5.77ppm),B(5.10ppm) and C(5.04ppm) that appeared in the ^{1}HNMR for DEAM monomer (fig.4.19) were appeared as one peak (1.7-2ppm) in the spectrum of linear PDEAM(fig.4.20), peak of (F) was appeared on (1.1-1.2ppm)[56] this was indicate that the addition polymerization was occurred. The peak on 2.5 ppm was referred to DMSO and the peak of (G),(D) and (E) were the same shift as in the monomer spectrum.



linear PDEAM

^{1}H-NMR when the hydroxamic acid added to linear PDEAM showed in (fig.4.21), overlapping signal (8-11ppm) referred to O-H and N-H that formed the hydroxamic acid groups[57], (G) and (D) signals were remained as in PDEAM this indicate that not all ester groups(-$COOC_2H_5$) were replaced to hydroxamic acid groups there are mixture of both functional groups,other peaks remained as in linear PDEAM.

^{13}C-NMR spectrum for polydihydroxamate was observed in (fig.4.22), C=O signal appeared on 167.77ppm, **C**H_2-CH signal on 36.85ppm, **C**H_2-CH_2 signal on 32.67ppm and **C**H-C=O on 33.22ppm[58].

^{1}H-NMR for *Xl*-PDEAM prepared using 1% cross-linking agent (60-80C)(fig.4.23) the signal of H-benzene for cross-linking agent(paradivinyl benzene) was appeared on 7.79ppm[55] this indicated that cross-linking was occured. But when *Xl*-PDEAM(0.5% paradivinyl at room temperature) used to prepare *Xl*-Polydihydroxamate the signal of H-benzene for cross-linking agent(paradivinyl benzene) was not appeared(fig.4.24) this indicated that dihydoxamate group effect on cross-linking

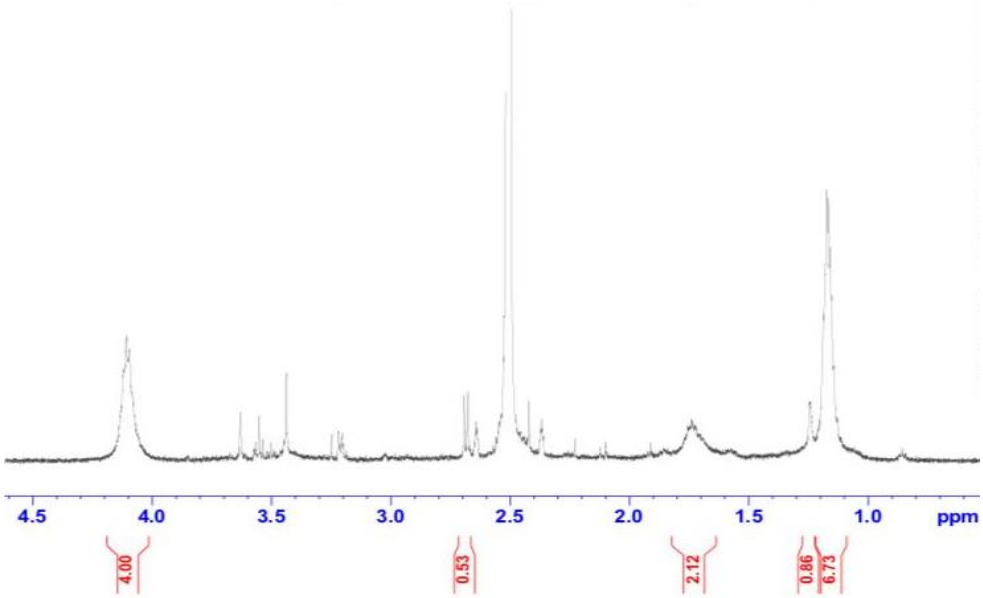


Fig.4.20: ^{1}H-NMR(DMSO solvent,500MHz) for linear PDEAM.

