جمهورية العراق
وزارة التعليم العالي و البحث العلمي
جامعة كربلاء
كلية التربية للعلوم الصرفة
قسم الكيمياء

تحضير بوليمر مشترك جديد ودراسة الدوال الحركية والثرموديناميكية

هذه الرسالة مقدمة إلى
مجلس كلية التربية للعلوم الصرفة - جامعة كربلاء ، كجزء من متطلبات نيل
درجة الماجستير في علوم الكيمياء

من قبل

مازن فاضل عناد الطفيلي

بكالوريوس كيمياء / جامعة الأنبار (2000/2001)

إشراف

الأستاذ الدكتور
محمد ناظم بهجت

الأستاذ الدكتور
حميدة عيدان سلمان

ذي الحجة - 1439هـ
أيلول- 2018 م

Ministry of Higher Education
And Scientific Research
University of Karbala
College of Education for pure Science
Department of Chemistry

Preparation of a New Co-Polymer and Studying Kinetic, Thermodynamic Functions

A Thesis
Submitted to the Council of College of Education for pure Science
University of Karbala/ In Partial Fulfillment of the Requirements for the
Degree of Master in Chemistry Sciences
By

Mazin Fadhel Enad AL-Tufaily

(B.Sc. in Chemistry / AL-Anbar University – 2000/2001)

Supervisors

Professor Dr.	Professor Dr.
Hamieda Edan Salman	**Mohammad Nadhum Bahjat**

2018A.D 1439A.H

بسم الله الرحمن الرحيم

﴿ويسألونك عن الروح قل الروح من
أمر ربي وما أوتيتم من العلم إلا قليلا﴾

صدق الله العلي العظيم /سورة الإسراء/ الآية ٨٥

Supervisors Certification

We certify that this thesis (**Preparation of a new co-polymer and studying kinetic , thermodynamic functions**) was papered under our supervision in the chemistry department-College of Education for Pure Sciences- University of Karbala, in partial Fulfillment of the requirements for the degree of Master in Chemistry Sciences by the student (**Mazin fadhel enad**).

Signature:	Signature:
Prof. Dr. **Mohammad Nadhum Bahjat**	Prof. Dr. **Hamieda Edan Salman**
Supervisor	Supervisor
Date: 2018 / /	Date: 2018 / /

In view of the available recommendations, I forward this thesis for debate by the examining committee.

Signature:

Name: Prof. Dr. **Hamieda Edan Salman**

Date: 2018 / /

Head of Chemistry Department

Committee Certification

We certify that, we read this thesis **(Preparation of a new co-polymer and studying kinetic, thermodynamic functions)** and as examining committee examined the student (**Mazin fadhel enad AL-Tufaily**) in its content, and that in our opinion it is adequate (**Excellent**) with standing as a thesis for degree of master in chemistry sciences.

Chairman

Signature:
Name:**Dr. Abbas Matrood Bashi**
Sci.Title: Professor
Address:
Date: 2018 / /

Member

Signature:
Name**: Dr.Mohanad Mousa Kareem**
Sci.Title: Asst. Professor
Address:
Date: 2018 / /

Member

Signature:
Name: **Mousa Omran Kadium**
Sci.Title: Asst. Professor
Address:
Date: 2018 / /

Supervisor & Member

Signature:
Name: **Prof. Dr. Hamieda Edan Salman**
Sci.Title: Professor
Address: University of Karbala/College of Education for pure Sciences
Date: 2018 / /

Supervisor & Member

Signature:
Name: **Prof. Dr. Mohammad N.A.L Baiati**
Sci.Title: **Professor**
Address: University of Karbala/College of Education for pure Sciences
Date: 2018 / /

Approved for the College Council……
Signature:
Name: Prof. Dr.
Sci.Title: Professor
Address: University of Karbala/College of Education for pure Sciences
Date: 2018 / /
Dean of the College of Education for Pure Sciences

Scientific Evaluation Report

This is to certify that I have read the thesis entitled (**Preparation of a new co-polymer and studying kinetic, thermodynamic functions**) and corrected the scientific mistakes I found. The thesis is, therefore, qualified for debate

Signature:
Name:
Sci.Title:
Address:
Date: 2018 / /

Amendment Report

This is to certify that I have read the thesis entitled (**Preparation of a new co-polymer and studying kinetic, thermodynamic functions**) and corrected the grammatical mistakes I found. The thesis is, therefore, qualified for debate .

Signature:
Name:
Sci.Title:
Address:
Date: 2018 / /

Dedication

THIS WORK
IS DEDICATED
TO GREAT ALLAH

Acknowledgements

Thanks to Allah : the Almighty , the Merciful the Generous for helping me in completing this work .

