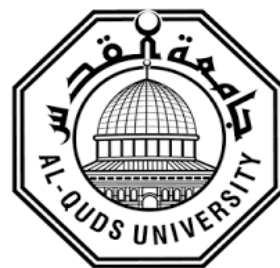


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**Synthesis and characterization of novel polymers based
on hydroxamic acid**

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M.Sc. Thesis

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**Synthesis and characterization of novel polymers based on
Hydroxamic acid**

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A thesis

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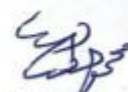
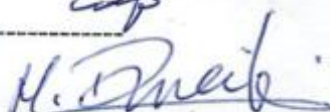

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Declaration

I certify that this thesis is submitted for the degree of Master of science is the results of 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.

Signed: Rawdah Sunoqrot

Date: 14/08/2021

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There must be a hero in every human's life, a true hero and a role model, someone who inspires you, charms you, makes you do the impossible for him out of love, and with the motive of returning the favor that he did for you, and my hero is my father, who has always flooded me with his giving. He was always my guide, my idol with his wisdom and knowledge. Thanks to my source of strength 'my mother, thanks to my siblings especially my sister Reem.

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Abstract

Water-soluble polymers based on Hydroxamic acids are becoming increasingly important in several applications for their impressive chelating ability with heavy metals. In this study Acrylo- hydroxamic acid monomer was prepared from the reaction of n-butyl acrylate with hydroxylamine hydrochloride using potassium hydroxide as a base in methanol. The linear polymer was prepared at room temperature in degassed distilled water using free-radical initiators, potassium persulfate ($K_2S_2O_8$), and sodium metabisulfite ($Na_2S_2O_5$) under inert gas (N_2) conditions. A cross-linked polymer was prepared by using potassium persulfate ($K_2S_2O_8$) as a free radical initiator and *N,N'*-methylen bis(acrylamide) as a cross-linking agent at 70 °C. The polymers produced in this work have a high weight average molecular weight (Mwt). The average weight of linear and cross-linked polymers were determined by light scattering and they were 488,000, 431,000 gm/mol respectively.

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Abbreviation

HA: Hydroxamic Acid

PHA: Poly (Hydroxamic Acid)

AA: Acryl amide

HEMA: Hydroxyethyl methacrylate hydroxyethyl acrylate

HEA: Hydroxyethyl acrylate methacrylate

VP: Vinylpyrrolidone

PVA: Polyvinyl Alcohol

GPC: Gel permeation chromatography

SLS: Static light scattering

DLS: Dynamic light scattering

FTIR: Fourier transform infrared

NMR: Nuclear magnetic resonance

PMMA: poly (methyl methacrylate)

SBHA: Suberic bishydroxamic acid

SAHA: Suberoylanilide hydroxamic acid

PDI: Polydispersity index.

PMA: Polyacryl amide

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CHAPTER ONE

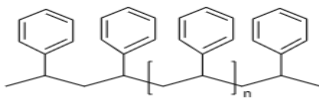
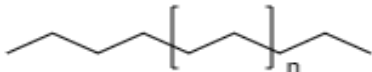
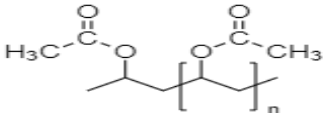
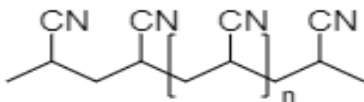
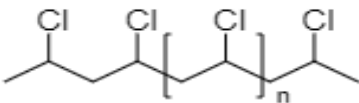
INTRODUCTION

1. Introduction

1.1 Common organic soluble polymers

Polymer science produces new materials for new applications with unique properties, depending on the nature and the average molecular weight of the polymer backbone. Polymers are macromolecules made of repeating units by a process called polymerization [1]. Most common polymers are known for their solubility in organic solvent and are not water- soluble. Some are listed in the table below.

Table (1): common organic soluble polymers (2)

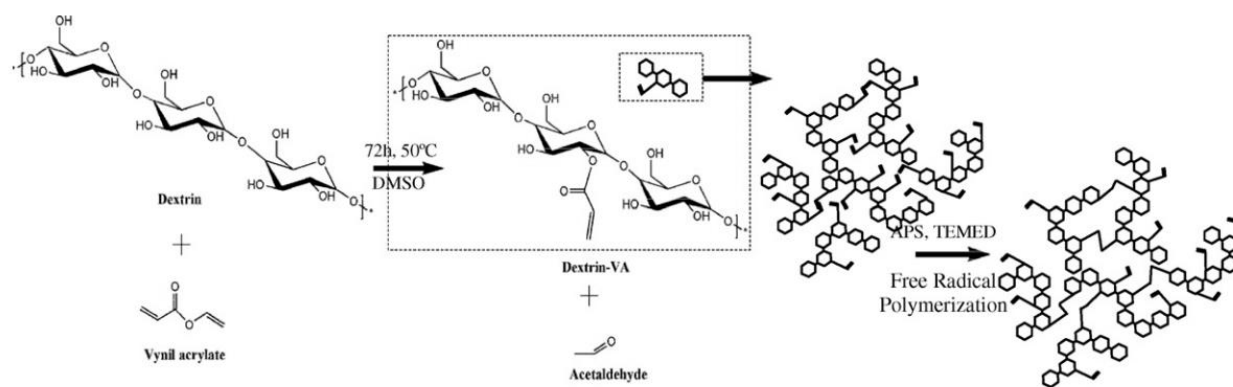
Polymer	Polymer structure	Solubility
Polystyrene		Soluble in aromatic hydrocarbons, higher ketones and esters.
Polyethylene		Soluble in hexane
Polyvinyl acetate		Soluble in different organic solvents.
Polyacrylonitrile		Soluble in DMF.
Polyvinyl chloride		Soluble in ketones and esters.

1.2 Water soluble and water swellable polymers

1.2.1 Overview

Water-soluble polymers are one of the most interesting classes of polymers for their ability to dissolve or swell in water to form solution or hydrogel respectively. They have known a wide range of applications in many areas, including water treatment, cosmetics, personal care products, pharmaceuticals, oil recovery, production of pulp and paper, mineral processing, agriculture, etc. There are many techniques that are used to produce this type of polymers, such as aqueous solution polymerization, inverse suspension polymerization, and inverse emulsion polymerization, which are triggered by either thermal initiators or redox couple initiators [3].

Cross-linked or hydrogels polymers behave differently from other classes of polymers, they can absorb a large amount of water without dissolving into it, Franklin et al. (2014) reported that the reason for hydrogel different behavior is the presence of hydrophilic groups such as OH , CONH , CONH_2 , and SO_3H . Polymers can be imbibing the water or biological fluids in different percent depending on the medium and polymer compositions [4]. Carvalho et al. (2007) outlined the preparation mechanism of dextrin vinyl acrylate (dextrin-VA) hydrogel by free radical polymerization (Scheme 1) [5]. This hydrogel polymer shows a wide range of applications, especially in pharmaceutical and drug delivery system.



Scheme1: Synthesis mechanism of dextrin-VA hydrogel by free radical polymerization adopted from [5].

1.2.2 Water-soluble polymer classification

Water-soluble polymers are classified into three classes:

1.2.2.1 Natural polymers.

Proteins

Such as Albumin and Hemoglobin

Polysaccharides

Polysaccharides include polymeric compounds made up of monosaccharide long chains linked together by glycosidic linkages. Natural polysaccharides have different structural characteristics due to their molecular weight, the content of the monosaccharides, glycoside patterns of linking, orientation (α or β), and branching degrees. Polysaccharides include starch, gum arabia, amylase and pullulan are water-soluble [6].

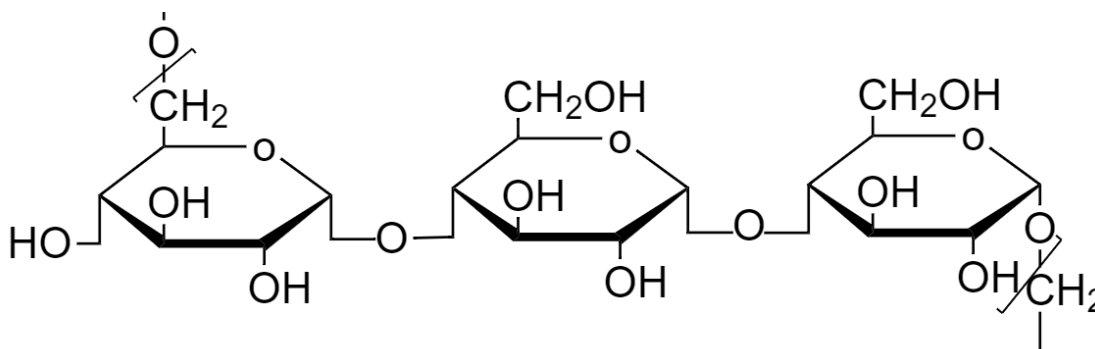


Fig (1): Chemical structure of pullulan

Xanthan is another example of water soluble polysaccharide, which is classified as microbial polysaccharide. Application of this polysaccharide include the usage of xanthan as thickeners, stabilizers, gelling agents and emulsifiers [7].

1.2.2.2 Semi-synthetic polymers

This category of polymer includes cellulose ethers and starch derivatives. Cellulose ethers utilize in medicines, personal care products, food, chemical oil fields, building paper, adhesives, stabilizers, densification, viscosity modifiers and textiles.

1.2.2.3 synthetic water-soluble polymers

Some important examples of synthetic water-soluble polymers are listed in Table (2) [8].

Table (2): Common synthetic water- soluble polymers.

Nonionic water-soluble polymers	Anionic water-soluble polymers	Cationic water-soluble polymers
$\left[\text{H}_2\text{C}-\underset{\text{CONH}_2}{\text{CH}} \right]_n$ <p>Polyacrylamide</p>	$\left[\text{H}_2\text{C}-\underset{\text{COOH}}{\text{CH}} \right]_n$ <p>Polyacrylic acid</p>	$\left[\text{H}_2\text{C}-\underset{\text{NH}_3}{\text{CH}} \right] +$ <p>Polyvinyl amine</p>
$\left[\text{H}_2\text{C}-\underset{\text{OH}}{\text{CH}} \right]_n$ <p>Polyvinylalcohol</p>	$\left[\text{P} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \\ \text{OH} \end{array} \text{O} \right]_n$ <p>Polyphosphoric acid</p>	$\left[\text{HC} \begin{array}{c} \text{CH}_2 \\ \text{H}_2\text{C}-\text{N}-\text{CH}_3 \\ \text{H} \end{array} \text{CH} \right]_n \text{Cl}^-$ <p>Polydimethyldiallylammoniumchloride</p>
$\left[\text{CH}_2-\underset{\text{H}_2\text{C}-\text{N}-\text{C}=\text{O}}{\text{CH}} \right]_n$ <p>Polyvinylpyrrolidone</p>	$\left[\text{CH}_2-\underset{\text{SO}_3\text{H}}{\text{CH}} \right]_n$ <p>Polystyrene sulphonic acid</p>	$\left[\text{CH}_2-\underset{\text{N}^+\text{RX}^-}{\text{CH}} \right]_n$ <p>Poly4-vinyl-N-alkyl-pyridinium salts</p>

1.2.3 Applications of water soluble polymer.

Water-soluble polymers have a wide range of applications such as superabsorbent, soluble packaging, soft contact lens, etc. The reason of this wide range of applications because of their solution properties. In particular from their ability to alter the rheology of an aqueous medium and to adsorb particles or surfaces from the solution [9].

Applications of Hydroxamic acid in medicine

The main key of medical applications of hydroxamic acid is high ability to inhibit some enzymes effectively, which would cause imbalance within the body. In addition to the high ability to form a strong complex with heavy metal ions.

Histone Deacetylase is one of the enzymes that eliminate the group of acetyls from Histon protein. This elimination will make the DNA less reachable to the factor of transcription. The cell cycle depends on Histone and the lack of it may cause cancer. Marks et al. (2007) studied the inhibition activity of suberoylanilide hydroxamic acid on different histone deacetylases classes. Fig (5) shows the histone deacetylases inhibitors based on hydroxamic acid. The results showed an effective inhibition from SBHA, SAHA onto Histone Deacetylase [10].