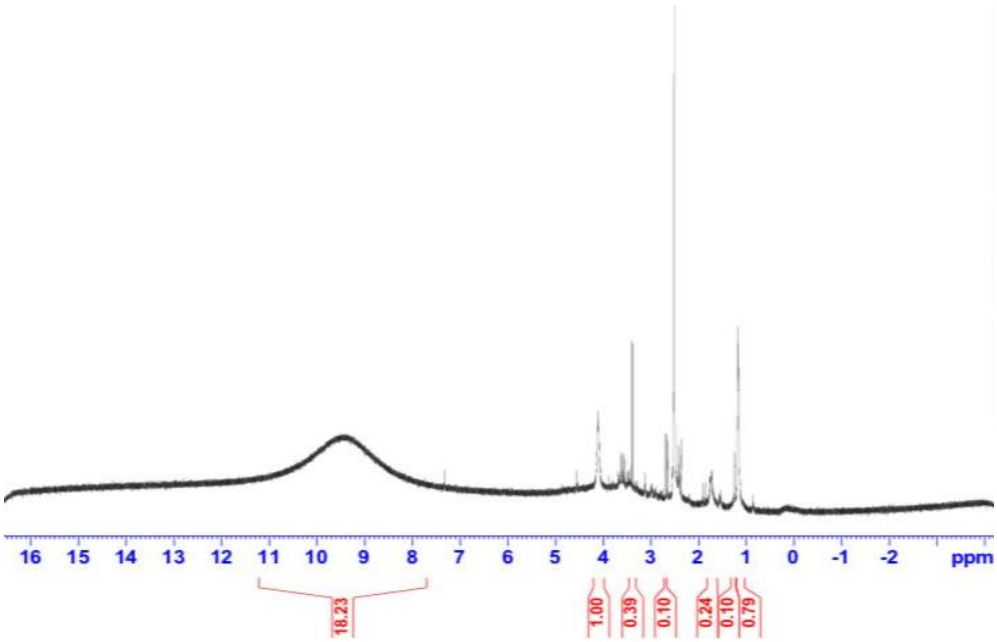


Fig.4.21: ^{1}H-NMR(DMSO solvent, 500MHz) for linear Polydihydroxamate prepared by addition of hydroxamic acid to linear PDEAM.

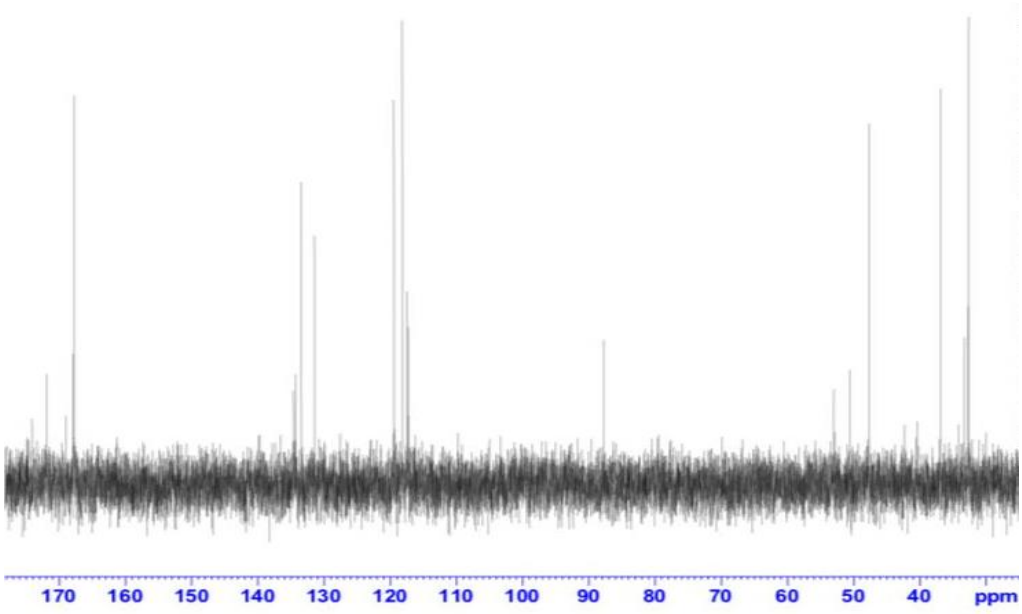


Fig.4.22: ^{13}C-NMR(HD_2O solvent, 500MHz) for linear Polydihydroxamate prepared by polymerization of dihydroxamate monomer.