I would like to extend my deepest gratitude to my supervisors, Prof. Dr. Mohammad Nadhum Bahjat,and Prof. Dr. Hamieda Edan Salman. whose expertise, understanding, patience, generous guidance and support made it possible for me to work on a topic that was of great interest to me, it was a pleasure working with them.

I would like to thank the Dean of College of Education and the head of Chemistry Department Prof. Dr. Hamieda Edan Salman.

I would like to extend my deepest gratitude to all professors who taught me at the postgraduate levels .

I owe especial thanks to : My family and all my friends for standing with me and encouraging me.

I take this opportunity to record my sincere thanks to all of the gentlemen chairman and members of the committee discussion.

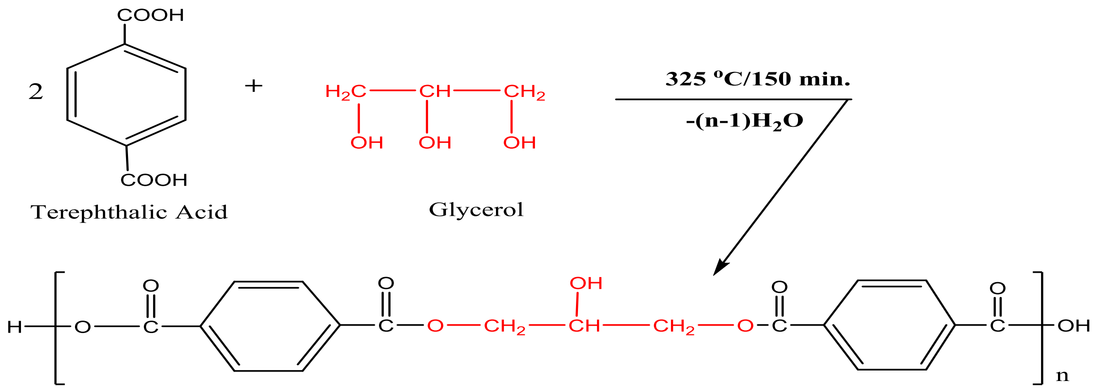
✍

Mazin

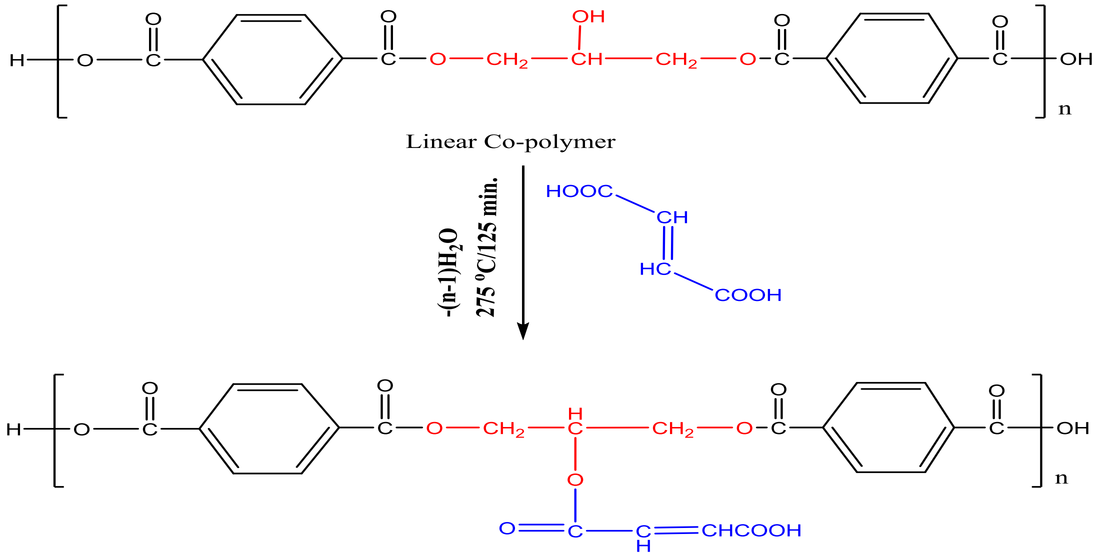
Abstract

In this work, a new graft co- polymer was synthesized by two methods (fusion and solubilization) by the reaction of one mole of glycerol with two moles of terphthalic acid to form the linear co-polymer. The graft co-polymer was synthesized by the reacted of the linear co-polymer with 0.5mole of fumaric acid:-

<u>First:</u> fusion process, the linear co- polymer was prepared in 150 Min. at 325 °C, and the graft co-polymer at 275 °C in 125 Min., as shown in the following schemes. The product was identified by FT-IR and ^{1}HNMR spectroscopies.