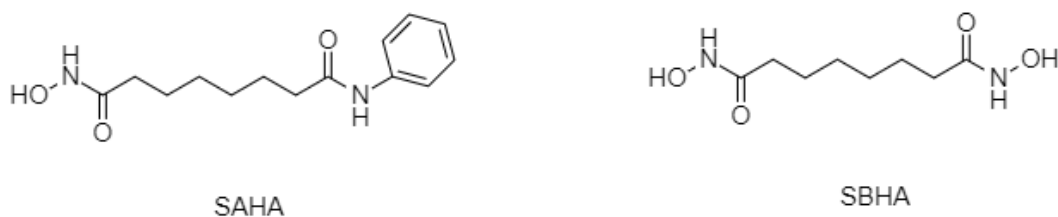
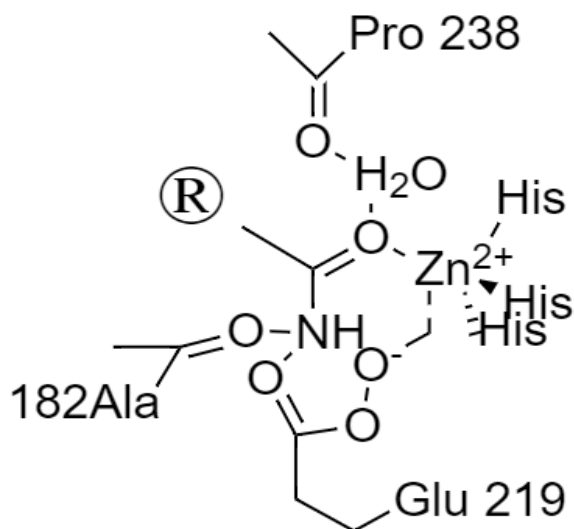


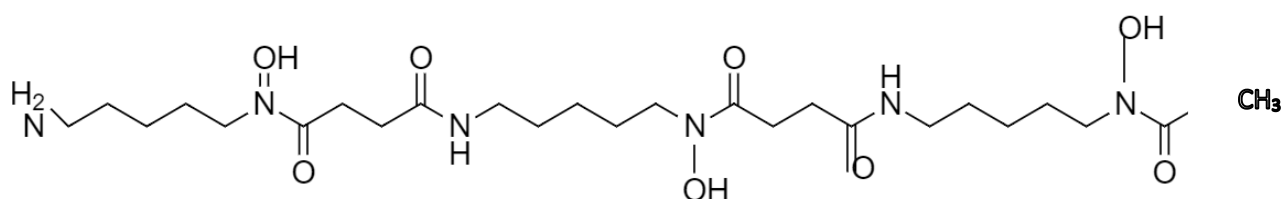
Fig (2): SBHA, suberic bishydroxamic acid; SAHA, suberoylanilide hydroxamic acid.

Browner et al. (1995) showed in the following schematic diagram the reaction of hydroxamat with zinc containing enzyme (matrilysin). Scheme (8) shows the general mechanism of inhibition [11]:



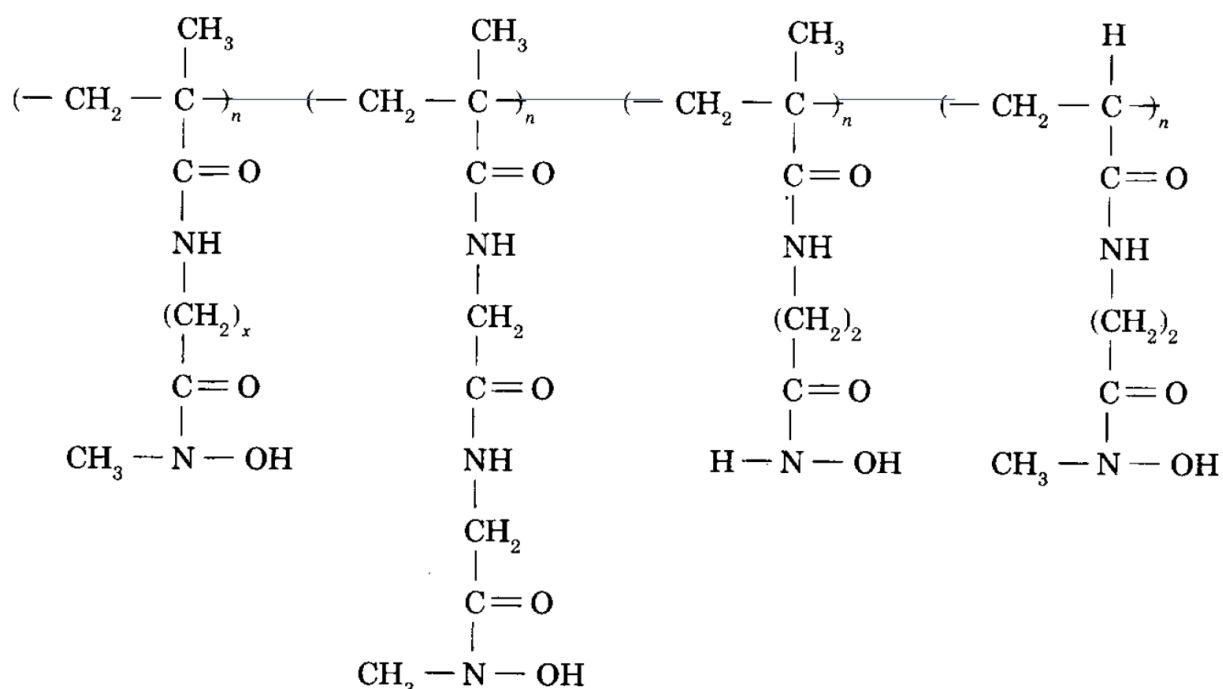
Scheme 2: Reaction of hydroxamat with zinc containing enzyme (matrilysin)

Keth et al. (2011) discussed the treatment of iron overload by hydroxamic acid according to its strong chelating with iron ions. In some cases, in inherited, blood disorders and thalassemia's describe by a decrease in hemoglobin production, Deferoxamine (DFO) (Scheme 3) which is well known for its high stability constant for iron complex preventing iron accumulation [12].



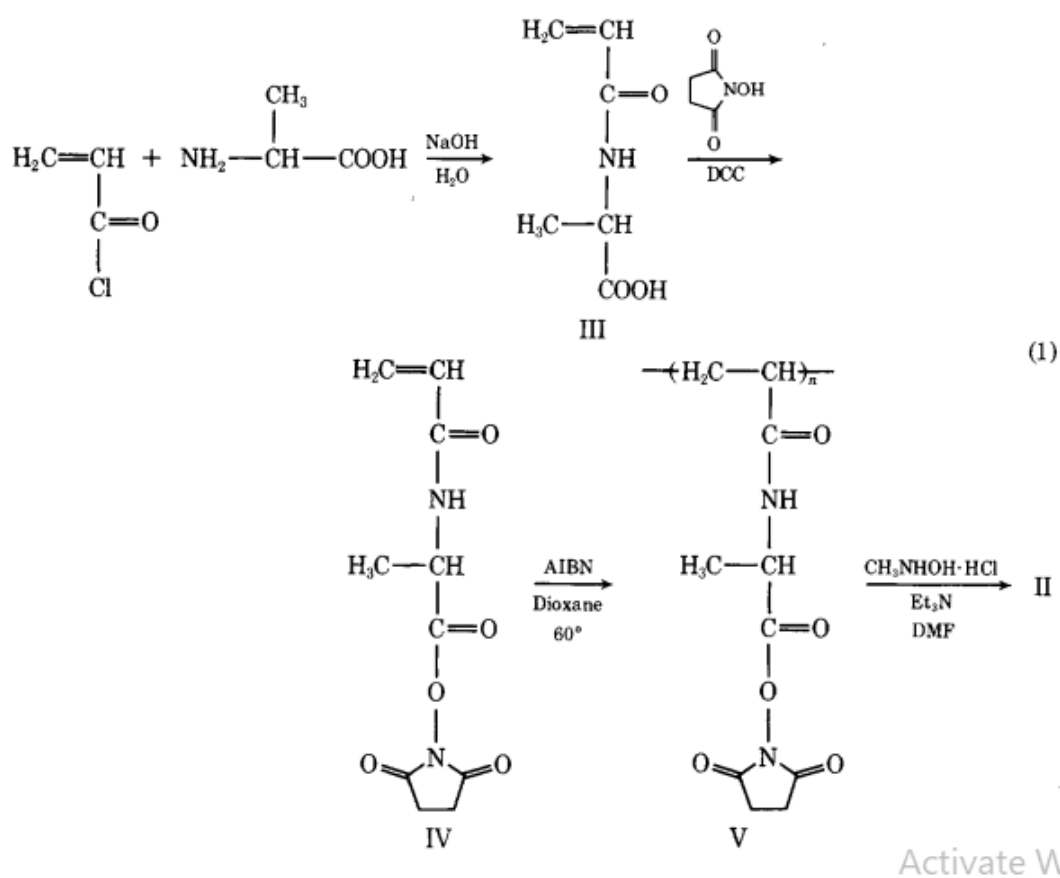
Scheme 3: Chemical structure of Deferoxamine

Winston et al. (1978) prepared poly (Hydroxamic acid) with very high stable complexation properties according to its design, which is designed form to an octahedral iron complex. scheme (4) [13]:



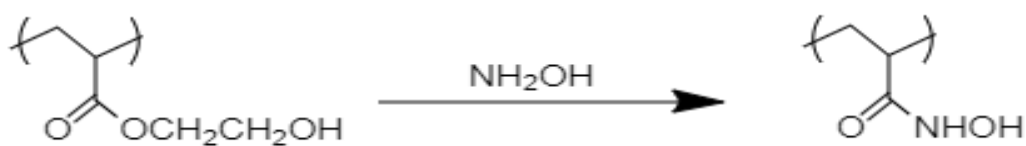
Scheme 4: Chemical structure of the novel deferoxamine (II) adopted from [13].

Scheme (5) outline all steps in details for synthesis of novel deferoxamine in scheme (10):



Scheme 5: Series of reactions for synthesis of deferoxamine adopted from [13]

Polomoscanik et al. (2005) synthesized poly functionalized Hydroxamic acid gel that swell in water and uptack iron ions effectively. The synthesis process includes the reaction of hydroxylamine with polymer gel based on acryloyl chloride-Divinylbenzene, (2- hydroxyethyl) acrylate and N-acryloxysuccinimide monomer. Scheme (6) representing the synthesis reaction of poly (Hydroxamic acid) from Poly(2-hydroxyethyl) acrylate [14].



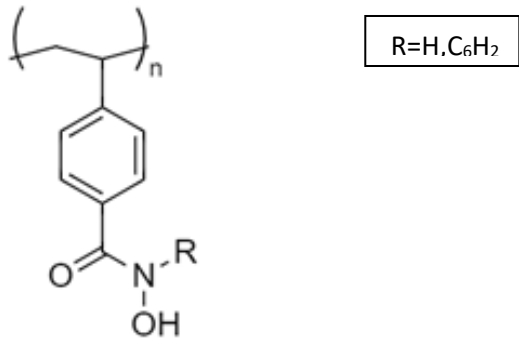
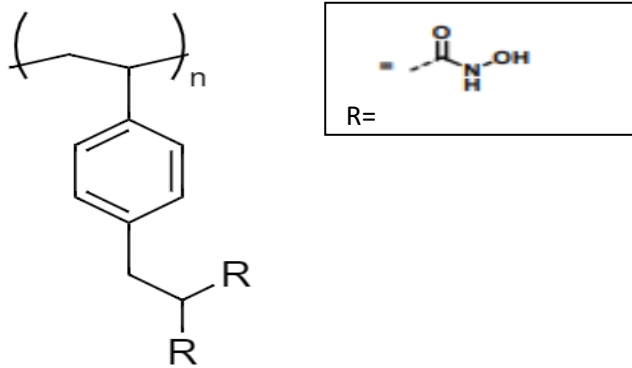
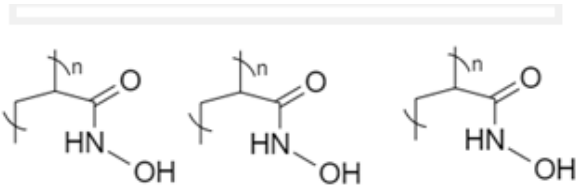
Crosslinked gel

Scheme 6: Synthesis of poly (Hydroxamic acid) from Poly(2-hydroxyethyl) acrylate

In vivo iron binding study on groups of hydroxamic acid polymers gel rats showed impressive efficiency to overcome iron overload. They gave one group of rats a specific diet with iron overdose and the other group was a control group with no iron overdose, the group with iron overdose was given the chelating polymer gel orally. Results show the effective uptake of excess iron from rats' gastrointestinal track.

The table below shows some of the hydroxamic acid polymer and their applications.

Table (3): Examples of poly (hydroxamic acids) and their application ⁽¹¹⁾.

Polymer Structure	Application
	Removal of earth metals by poly (Hydroxamic acid) resin
	Seawater treatment from uranium
	Used as packaging material for reducing of lipid oxidation

1.3.2 Chemical synthesis of hydroxamic acids.

Keth et al. (2020) summarized various methods of synthesis of hydroxamic acid [14]. In general, hydroxamic acids are the product of the reaction of hydroxylamine (or its derivatives) and a carbonyl compound. A mixture of mono, di- or tri-substituted products could be produced when employing acyl chlorides in the reaction with hydroxylamine which is a highly reactive carbonyl compound. Reaction(B) in figure (4) below illustrates that one single step reaction can be achieved by using ester derivative as starting material with using a base to ensure complete deprotonation of hydroxylamine, the reaction can be carried out in an aqueous solution. In 1896 Angeli et al. were the first who reported the preparation of hydroxamic acids from aldehydes by using an oxidizing agent such as N-hydroxybenzenesulfonamide to oxidize aldehydes into hydroxamic acids (E) in figure (4). Folkers et al. (1995) clarified that synthesis of hydroxamic acids could be achieved under mild condition by incorporation of carboxylic acids with protected hydroxylamines (H) [17].