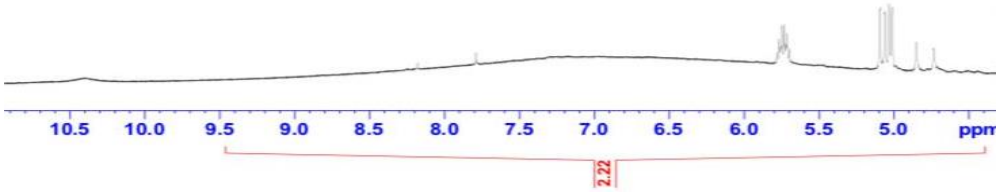


Fig.4.23: ^{1}H-NMR(DMSO solvent, 500MHz) for *Xl*-PDEAM prepared using 1% cross-linking agent (60-80℃).

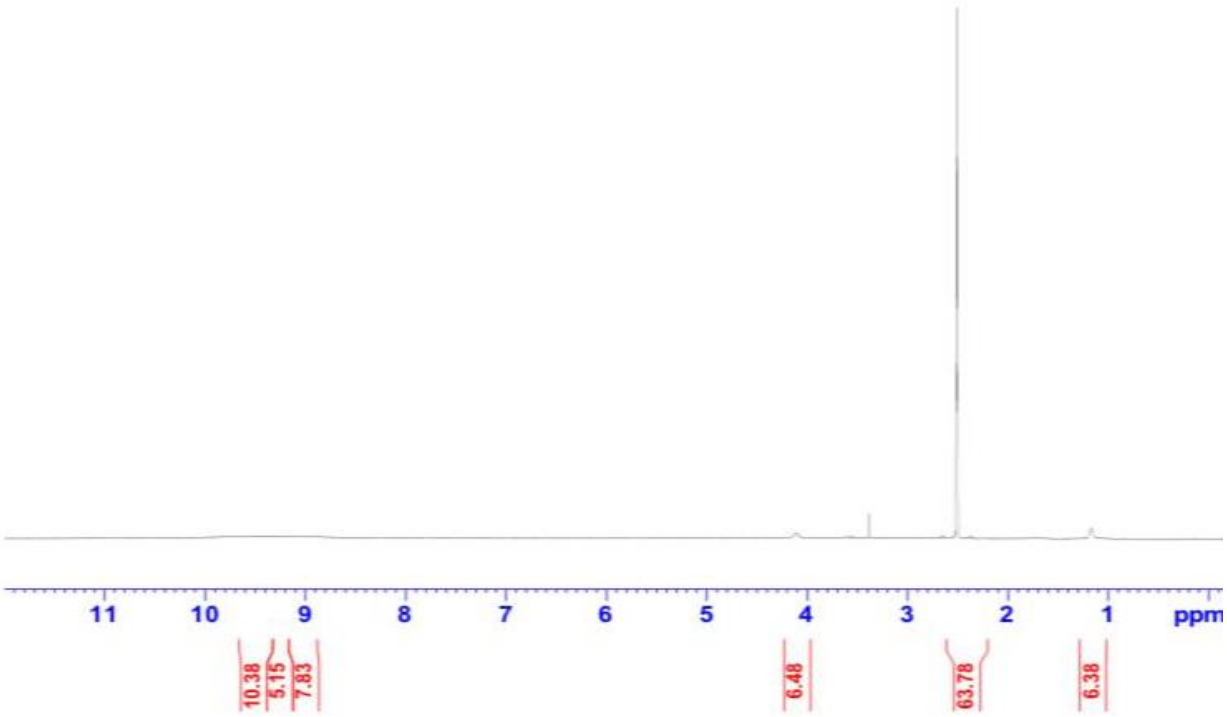


Fig.4.24: ^{1}H-NMR(DMSO solvent, 500MHz) for product of *Xl*-PDEAM(0.5% paradivinyl at room temperature) and hydroxamic acid.

4.4 % HA on the polymers ($FeCl_3$ Test):

Concentration for HA monomer and PHA is 4ppm in all solutions.

Table 4.3: Different concentrations of $FeCl_3$ in dihydroxamate monomer solution and their absorbances.