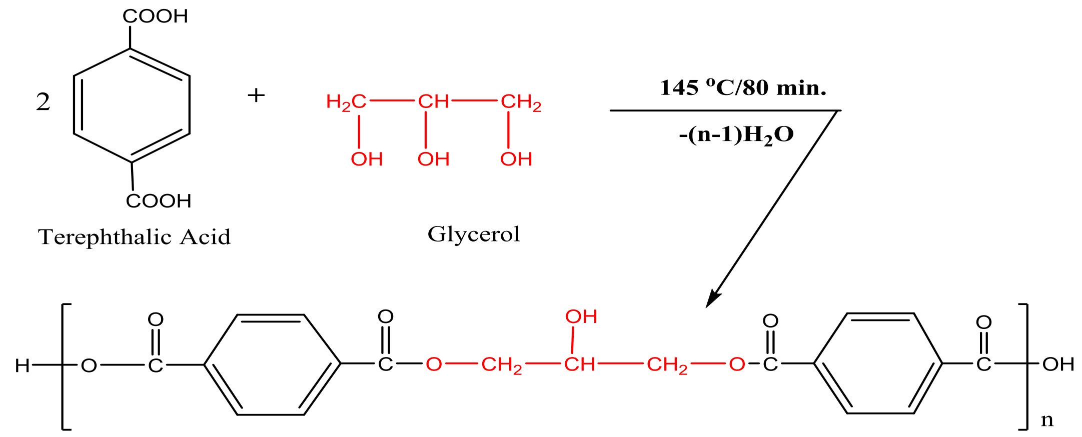


Linear Co-polymer

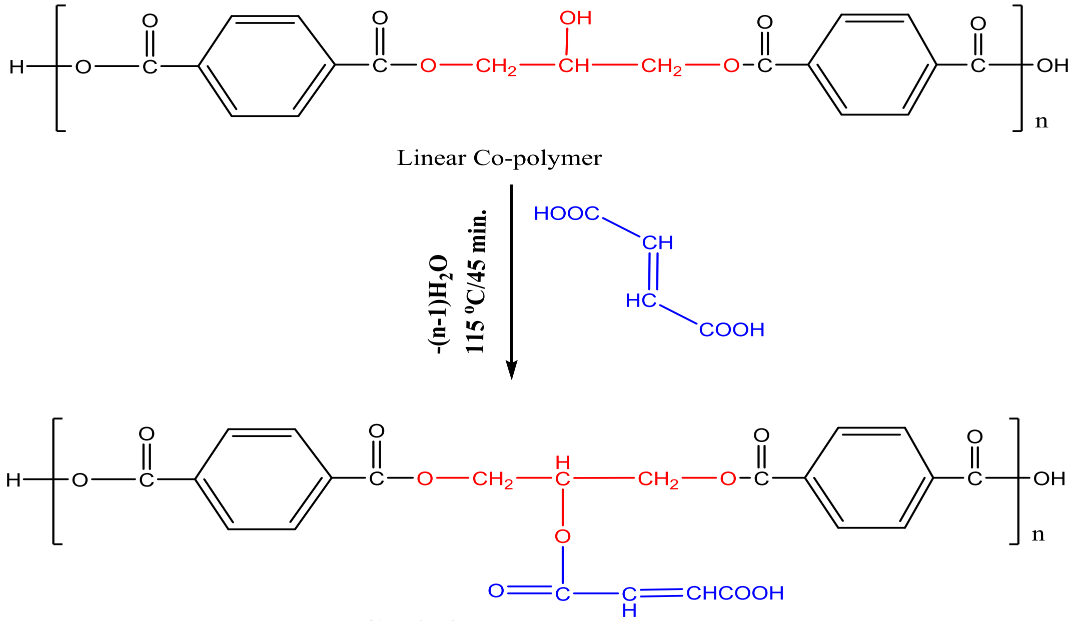


Graft Co-polymer

<u>Second:</u> solubilization process, the linear co- polymer was prepared in 80 min. at 145 °C, and the graft co-polymer at 115 °C for 45 min., as shown in the bellow schemes. The AFM used to the molecules that produced by solubilization process, and the test was shown as nanoparticles. The roughness coefficient of a linear co-polymer surface was 1.19 nm and the square root was equal to 1.37 nm and the molecular size of the linear co-polymer nanoparticle was 94.09 nm. The roughness coefficient of a graft co-polymer surface was 1.68 nm and the square root was equal to 1.96 nm and the graft co-polymer nanoparticle was 56.80 nm