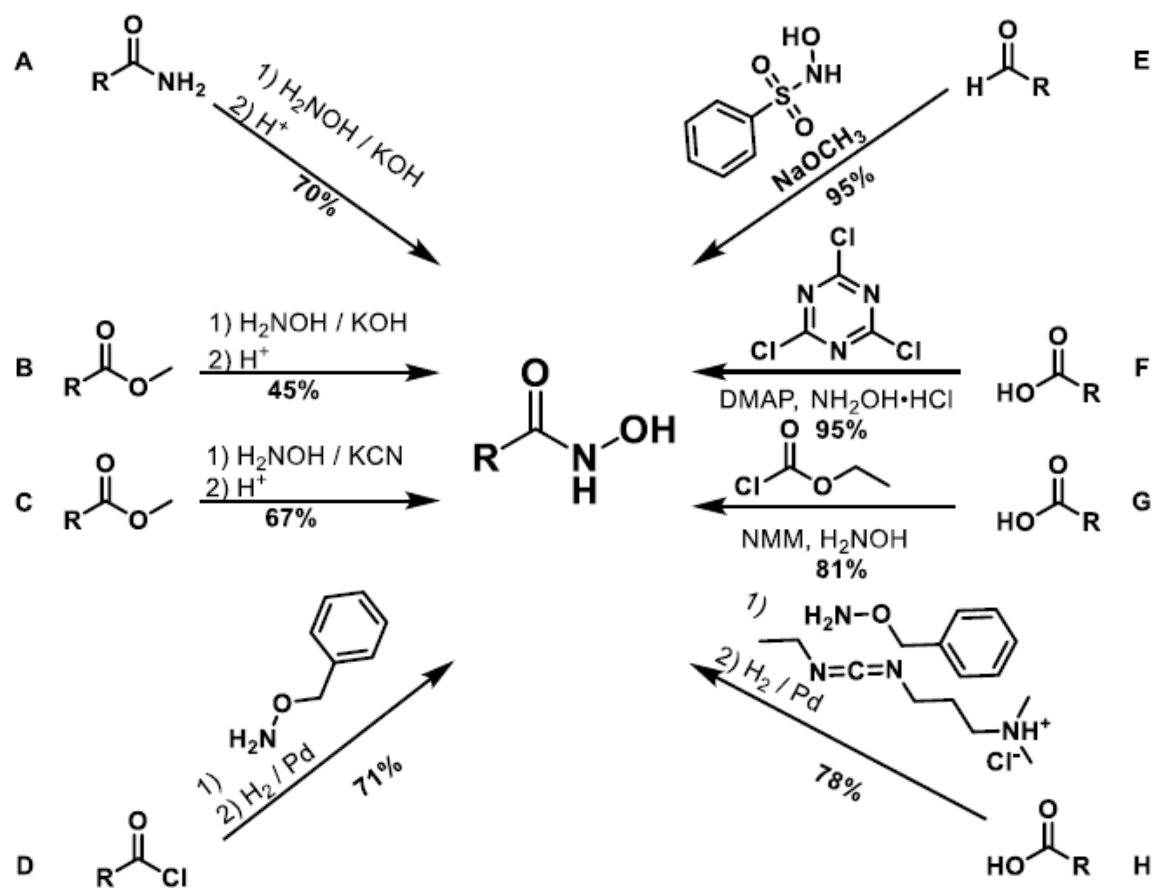


Fig. (5): Various synthetic approaches for the preparation of hydroxamic acids adopted from [16].

1.4 Aim and objective

This thesis addresses method of water-soluble and water-swellaable poly (hydroxamic acid) synthesis. The key objective of this research is to synthesize a novel water-soluble poly (hydroxamic acid) starting from n-butyl acrylate to obtain poly (acrylo-hydroxamic acid) by free radical polymerization and cross-linking and then characterize them.

This work aims to produce linear and hydrogel polymers that have a very high potentiality of chelating and removing heavy metal ions from water.

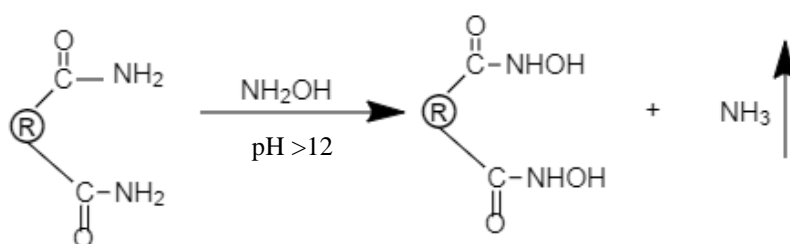
Chapter two

Literature review

2. Literature review

2.1 Linear and hydrogel Poly (hydroxamic Acid) from Poly(acrylamide)

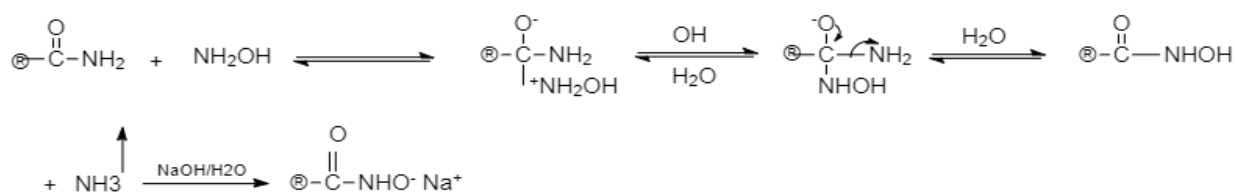
Domb et al. (1988) reported a method to synthesize poly (hydroxamic acid) from poly(acrylamide) as starting material, poly(acrylamide) reacted at 26 °C with hydroxylamines by using a base, the description of the method is shown below (2) [18].



Where R is backbone of polymer

Equ. 2: Reaction of poly(acrylamide) and hydroxylamines

About 70% of amide groups converted to hydroxamic acid groups, not more than 5% of carboxylic acid groups and 25% of unreacted amide groups which is obtained by titration of the polymer with sodium bicarbonate. Domb et al. (1988) mentioned that using poly(acrylamide) as starting material instead of other common polymers like: poly(acrylonitrile) would overcome some disadvantages which the outcome of the heterogeneous reaction in water medium are. Jenkes et al. (1985) suggest a mechanism for the reaction of hydroxylamines and carbonyls in basic solution (pH>10), which is outlined in the following equation (3):



Where R is backbone of polymer.

Equ. 3: Mechanism reaction of carbonyls and hydroxylamines under basic conditions (pH >10)

By using another method, with the same starting material, Isikver et al. (2001) prepared hydroxamic acid from the reaction of poly(acrylamide) and hydroxylamine by using *N,N'*-methylene bis(acrylamide) as a cross-linking agent and ammonium persulfate as initiator by free radical polymerization. But first, the poly(acrylamide) was prepared as hydrogel then reacted with hydroxylamine in a basic medium using potassium hydroxide (KOH). [19].

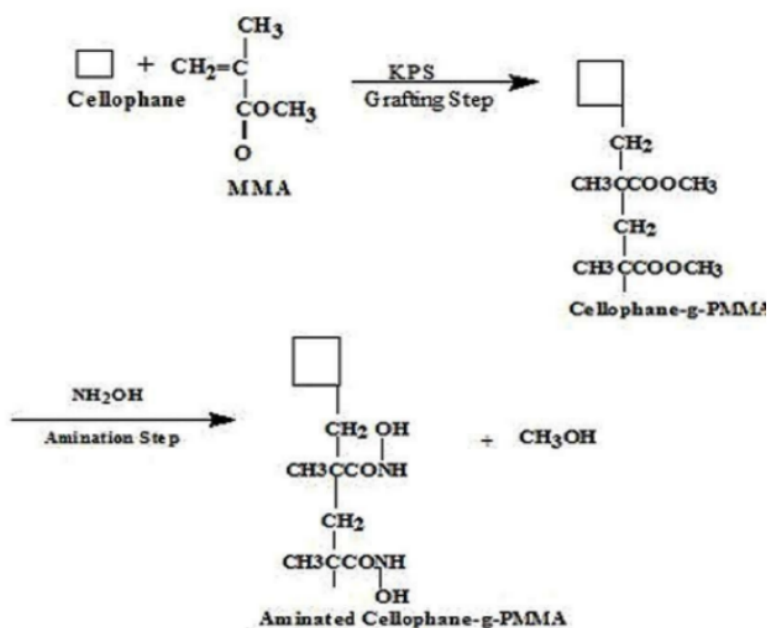
The binding affinity of heavy metal ions onto polymer was studied, and the results indicated the uptake of some ions such as Ni^{2+} , UO_2^{2+} , Co^{2+} , Cu^{2+} and Cr^{3+} . An aqueous solution of heavy metal ions was prepared, then PHA hydrogel and PAAm was added to the solutions separately, after two days, when the solutions were left to reach the equilibrium. The solution with PHA hydrogel showed dark color but the solution with PAAm did not .

Saraydin et al. (2001) [20], synthesized PHA using the same method but they did an additional study about binding properties of PHA hydrogel with uranyl ion. Two sources of uranyl ion were used, uranyl acetate and uranyl nitrate. PHA was transferred into aqueous solutions containing a uranyl ion source, the solutions were allowed to reach equilibrium for two days. The solutions showed orange-red color due to the binding of PHA hydrogel and uranyl ions. Maturana et al. (1995) [21] explained this coloration based on the ionizable hydroxamic acid groups, whereas the reaction of polymer and uranyl groups increase when the ionizable hydroxamic acid groups increase.

2.2 Synthesis of poly (Hydroxamic acid) from poly(methacrylate) and poly (ethyl acrylate)

Poly (Hydroxamic acid) prepared from poly(methacrylate) hydrogel by Haron et al. (1994) in one step. The starting material poly(methacrylate) converted to resin. Poly (methacrylate-divinyl benzene) prepared by using suspension polymerization of divinylbenzene methacrylate solutions, then the product reacted with hydroxylammonium chloride to produce hydroxamic acid under basic medium in the presence of potassium hydroxide (KOH) at 45C° for 24 hr. [22].

Fawal et al. (2021) also synthesized poly (Hydroxamic acid) from Poly (methyl methacrylate) with a different approach. First, Poly (methyl methacrylate) grafted with cellophane membranes under specific conditions. Second, the reaction of hydroxylamine with PMMA was carried out to functionalize the polymer with hydroxamic acid at 40°C. Scheme (7) proposed the possible mechanism of the reaction [23]:

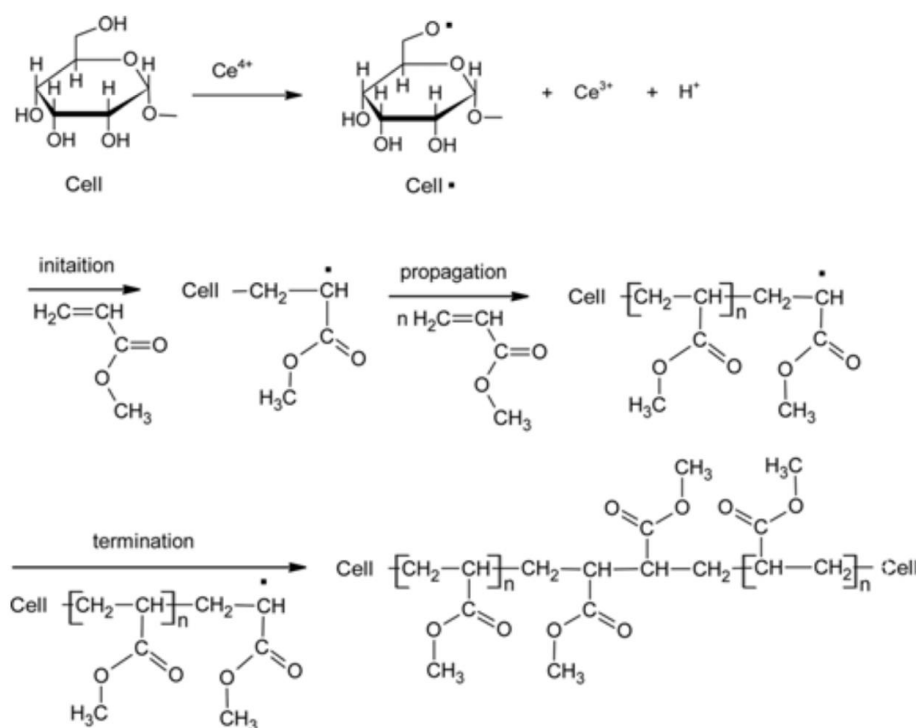


Scheme 7: Schematic diagram of the amination process of the cellophane-g-PMMA membranes adopted from [23].