$FeCl_3$ concentration(ppm)	Absorbance for HA monomer and $FeCl_3$ solution
48.6	0.0826
97.0	0.0990
146.0	0.1100
195.0	0.1300

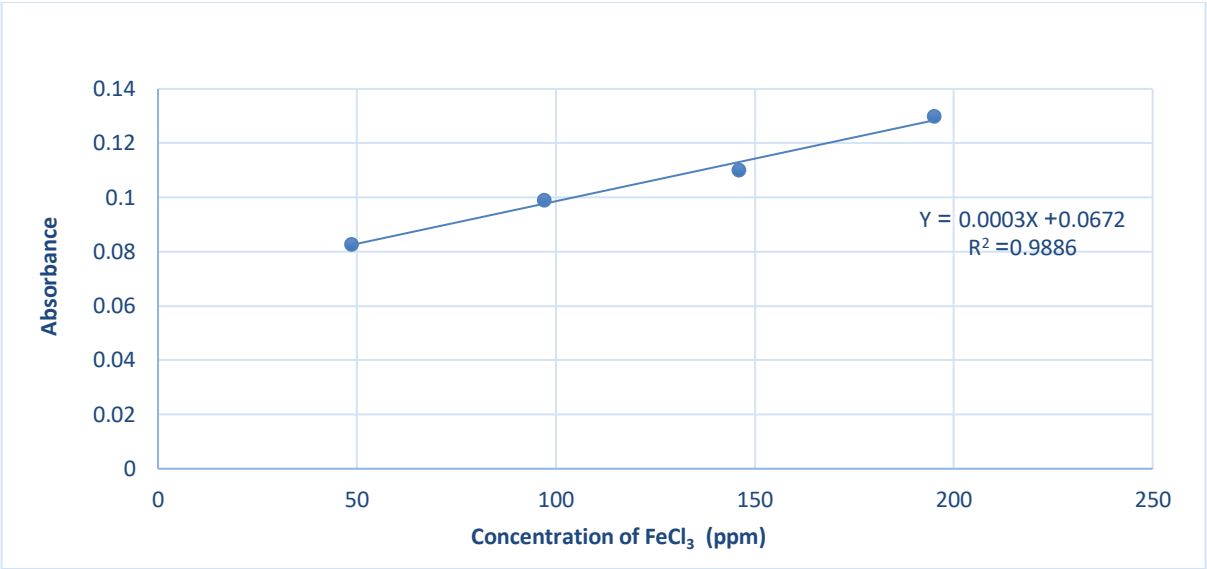


Fig.4.25 Calibration curve (concentration of $FeCl_3$ in HA monomer solution versus absorbance).

Table 4.4: Different concentrations of $FeCl_3$ in PHA_1 solution and their absorbances.

$FeCl_3$ concentration(ppm)	Absorbance for PHA_1 and $FeCl_3$ solution
48.6	0.0424
97.0	0.0468
146.0	0.0533
195.0	0.0600

PHA_1 : Poly dihydroxamate prepared by the addtion of HA group to PDEAM.

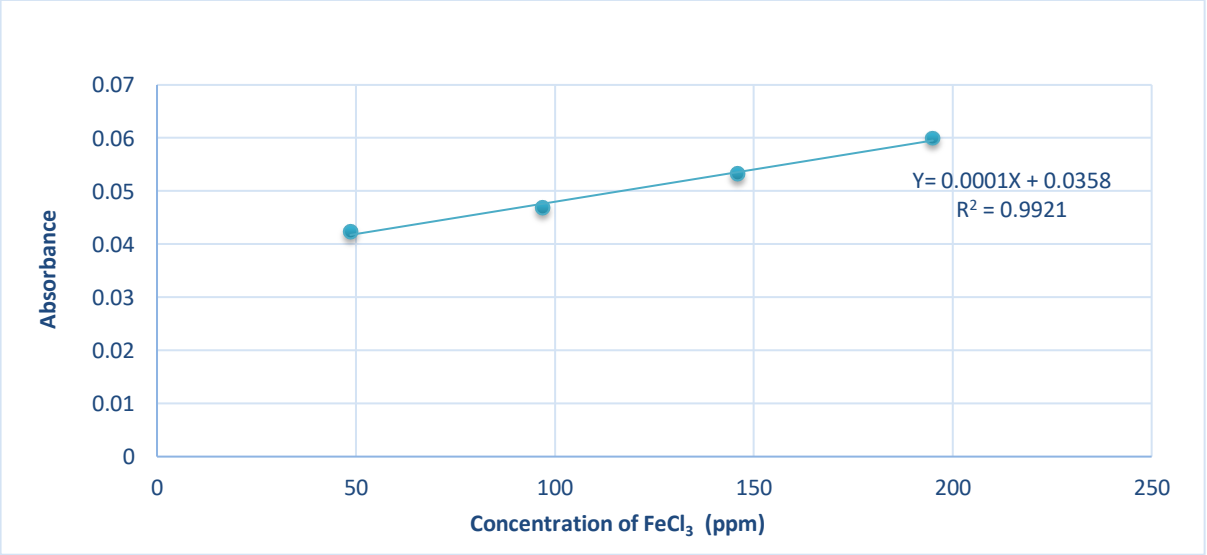


Fig.4.26: Calibration curve (concentration of $FeCl_3$ in PHA_1 solution versus absorbance)

Table 4.5: Different concentrations of $FeCl_3$ in PHA_2 solution and their absorbances.