Linear Co-polymer



Graft Co-polymer

The rate of polymerization and the activation energy for the linear co-polymer were calculated. It was found 120 Sec.$^{-1}$ and 242.3531 J/mole respectively. The thermodynamic function for the linear co-polymer was calculated in different temperatures, it was found as in the following

no	**T (K^o)**	**1/T**	**lnK**	**ΔH (KJ/mol)**	**ΔG (KJ/mol)**	**ΔS (KJ/mol.K)**
1	563	1.776×10^{-3}	-0.1003	2.9×10^{3}	0.469	5.150
2	568	1.7605×10^{-3}	-9.2992		43.914	5.097
3	573	1.7452×10^{-3}	-10.733		51.131	4.971
4	578	1.7301×10^{-3}	-15.232		73.197	4.890
5	583	1.7152×10^{-3}	-24.063		116.634	4.774

The swelling ratio was measured for all the hydrogel samples, in three different media (pH=2.2), (pH=7.0) and (pH=8.0) at constant temperature, as function of time; The results obtained showed that the swelling ratio in the basic medium were higher than in the acidic medium, indicating that the combined graft co-polymer is selective in the medium. On the other hand, the swelling ratio of the graft co-polymer which prepared by solubilization process was higher than the graft co-polymer which prepared by a fusion process.

When we compare the results obtained for the polymers which prepared by fusion process and polymers which prepared by solubilization process, we note that the solubilization polymers were far higher than the fusion polymers, and this Indicates the advantage of the solubilization process from fusion process, as the nanoparticles have played an important role in the effectiveness of polymers in the swelling.

List of Contents

List of Tables

Pages	**List of Figures**	Serial No.

List of Abbreviations

Symbol	**Description**	
HDPE	High density polyethylene	
SMCs	sheet molding compounds	
MEKP	Methyl ethyl ketone peroxide	
TG	Degree of Glass transition	
PETP	Poly ethylene terephthalate	
ATRP	Atom transfer radical polymerization	
pH	Acid value	
IUPAC	International Union of Pure and Applied Chemistry	
Q	temperature coefficient	
kJ/mol	kilojoules per mole	
kcal/mol	kilocalories per mole	
NP	Nano particles	
FT-IR	Fourier transform infrared	
^{1}HNMR	Proton nuclear magnetic resonance	
AFM	Atomic Force Microscope	
$\overline{Mn}$	Average number of molecular weight	
ppm	Part per million	
AA/BB	Alternative co-Polymer	

1. Introduction

1.1General Consideration

Most chemists and chemical engineers are now involved in some phase of polymer science or technology; some have called this "the polymer age". Actually, we have always lived in a polymer age [1].

The ancient Greeks classified all matter as animal, vegetable and mineral. The last was emphasized by the alchemists and medieval artisans; animal and vegetable matter, which are largely polymers, have, for the most part, always been more important than minerals [2].

Most linear polymers such as high density polyethylene (HDPE) are thermoplastic, i.e., they may be softened by heat and hardened by cooling in a reversible physical process. However, linear polymers, like cellulose which have very strong intermolecular forces (hydrogen bonds), cannot be softened by heating below the decomposition temperature [3]. Thermoset polymers are cross-linking and cannot be softened by heating. Thermoplastics such as natural rubber and stage–A resole Bakelite resins can be transformed to thermosetting polymers by having a cross-linking agent between the polymer chains[4], Some naturally occurring polymers, such as proteins , are mono-disperse, while most Synthetic polymers, such as, cellulose and polyethylene, are polydisperse [4].

Many rubbers like polymers are flexible because the free rotation of carbon–carbon single bonds allows the formation of many different shapes or conformations [5]. This segmental motion is restricted by bulky pendant groups by stiffening groups in the polymer chains and strong intermolecular forces. Hydrogen bonding which is the strongest of these intermolecular forces is essential for most of the strong fibers [6].

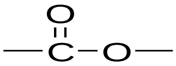
Free rotation of covalently bonded atoms is also prevented by the presence of double bonds. Thus, stable (Trans) and (Cis) configurations are possible for polymers such as polyisoprene. The (Trans) and (Cis) isomeric forms of the latter are known as flexible and have rubber and hard plastic gutta – percha, respectively [7].

1. 2 Polymerization Processes

Traditionally, polymers have been classified into two main groups (Addition polymers) and (Condensation polymers). This classification, first proposed by Carothers, addition polymerization, is based on whether or not the repeating unit of the polymer contains the same atoms of the monomer in its repeating unit, while condensation polymers contain fewer because of the formation of byproducts during the polymerization process. The corresponding polymerization processes would then be called (addition polymerization) and (condensation polymerization)[8].