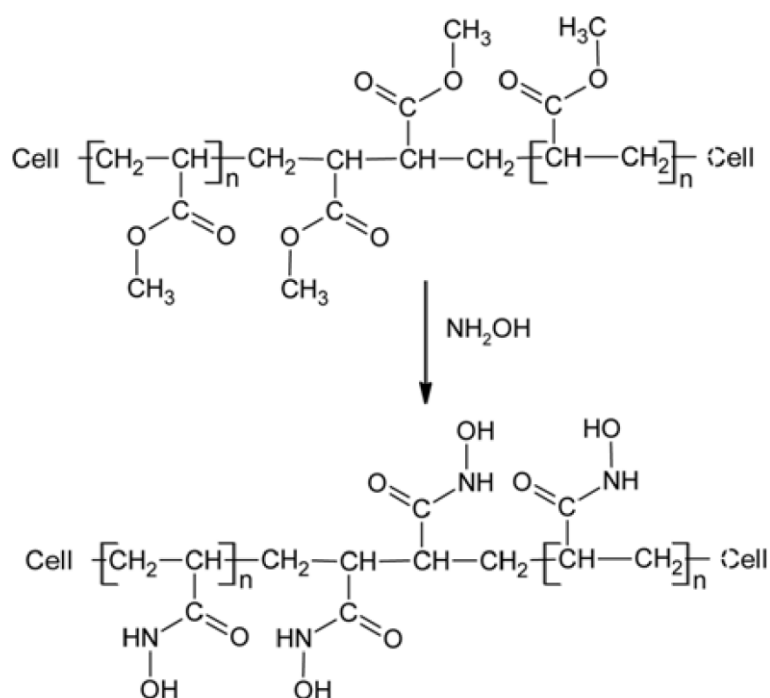
Both studies investigated the chelating affinity of hydroxamic acid polymers with heavy metal ions. Purple, dark green, and brown coloration appeared when poly (hydroxamic acid) placed into three solutions containing vanadium(V), copper(II), and iron(III) ions, respectively according to Haron et al. (1994) study [22].

Fawal et al. (2021) tested the ability of poly (hydroxamic acid) to adsorb Cu^{+2} from CuSO_4 solution, the solutions turned to dark blue, which indicates successful adsorption of copper [23].

Cellulose is one of the most widespread natural polymers and the most widely used in scientific research, due to its low cost, and its interesting chemical and physical properties. Rahman et al. (2016) used cellulose to prepare hydroxamic acid by adding methyl acrylate to the surface of cellulose and then converting it into hydroxamic acid ligand by free radical polymerization using Ce^{4+} as initiator because it's highly reactive at different positions on the surface of cellulose. After preparation of cellulose grafted with poly (methyl acrylate) which cellulose obtained from Khaya plant, the grafted cellulose reacted with hydroxylamine hydrochloride in basic solution at 70°C for 6 hours. FT-IR results confirmed the conversion of Poly (methyl acrylate) groups into poly (hydroxamic acid) groups by the appearance of the hydroxamic acid group in the spectrum. Schemes (8-9) shows all reactions mechanism for preparation of poly (hydroxamic acid) by free radical polymerization [24]:

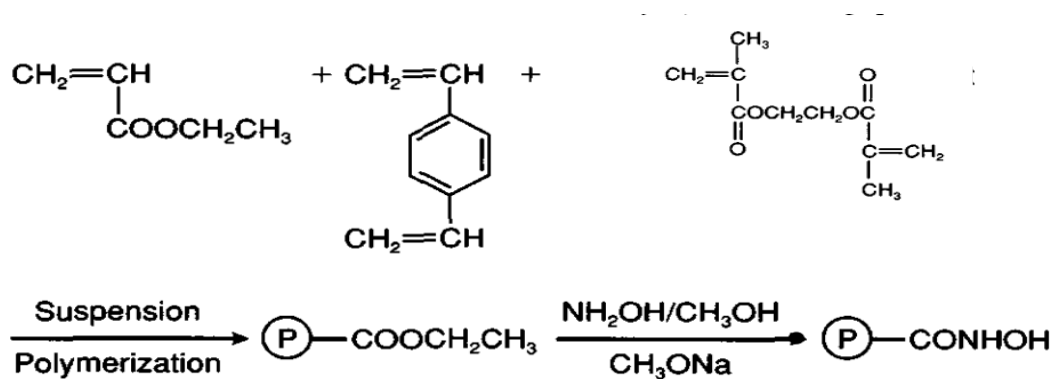


Scheme 8: Graft copolymerization of methyl acrylate onto khaya cellulose (Cell • is a glucose unit of cellulose) adopted from [26].



Scheme 9: Khaya cellulose-g-PMA converted into poly (hydroxamic acid).

Lee et al. (1995) prepared poly (hydroxamic acid) from poly (ethyl acrylate) as starting material by suspension polymerization. divinylbenzene ethylene and glycol dimethacrylate (EGD) used to crosslinked poly (ethyl acrylate), the following scheme (10) shows all reaction steps to prepare poly (hydroxamic acid) from poly (ethyl acrylate) [25]:



Scheme 10: Reaction steps of preparation poly (hydroxamic acid) from poly (ethyl acrylate) crosslinked with divinylbenzene and hydrophilic crosslinking agent adopted from [27].

Poly (Hydroxamic acid) resin showed impressive binding ability towards heavy metal ions due to the high hydrophilic group.

Hydroxamic acid polymer has been studied broadly. Various starting materials were used to synthesize it by different polymerization method. As noted in the literature review, poly Hydroxamic acids mostly synthesized by converting functional groups of monomers to hydroxamic acid groups, taking into consideration that most of the starting materials were polymers and the functionalized of hydroxamic acid groups has not been 100% in any cases. Many obstacles may face functional groups during the conversion process such as the shielding that may occur because of the high-molecular-weight monomer. In contrast, starting with hydroxamic acid monomer then polymerization could produce high-molecular-weight polymer with a higher percentage of hydroxamic acid groups as we assumed in this research.

Chapter three

Methodology

3. Methodology

3.1 Chemicals:

N,N'-methylene bis(acrylamide) 99% (Sigma-Aldrich), potassium persulfate 99% (Sigma-Aldrich), Sodium metabisulfite (Riedel-de Haen), hydroxylamine hydrochloride 99% (Sigma-Aldrich), potassium hydroxide 99% (Sigma-Aldrich).

Solvents: Methanol 98% (Sigma-Aldrich), Distilled water.

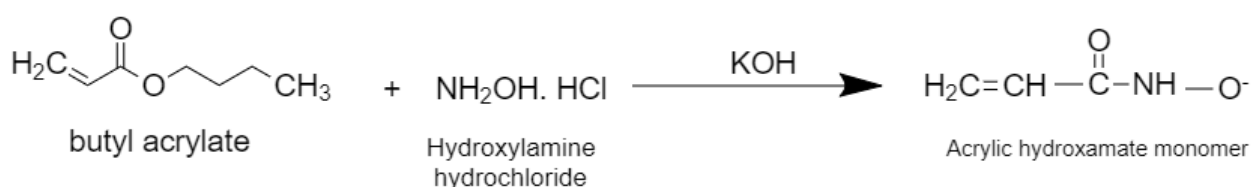
3.2 Instruments:

Fourier transform infrared spectroscopy (FT-IR) (BRUKER-Tensor II) Abu-Dies/Al-Quds University, *Uncle* instrument which combines Dynamic light scattering (DSL) and single light scattering (SLS), ZURICH University/Switzerland, Nuclear magnetic resonance (NMR) (BRUKER 300 MHz) Genève University/Switzerland.

3.3 Experiments

3.2.1 -Preparation of acrylic hydroxamate monomer:

Fieser et al. (1967) procedure for the general synthesis of hydroxamic acid was used in this research to synthesize acrylic hydroxamate monomer [26]. 46.7 gr. of hydroxylamine hydrochloride (672.0391 millimoles) was transferred to a beaker then 240 ml of methanol was dissolved. In another beaker, 56 gr. of potassium hydroxide (998.1178 millimoles) in 140 ml of methanol was prepared and boiled. The two solutions cooled to 30-40 °C, and the second solution was added to the first. After cooling in ice to ensure complete separation of potassium chloride, 26 ml of butyl acrylate (180.54147 millimoles) was added with shaking then the mixture was filtered quickly. The monomer was weighed and stored in the fridge

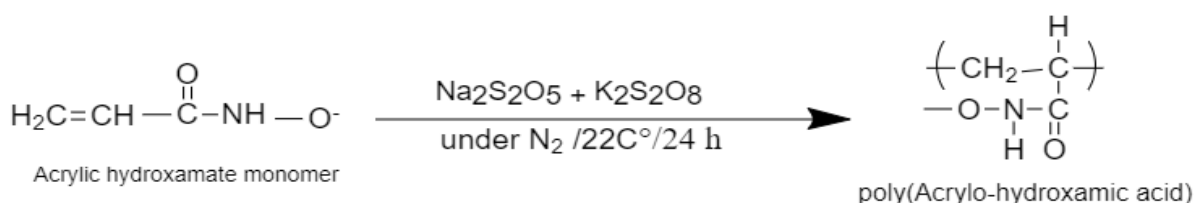


Equ. (4): Reaction of butyl acrylate and hydroxylamine hydrochloride

3.2.2 - Free radical polymerization:

1.12 gr. of Acrylo-Hydroxamic acid (monomer) was weighed out and transferred to a 50 ml round bottom flask. 15 ml of degassed Distilled water was added to the round bottom flask which was immediately sealed with the septum. Nitrogen gas bubbled into the RBF by needle through a balloon. 0.057gr. of Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and 0.104 gr. of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) were weighed and dissolved in 1 ml degassed water. A syringe is used to transfer the initiator to the reaction. The second needle was also inserted into the septum to release some pressure built up. The reaction was carried out (20-22 °C). The polymerization reaction continued for 24 hours. Then a solution of 1% of methanolic sodium acetate was used to precipitate the polymer. The polymer was dried under vacuum for 2 hours at 40 °C.

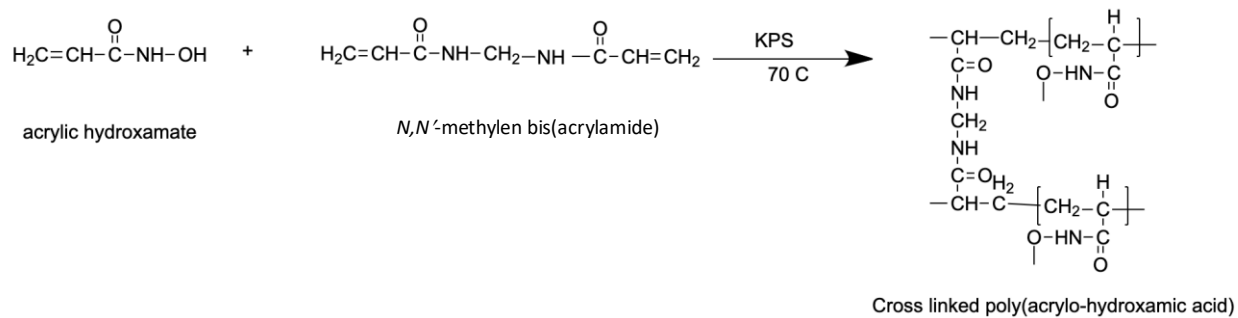
The percentage yield of linear polymer = 89.38%.



Scheme 11: Polymerization of poly (Acrylo-hydroxamic acid).

3.2.3 - Cross-linked polymerization:

2.35 gr. of Acrylo-Hydroxamic acid (monomer) and 1.12gr. cross-linking agent *N,N'*-methylene bis(acrylamide) were dissolved in 25ml of degassed water and placed in a 50 ml round bottom flask. The RBF immediately sealed with the septum. Nitrogen gas bubbled into the RBF by needle through a balloon. The reaction mixture of was heated at 70°C and deoxygenated for 30 min. Then, 13.5 mg of KSP was added to initiate polymerization. The polymerization reaction continued for 24 hours. The percentage yield of crosslinked polymer = 84.82%.