FeCl3 concentration(ppm)	Absorbance for PHA_2 and $FeCl_3$ solution
48.6	0.0433
97.0	0.0521
146.0	0.0608
195.0	0.0668

PHA_2 : Poly dihydroxamate prepared by polymerization of poly dihydroxamate monomer.

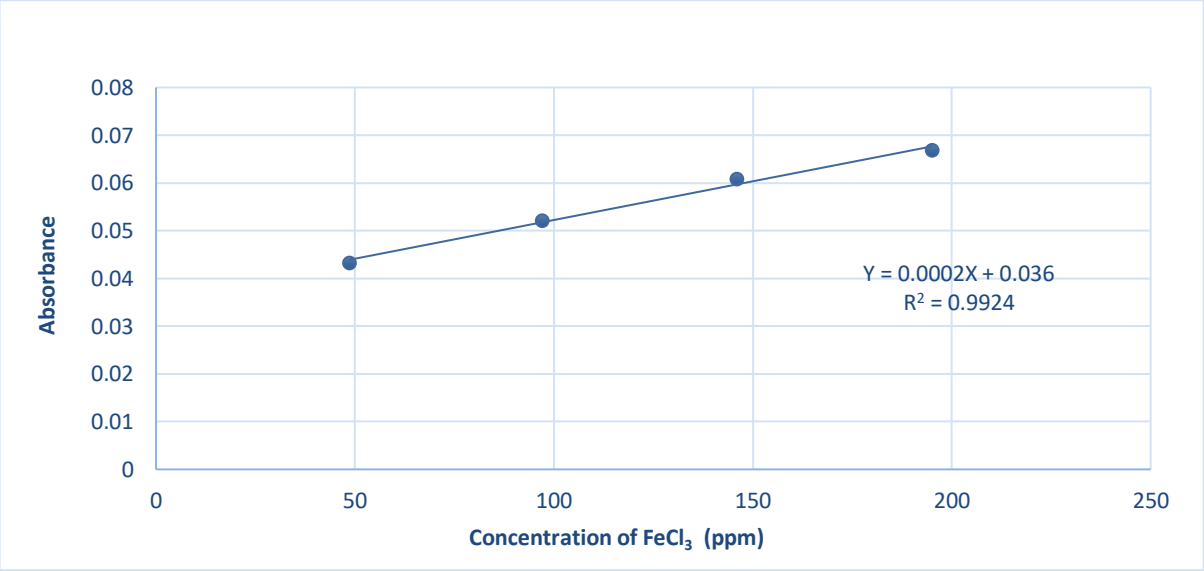


Fig.4.27: Calibration curve(concentration of $FeCl_3$ in PHA_2 solution versus absorbance).

%HA groups for PHA_1 = (0.0600/0.1300)*100%

= 46.15 %

%HA groups for PHA_1 = (0.0424/0.0826)*100%

= 51.30 %

Average % PHA_1 = (46.15% + 51.30%)/2

= 48.73%

%HA groups for PHA_2 = (0.0668/0.1300)*100%

= 51.38%

%HA groups for PHA_2 = (0.0433/0.0826)*100%

= 52.42%

Average %PHA_2 = (51.38% + 52.4%)/2

= 51.9%

Through this experiment, we note that the percentage of the HA groups on PDEAM was about (46% - 52%) in both ways, whether the addition of HA groups to the polymer after polymerization or added to the monomer before polymerization and then polymerization. According to Takahiro Hirotsu.et al (1986), in addition to hydroxamate groups, part of the ester groups is expected converted to carboxylic acid groups, carboxylic acid groups can not be explained well, but hydroxamic acid groups catalized the hydrolysis of ester groups under basic conditions[39].

Chapter five

5. Conclusion:

Due to the wide applications of polymers, the world of polymers has received great interest from scientists, as everyone is looking for the most applicable polymer in medicine, the environment and all aspects of life.