Scheme 12: Cross linked poly (acrylo-hydroxamic acid)

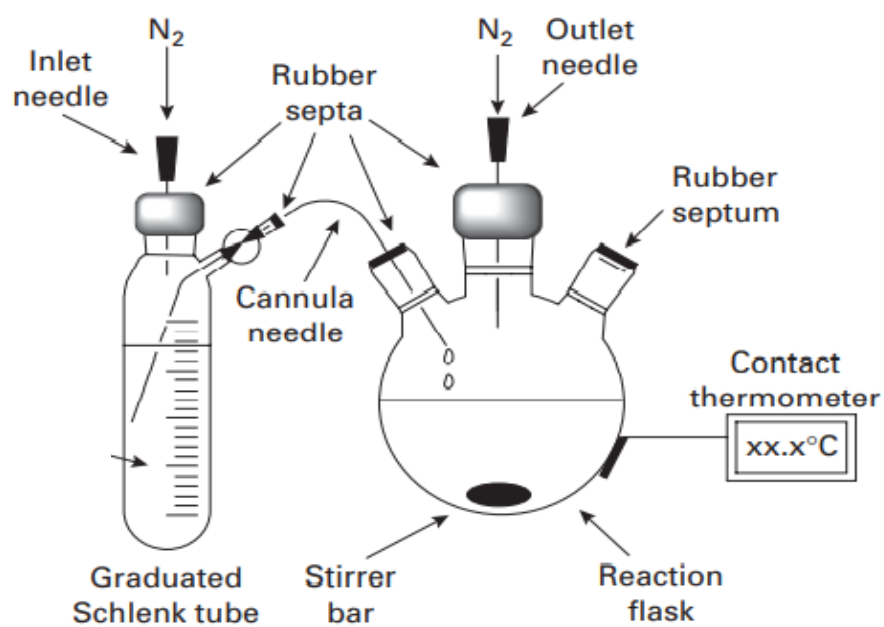


Fig. (6): Free radical polymerization system under N_2 gas.

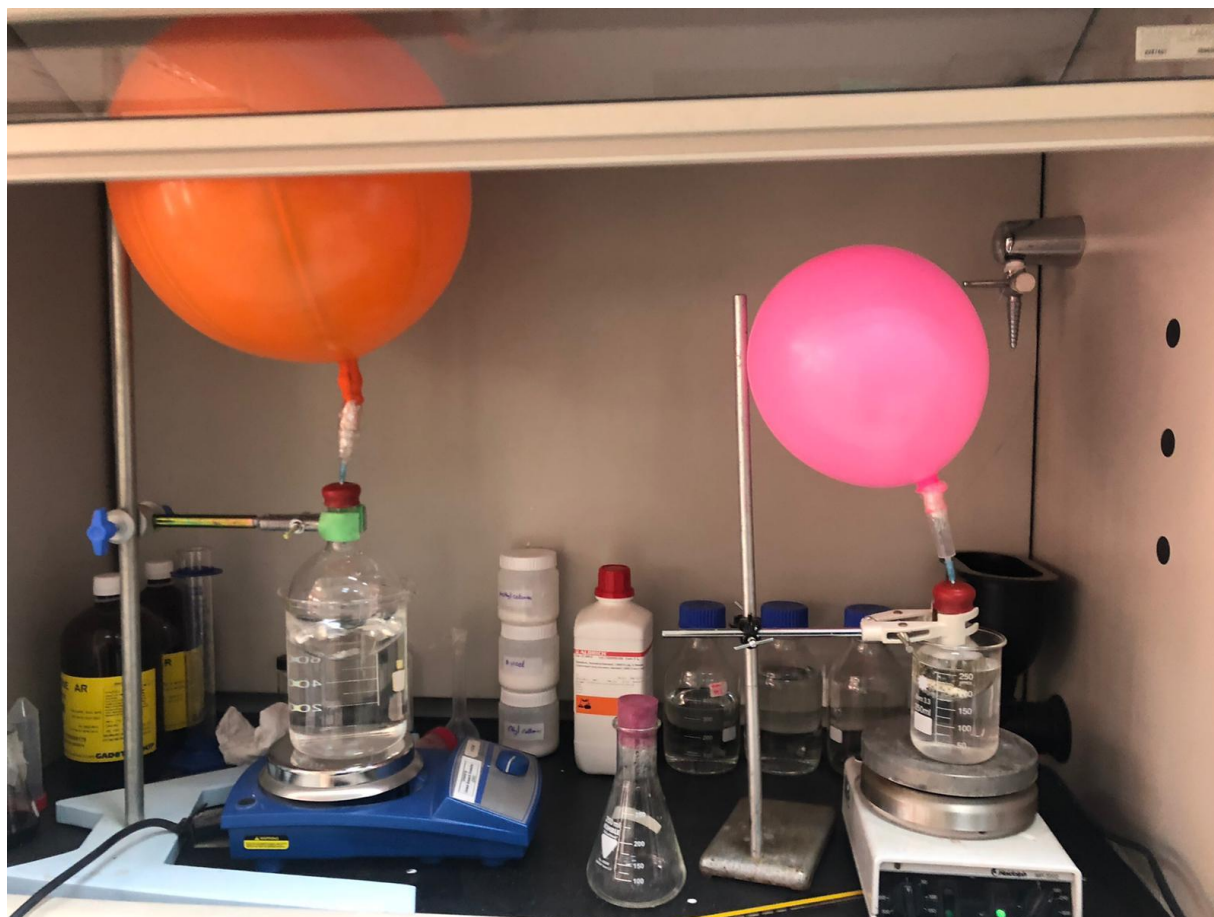


Fig. (7): Polymerization of acrylo-hydroxamoc acid polymer under N₂.

Chapter four

Results and discussion

4.Results and discussion

Acrylo hydroxamate monomer appeared in the form of a white fine crystal that dissolves in water, while the highly viscous linear poly (acrylo-hydroxamic acid) was effectively soluble in water, in contrast to the cross-linked poly (acrylo-hydroxamic acid) that did not dissolve in water. cross-linked poly (acrylo-hydroxamic acid) appeared as pale-yellow powder. Acrylo hydroxamate monomer, linear and cross-linked poly (acrylo-hydroxamic acid) formation from butyl acrylic acid was confirmed by making a magenta complex with Fe^{3+} ions in aqueous solution. While the starting material (butyl acrylate) gives negative result with Fe^{3+} [27].

4.1 FT-IR:

Table (4) below shows the functional groups of butyl acrylate monomer.

Functional groups	Frequency(cm^{-1})
C=O	1722
C-H	2875-2961
C=C	1637
CH ₂	1408

For Acrylo-Hydroxamic acid monomer. C=O band at around 1641cm^{-1} . The band 1622 cm^{-1} belong to C=C stretching. The band at around 1133cm^{-1} refers to C-N stretching band. In addition, N-H stretching band was around 1542 cm^{-1} . The peak 3050cm^{-1} for C-H stretching vibrations. $-\text{CH}_2-$ group observed at 2878cm^{-1} . A signal at 3675 cm^{-1} and another signal at 3246cm^{-1} was attributed to stretching vibrations of $-\text{OH}$. The FT-IR spectrum of the monomer confirmed the presence of hydroxamic acid functional group.

Table (5): frequencies observed from the corresponding functional groups of hydroxamate monomer.

Bond	Frequency (cm⁻¹)
C=O	1641
C=C s	1622
C–N s	1133
N–H	1542
C–H s	3050
CH₂–	2878
–OH s	3675, 3246

S=stretching

In a comparison between butyl acrylate and hydroxamate monomer FT-IR spectrum, the presence of hydroxamic acid functional groups confirmed.

FT-IR spectrum can indicate the successful polymerization process by observing the disappearance of the C=C double bond from the spectrum and that's what linear poly (acrylo-hydroxamic acid) table (5) shows. The peak around 3190 cm⁻¹ refers to the O–H bond. FTIR spectra showed that around 1552 cm⁻¹ N–H stretching bond was apparent. –CH₂– group observed at 2819 cm⁻¹. The band at around 1202 cm⁻¹ belong to C–C. The band around 1701 cm⁻¹ refer to C=O.

Table (6): frequencies observed from the corresponding functional groups of linear polymers.

Bond	Frequency(cm^{-1})
O-H	3190
C-C	1202
-CH₂-	2819
C=O	1701
N-H	1552

For cross-linking polymerization spectrum showed that around 1637 cm^{-1} C=O band appeared. 1541 cm^{-1} refers to the N-O single bond. The band at around 1122 cm^{-1} refers to C-N stretching band. 1202 cm^{-1} related to C-O bands. 1232 cm^{-1} for single bond C-C stretching vibrations. the peak around 3269 cm^{-1} refers to the O-H bond.

Table (7): frequencies observed from the corresponding functional groups of cross-linked polymers.

Bond	Frequency(cm^{-1})
C=O	1637
N-O	1541
C-N	1122
C-O	1202
C-C	1232
O-H	3269

Apparently, the C=C double bond disappear as shown in figures (14,15), this is sign that the polymerization process successfully done.

FT-IR spectrum in the appendix.

4.2 NMR:

Szarka et al. (2000) [28] synthesized hydroxamic acid using different starting materials, NMR analysis of their works used in this research as a reference. Fig. (10) showed the ^1H NMR spectrum for the monomer. C-H (3.95ppm), O-H (3.44ppm), N-H (4.22 ppm) and the signals (0.99-2.71 ppm) corresponds to the butanol residuals. The ^{13}C NMR spectrum of Acrylo-hydroxamic acid monomer that was analyzed by D_2O as a solvent is shown in Fig. (11). The peak at 160.02 ppm corresponds to the $\text{C}=\text{O}$, signal at 168.89 ppm refer to $\text{C}=\text{C}$ double bond. The peak 55.75 ppm corresponds to the $\text{H}_2\text{N}-\text{C}$ (amine). Signals (30.44-34.90 ppm) corresponds to CH . the peak at 36.55 ppm corresponds to the CH_2 .

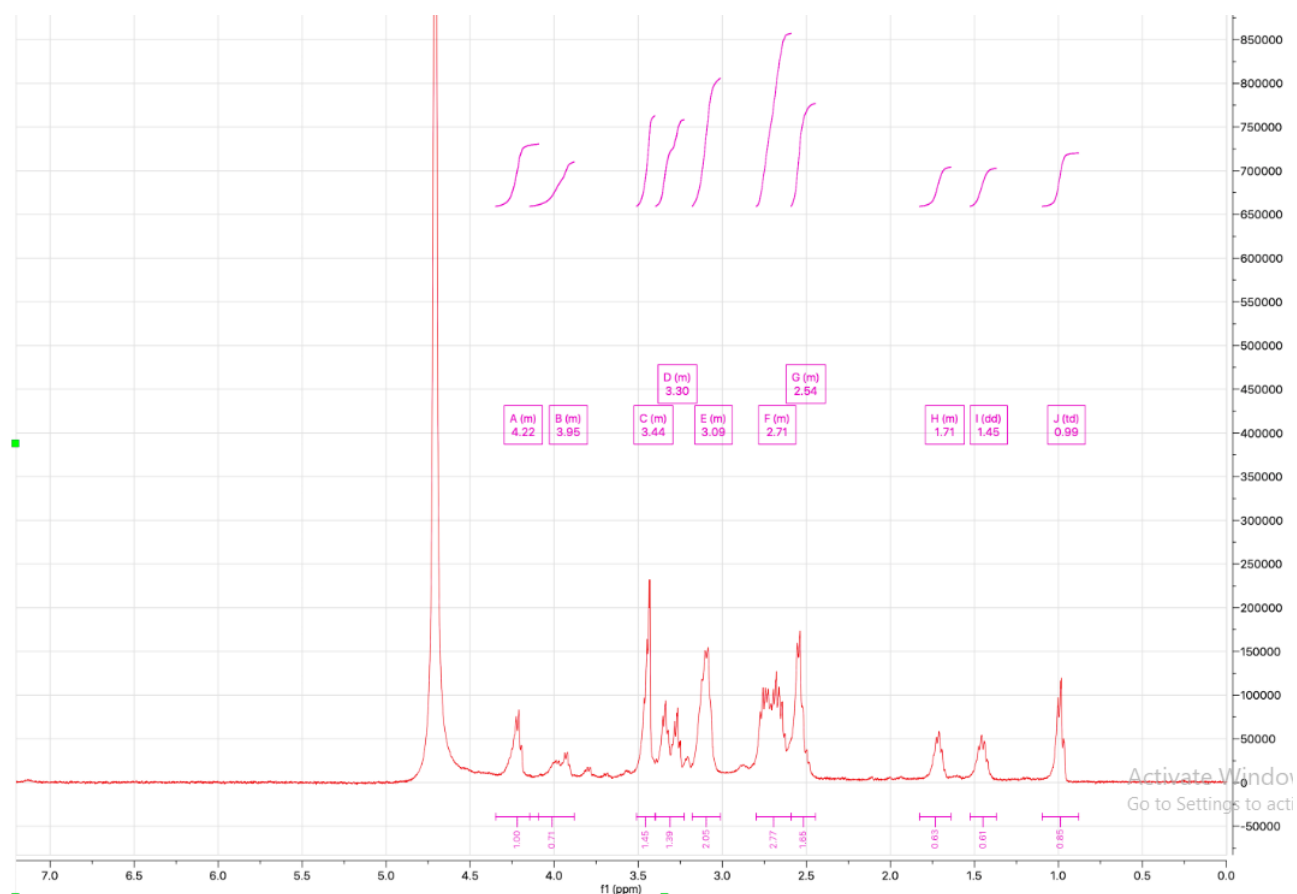


Fig. (8): ^1H NMR for acrylo-hydroxamic acid monomer

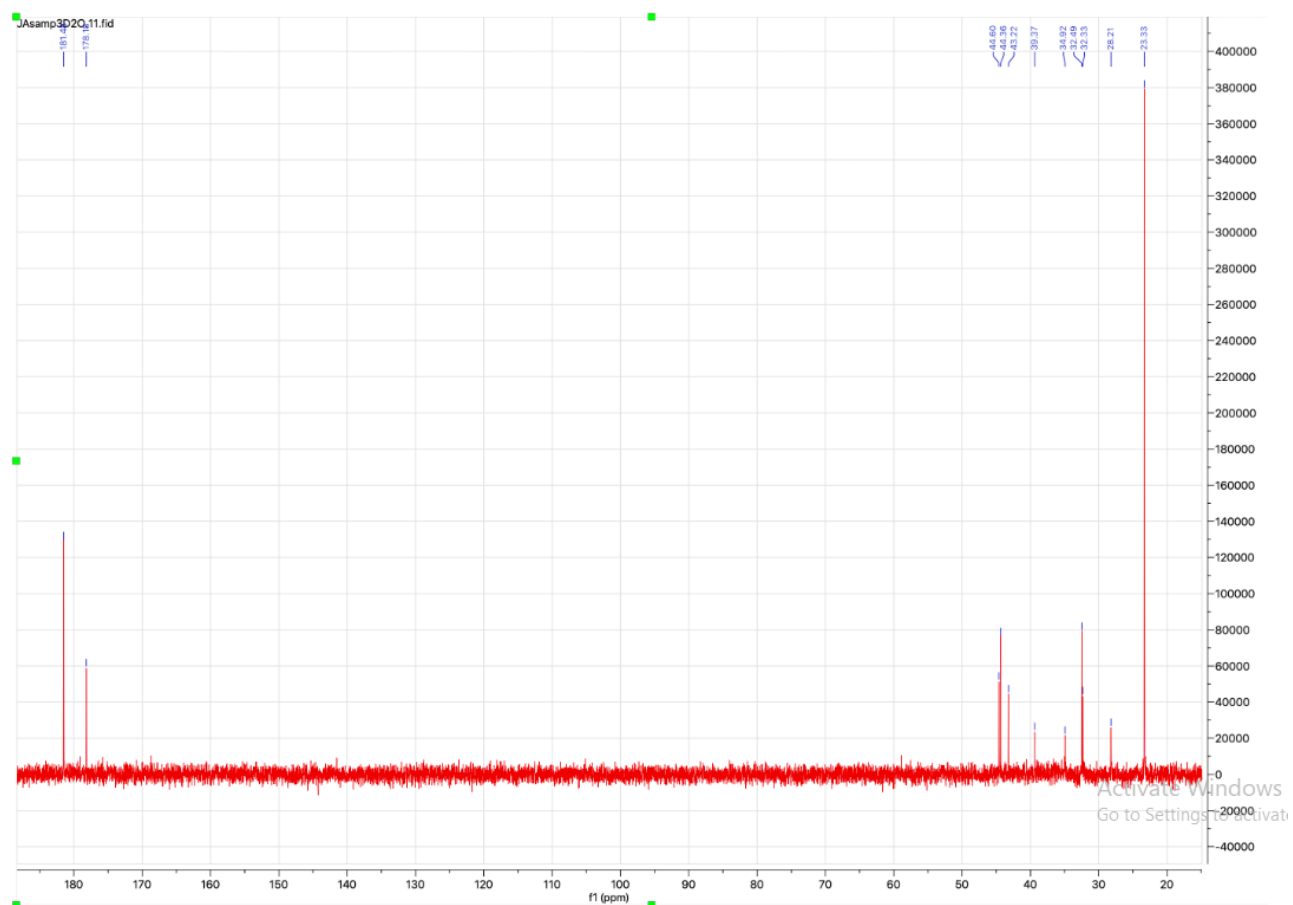


Fig. (11): ¹³C NMR for linear poly (acrylo-hydroxamic acid)

For cross-linked polymer, ^1H NMR spectrum shown in fig. (14). The protons of CH appeared at 3.08 ppm. The protons of NH group appeared in the region 4.40 ppm. Cross linked poly (acrylo-hydroxamic acid). The signal (2.16-2.73ppm) expected to corresponds to cross linking agent residuals.

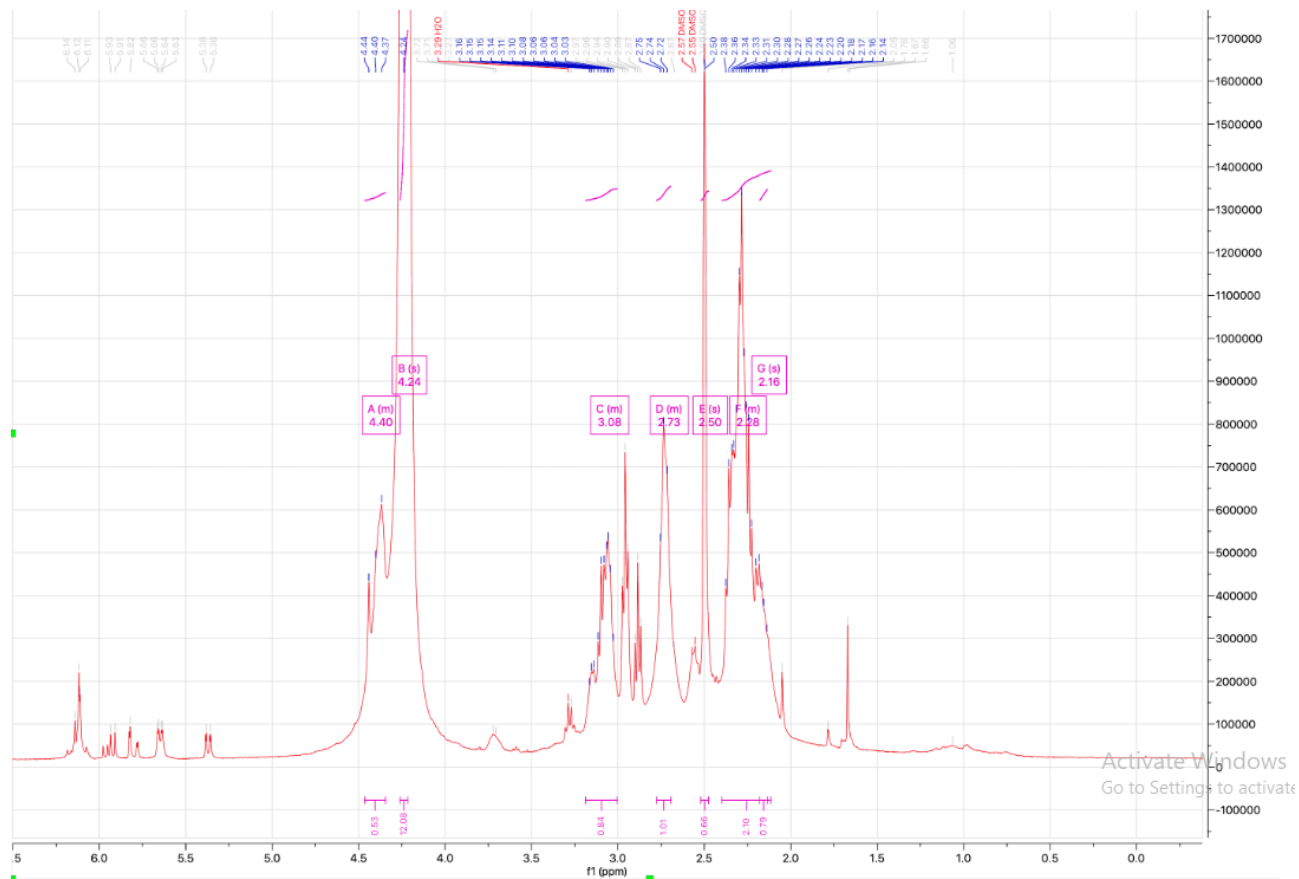


Fig. (12): ^1H NMR for cross-linked poly (acrylo-hydroxamic acid).

4.3 Characterization by Light scattering:

Table (8): linear and cross-linked poly (acrylo- hydroxamic acid) characteristic by SLS.

	Linear polymer	Cross-linked polymer
Poly dispersity index	0.209	0.257
Peak of interest Est. MW (kDa)	488000	431000
Temperature (C°)	28.23	28.23

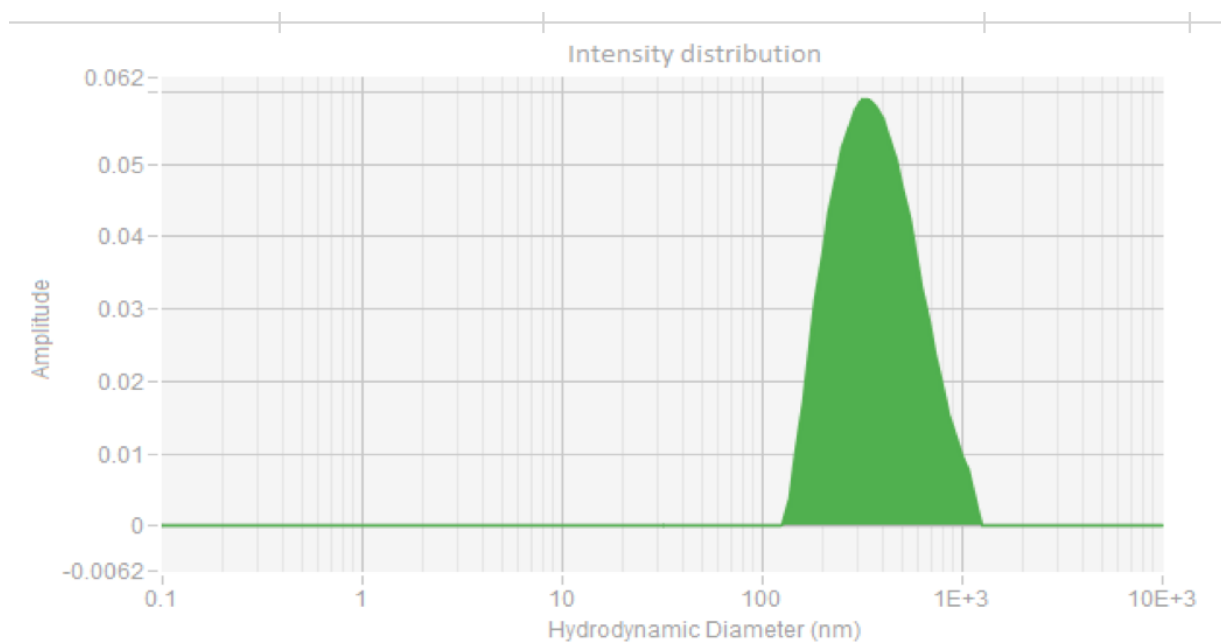


Fig. (13): Particle size distribution of poly (acrylo-hydroxamic acid) by free radical polymerization.

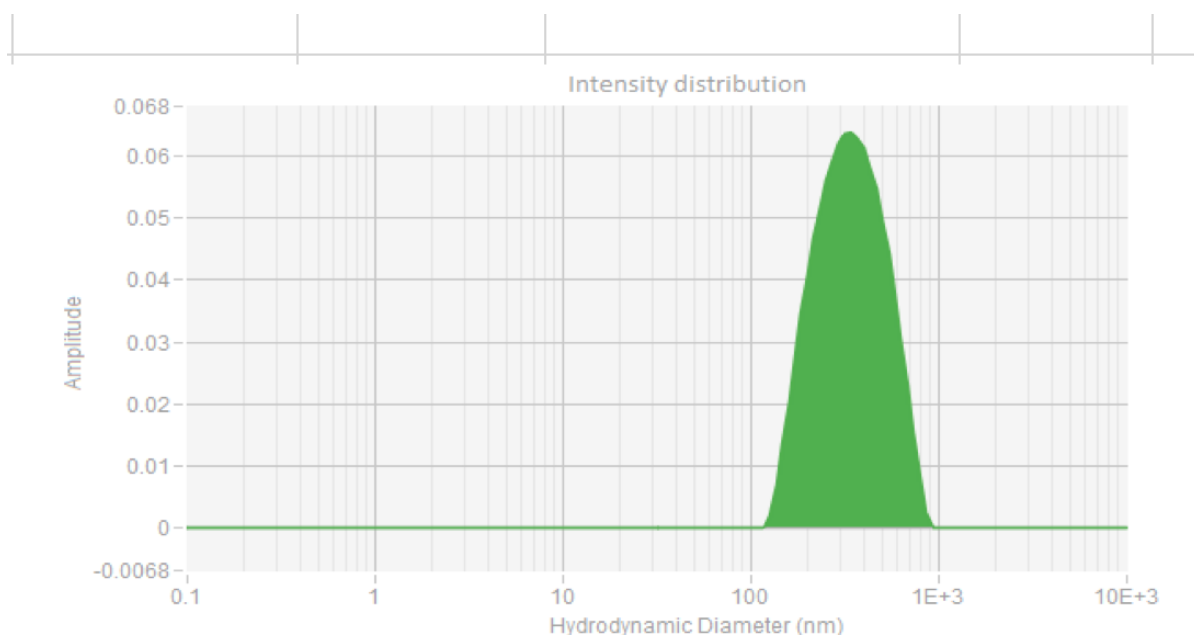


Fig. (14): Particle size distribution of poly (acrylo-hydroxamic acid) by cross-linking.