The important feature of DEAM monomer is that it is available, cheape, easly to polymerized and it contains two functional groups (two ester groups), The ester groups may be convert to carboxylic acid groups and made a hydrogel polymers. There are a class of three-dimensional, highly hydrated polymeric networks and are opening up new possibilities for the creation of numerous medical applications[59]. In this work, new polymers linear and *Xl*-PDEAM were prepared from DEAM monomer. This polymers is insoluble in water, foam polymer can be made from it and used in many applications such as packaging. Also polydihydroxamate was prepared, PHA can act as chelating agent for heavy metals and it be used in medicine and surface coating, also it can be used in the treatment of iron overloading due to the ability of hydroxamic acid polymers to chelate iron(III)[53],[60].

Bulk polymerization (highly exothermic reaction) was not used to avoid the degradation of hydroxamic acid groups[25]. Suspension polymerization is economical not as emulsion polymerization that is expensive because require surfactant but it give higher degree of polymerization than suspension polymerization as I found, specially on 60-80 ℃. When HA groups added to DEAM monomer and then polymerized, the polymerization process is becomes easier because the dihydroxamic acid monomer is soluble in water, there is no need to use emulsion in the polymerization process.

Suggestions for further works of this research:

1) Determine the moleclar weight of polymers and study its mechanical properties.

2) Study the chelating ability, biological activity and application in medicine field of linear and *Xl*-polydihydroxamate with heavy metal ions and pharmaceuticals.

3) Study the affect of the amount and type of surfactant on the rate of emulsion polymerization.

Chapter six

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تحضير ودراسة خصائص بوليمر ثنائي إيثيل أليل مالونات الجديد ومشتق حمض الهيدروكساميك الخاص به

اعداد: ديانا محمد مصباح خضيرات

المشرف الأولي: د. محمود الخطيب

المشرف الثانوي: د. مهند قريع

الملخص:

البوليمرات بانواعها المختلفة اما ان تكون قابلة للذوبان أو قابلة للانتفاخ أو غير قابلة للذوبان في الماء لكل منها عدد كبير من التطبيقات، بوليمرات حمض الهيدروكساميك قابلة للذوبان في الماء ولها تطبيقات عدة في الطب والبيئة، خاصة قدرتها على الارتباط مع المعادن الثقيلة. في هذه الدراسة، تم تحضير بوليمر ثنائي إيثيل أليل مالونات غير قابل للذوبان في الماء بشكليه الخطي و الشبكي باستخدام بلمرة الراديكال الحر لمونمر ثنائي ايثيل اليل مالونات في وسط مستحلب وايضا في وسط معلق, وتم استخدام بيرسلفات البوتاسيوم($K_2S_2O_8$) كبادئ للراديكال واجراء البلمرة على درجة حرارة (60-80 درجة مئوية) لمدة ستة ساعات,في تفاعل اخر تم استخدام ميتابيسلفات الصوديوم ($Na_2S_2O_5$) مع بيرسلفات البوتاسيوم كعامل مساعد ومحفز لبادئ البلمرة بدلا من الحرارة عند درجة حرارة الغرفة لمدة 24 ساعة, بالإضافة إلى كبريتات لوريل الصوديوم كمادة خافضة للتوتر السطحي عند استخدام المستحلب للبلمرة. تم تحضير بوليمر ثنائي حمض الهيدروكساميك بطريقتين، الأولى تفاعل بولي ثنائي إيثيل أليل مالونات مع هيدروكسيل أمين هيدروكلوريد باستخدام هيدروكسيد البوتاسيوم كقاعدة في الميثانول والثانية تحضير مونمر ثنائي حمض الهيدروكساميك ثم بلمرته. تم الكشف عن جميع المجموعات الوظيفية للمونومرات والبوليمرات بواسطة طيف الاشعة تحت الحمراء(FT-IR). كما تم فحصها من خلال جهاز مسعر المسح التباييني (Differential Scanning Calorimeter) و جهاز الرنين المغناطيسي النووي (Nuclear magnetic resonance), كما تم ايضا تأكيد الحصول على مونمر ثنائي حمض هيدروكساميك و بوليمر ثنائي حمض هيدروكساميك الخطي والشبكي عن طريق تفاعلها مع ايونات الحديد(Fe^{+3}) واعطاء معقد لونه ارجواني او قريب من ذلك في محلول مائي.