To determine the molecular average weights of polymers, several analytical techniques based on separations, osmometry, light scattering, and spectroscopy are currently available. Light scattering has the ability to produce more precise molecular weight readings than other approaches and is widely used recently to study the average molecular weight of polymers.

The average molecular weight of each sample was estimated by light scattering (fig.15,16) at 28°C, the molecular weight of the linear polymer by free radical polymerization (which took 24 hr) was 488,000 g/mol. Hosseini et al. (2011) [29] synthesized Poly (Hydroxamic Acid) by three fractions. The number average molecular weight of these fractions was determined by the cryoscopy osmometric method. Fraction one (Acrylic acid) which took 24 hr. the Mwt obtained was 105,700, fraction two (Ethyl acrylate) with a reaction time of about 18 hr. the Mwt was 96,600, and fraction three (Acrylamide) Mwt was 87,400 after 12 hr. of reaction time. In 2000, George et al. synthesized poly (Hydroxamic acid) from methacryloyl as a starting material, the Mn was 33,200 gr/mol. Cross-linked poly (acrylo hydroxamic acid) have Mwt up to 431,000 g/mol [30]. As its obvious the Mw of Hydroxamic acid polymer with butyl acrylate as starting material greater than other polymers with different starting

materials. The degree of polymerization of linear poly (acrylo hydroxamic acid) was 5609.19 while the degree of polymerization of hydrogel polymer =4954.022.

The polydispersity index (PDI) found 0.209 by light scattering for linear polymer, and 0.257 for cross-linked polymer (Table 7). The PDI values < 0.05 are common to monodisperse samples and those > 0.7 to broad size values e.g., polydisperse) were defined by the International Standard Organizations (ISOs).

The very high M_w of poly (acrylo-hydroxamic acid) is the secret in the sticky and viscous appearance of the polymer. The longer the chains get, the more difficult it is to make them flow since they are intertwined more.

Apparently, there are several factors to synthesis a high molecular weight polymer. From this study we can conclude some of them such as, low monomer concentration, pure materials and chemicals, complete prevention of oxygen leakage into the reaction, and preventing termination caused by impurities. The consumption of initiators at an early stage of polymerization.

Linear (acrylo- hydroxamic acid) polymer UV spectrum shows λ_{\max} at 250nm(fig.17), which is within the Ultraviolet region. Otherwise, cross-linked polymer showed flocculation in the absorbance spectrum (350,300,630,730, etc), It is assumed that the cause of this flocculation is due to the cross-linking agent. The bonding between the polymer and cross-linking agent caused the presence of λ in the UV-Vis region(fig.18).

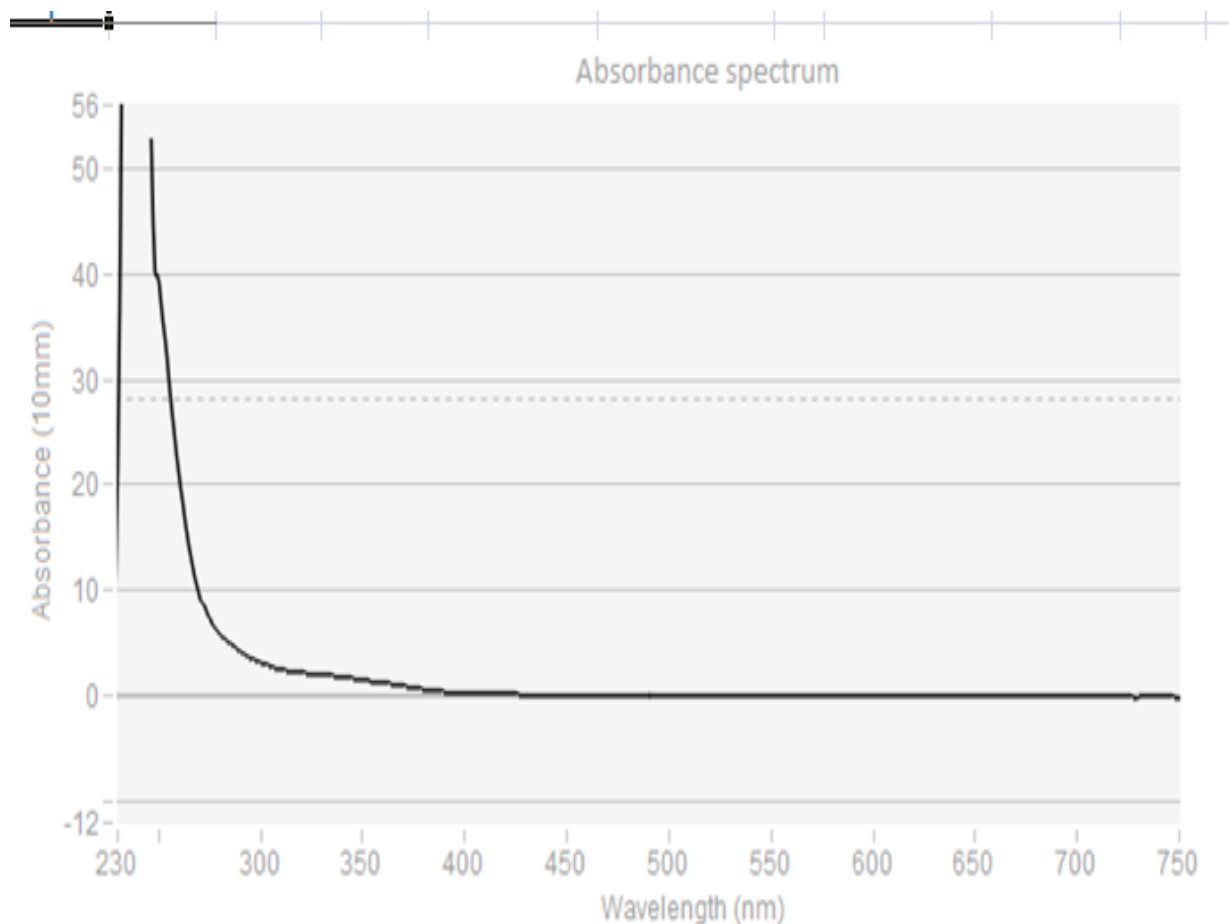


Fig. (15) UV-Visible spectrum of poly (arylo-hydroxamic acid) by free radical polymerization.

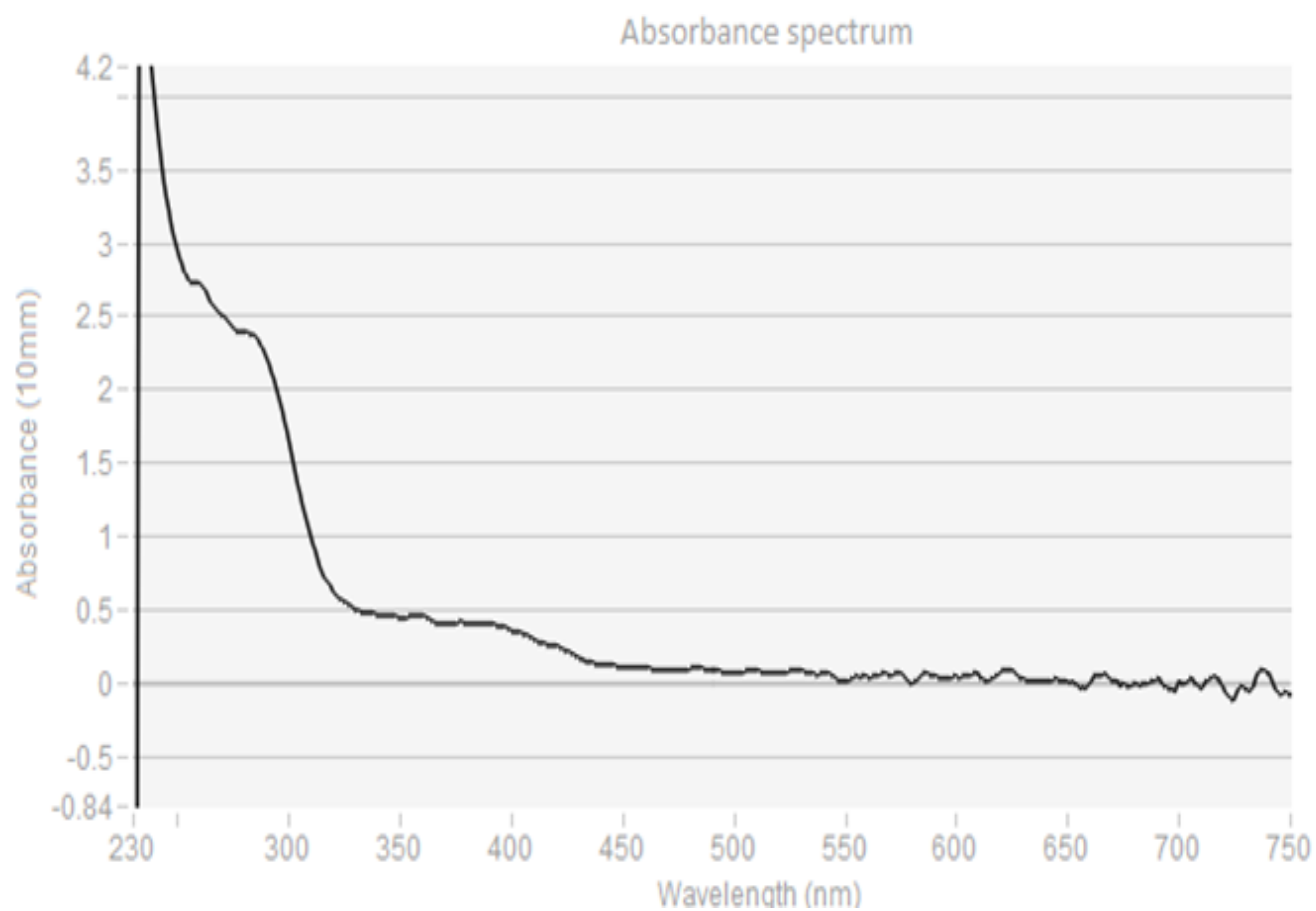


Fig. (16): UV-Visible spectrum of poly (arylo-hydroxamic acid) by cross linking polymerization

Chapter five

Conclusion

Conclusion:

Due to its great role as chelating agents, inhibitors of numerous enzymes, anticancer, antimicrobial, and many more purposes, hydroxamic acids find a variety of uses in chemistry, biology, and medicine in this study, linear and cross-linked poly (acrylo- hydroxamic acid) were prepared. The synthesized hydroxamic acid was characterized using FT-IR, light scattering and NMR. High molecular weight for both linear and cross-linked polymer was achieved. The chemical structure of the monomer and polymer was determined by NMR spectrum analysis. All functional groups of the monomer and polymer were detected by FT-IR spectrum. The swellable polymer has been prepared due to its ability to swell not dissolve and this characteristic is so important in many applications such as agriculture and medicine.

Suggestions for further work of this research:

- 1) Study the chelating ability of linear and cross-linked poly (acrylo-hydroxamic acid) with various heavy metal ions to apply this characteristic in removal, chelating or adsorption from water.
- 2) study its biological activity and its application in medicine field.
- 3) The percent of hydroxamic acid groups that synthesized in polymer estimating by [31].

Chapter six

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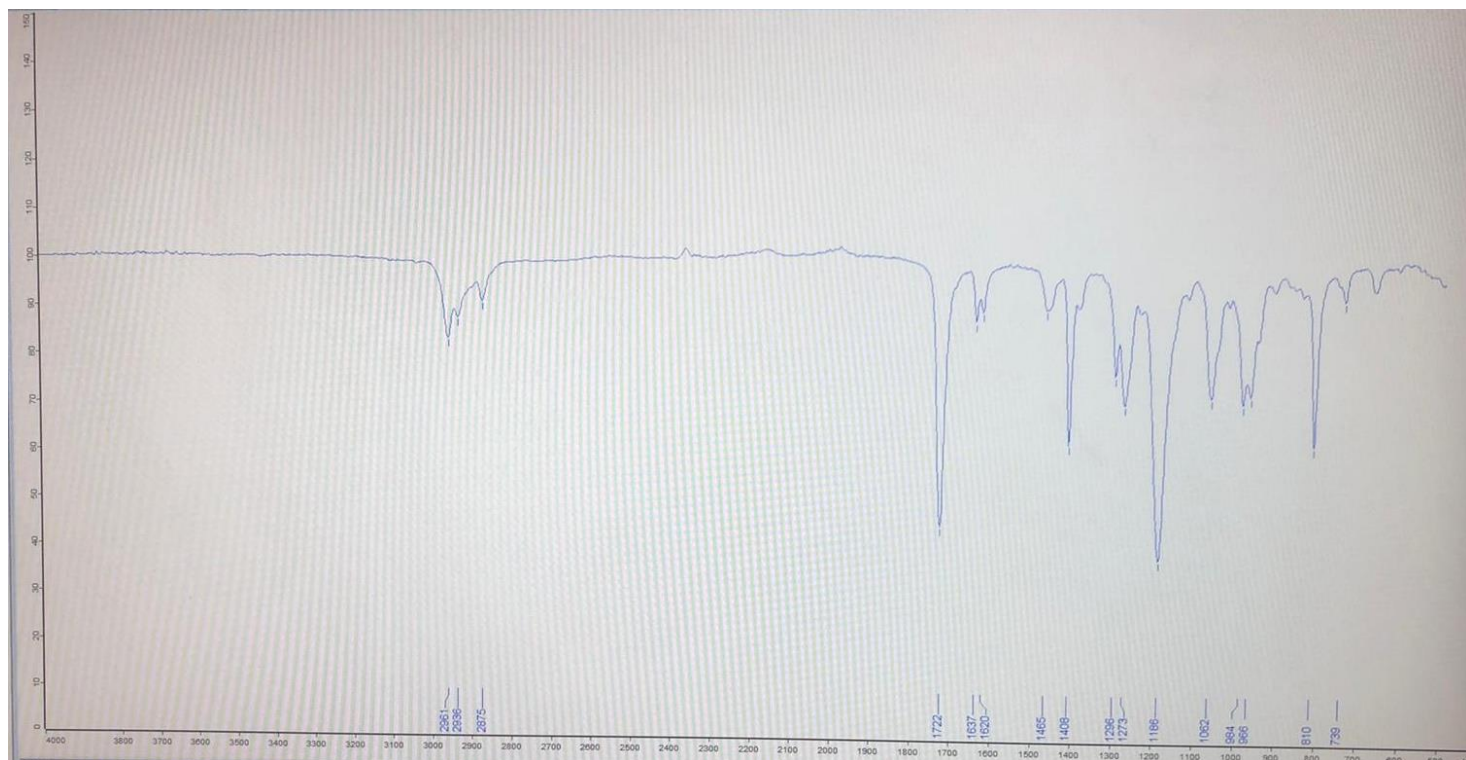
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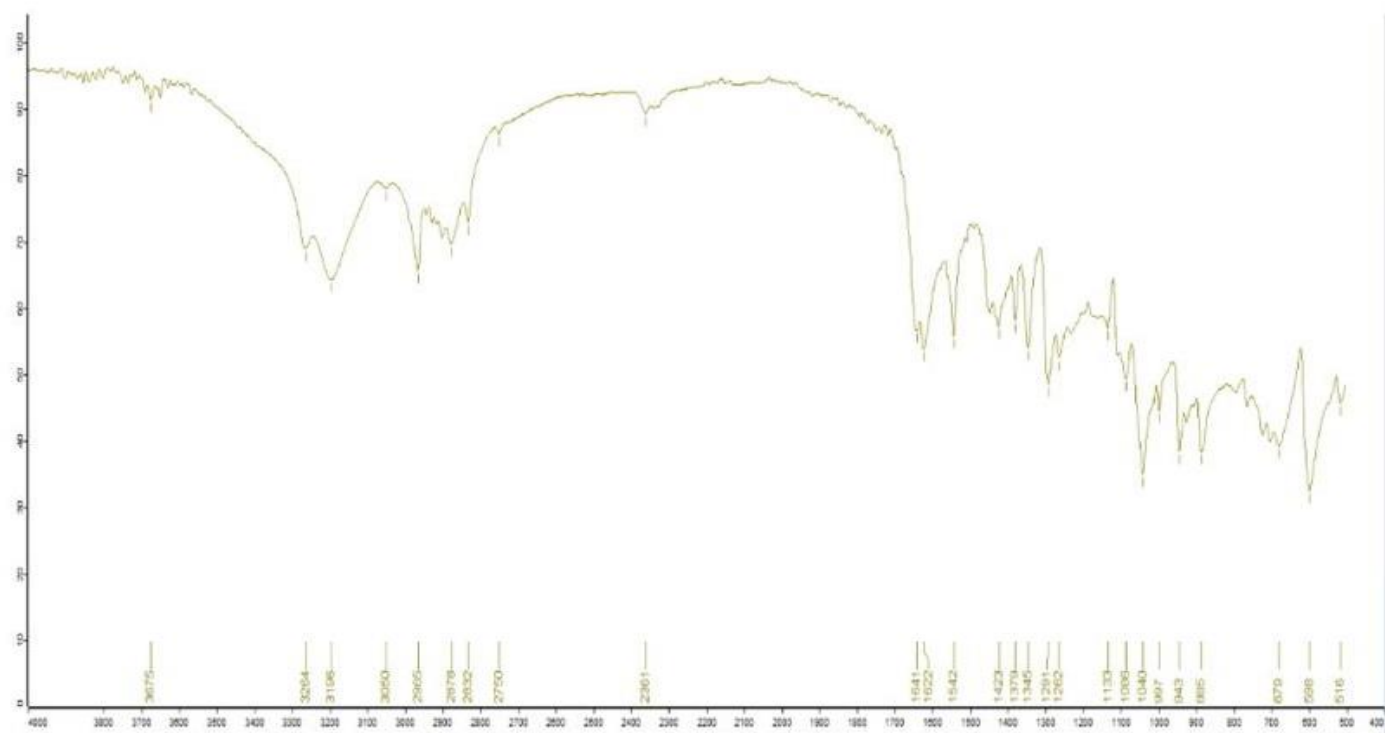
الملخص العربي:

أصبحت البوليمرات القابلة للذوبان في الماء القائمة على (أحماض الهيدروكساميك) مهمة في تطبيقاتها لقدرتها بيوتيل الرائحة على الارتباط مع المعادن الثقيلة. تم تحضير مونومر حمض أكريلو هيدروكساميك من تفاعل أكريلات مع هيدروكسيل أمين هيدروكلوريد بوجود هيدروكسيد البوتاسيوم كقاعدة في الميثانول. تم تحضير البوليمر الخطي عند درجة حرارة الغرفة في ماء مقطر منزوع الغازات باستخدام بادئ ذي جذور حرة، (N₂). تحت ظروف غاز خامل (Na₂S₂O₅) ، وثنائي كبريتات الصوديوم (K₂S₂O₈) بيرسلفات البوتاسيوم N, N'-كبادئ للجذور الحرة (K₂S₂O₈) تم تحضير بوليمر مترابط باستخدام بيرسلفات البوتاسيوم العمل () كعامل ربط متقاطع عند 70 درجة مئوية. البوليمرات المنتجة في هذا Methylen bis(acrylamide) تم تحديد متوسط وزن البوليمرات الخطية والمترابطة عن طريق تشتت (Mw). لها وزن جزيئي مرتفع الضوء وهي على التوالي 431000 ، 488000 جم / مول

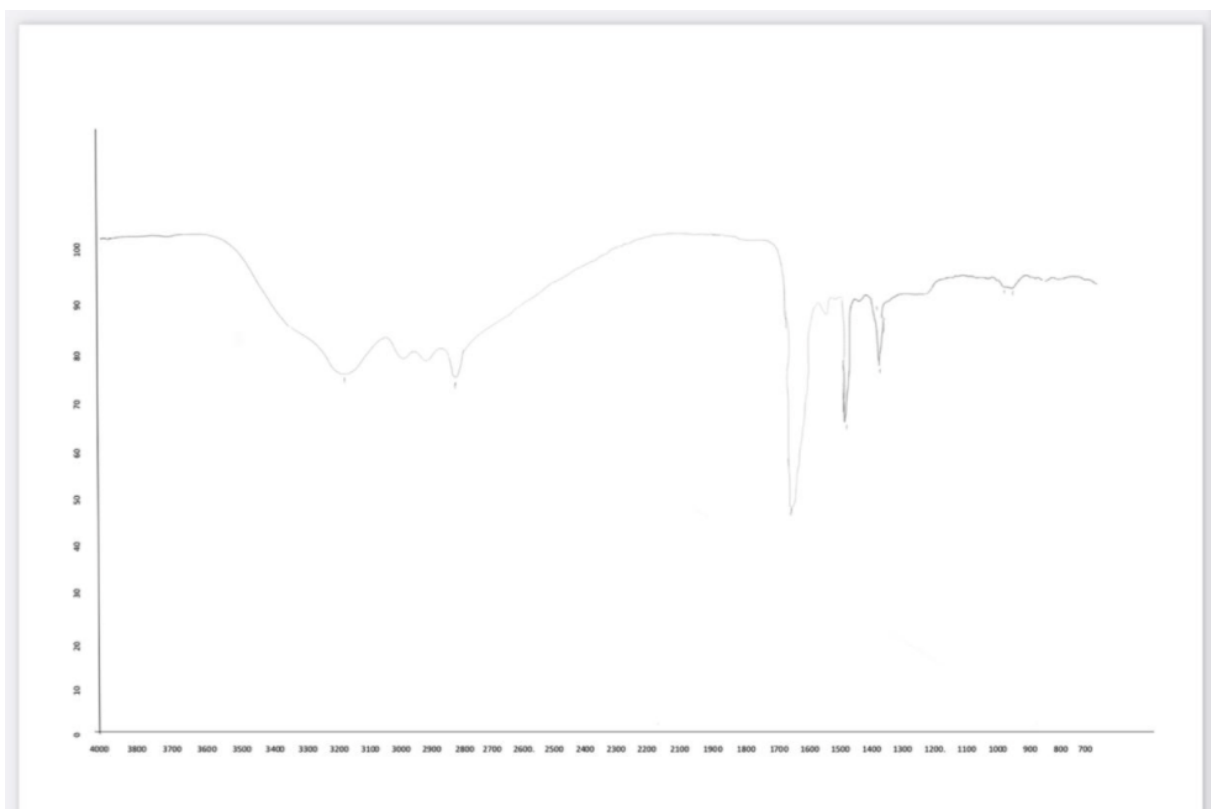
Appendix:



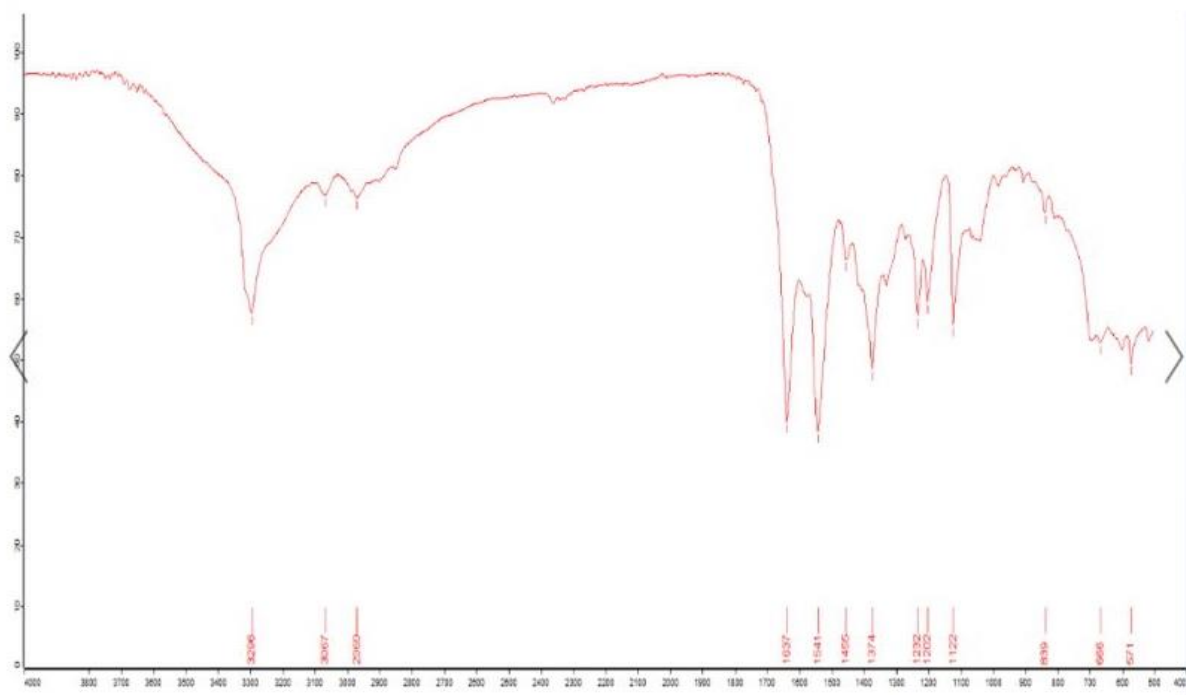
FT-IR spectrum for n-butyl acrylate



FT-IR spectrum of acrylic hydroxamate monomer



FT-IR spectrum of linear poly (acrylo-hydroxamic acid)



FT-IR spectrum of cross-linked poly (acrylo- hydroxamic acid)/