As was mentioned earlier, this classification can lead to confusion, since it has been shown in later years that many important types of polymers can be prepared by both addition and condensation processes. Recently, the emphasis has changed to classify polymers according to whether the polymerization occurs in a stepwise fashion (step growth)or by propagating from a growing chain (chain growth)[9].

1.3 Polyester Resin

Polyesters contain esters group  $-\overset{O}{\overset{\|}{C}}-O-$ in the main chain [10]. Credit for the first polyester is given to Gay- Lussac and Pelouze in 1833 and Berzelius in 1847 [11].Polyesters are hetero chain macromolecular substances characterized by the presence of carboxylate ester groups in the repeating units of their chains [12].

A linear homo- and Co- polyesters derived, whether actually or nationally, from the self- polycondensation of hydroxyl carboxylic acids or the polycondensation of dicarboxylic acids with dihydroxy compounds[13] . The first approach yields AB- type products having a unidirectional orientation of carboxylate ester groups in the molecular chain; the second leads to AA/ BB- type polymers with the ester groups recurring alternately in their oxycarbonyl and carbonyloxy forms[14] .

In homo polyesters the carboxylate ester groups are spaced regularly along the chains, but in co- polyesters their separations may vary with the nature of the intervening skeletal groups [15] .

Observations on polyesters were recorded from as early as 1833, but their first significance through empirical appearance was with the glyceryl phthalate (Glyptal) coating and impregnating materials of the world War- One period [16]. The rational study of polyesters dated from the 1990s with Kienle's observations, which led to the evolution of alkyd resin technology, and more outstandingly, with research of Carothers who, began with polyesters, laid the foundations of step- polymerization chemistry and the relationships among molecular structure, molar mass, and polymer properties [17].

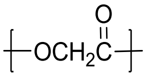
These principles were later elaborated systematically by Flory[18] . The resulting concepts formed the basis of Carother's discovery of nylon- 6,6 in 1935[19] and that of poly (ethylene terphthalate) by Winfield and Dickson in 1946[20] events which led in a large degree to the growth of the modern synthetic textiles industry. Other seminal discoveries were those of the late 1930s leading to the development of unsaturated polyester casting and laminating resins, and of impact- resistant polycarbonate resin in the mid- 1950s[21].

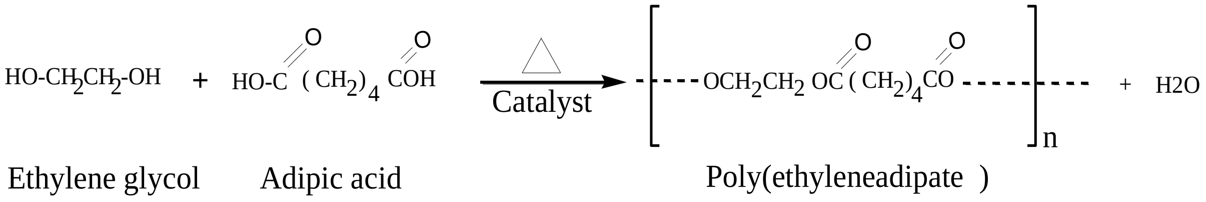
Saturated and unsaturated polyesters are conveniently prepared by melting co- polyesterification at elevated temperatures above the melting point of the resulting polyesters [22, 23].Unsaturated polyester resin are step- growth polymers formed by the interaction of stoichiometric mixture of saturated and unsaturated dibasic acids or anhydrides with dihydric alcohols or oxides[24]. The unsaturated acid component is fundamental to the reactivity of the low molecular weight polymers formed and is derived primarily from 1, 2- Olefinic dibasic acids such as maleic acid or anhydride [25] .

The commercial resins have established a significant position within the plastics industry [26]. They are typically solutions of unsaturated polyester polymers dissolved in unsaturated co- reactant liquid monomers such as styrene, to enhance reactivity and proccessibility [27]. Free- radical catalysts initiate cross- linking reactions involving the unsaturated polymer and the unsaturated co- reactant monomer, rapidly transforming the low viscosity resin into a rigid thermoset plastic state, comprising a three- dimensional polymer network [28]. Polyester resin as a plastic can be classified [29] into:

1. Aliphatic Polyesters

1.1 Aliphatic Saturated Polyesters

Poly(glycolide),is the simplest aliphatic polyester  $\left[-OCH_2\overset{O}{\overset{\|}{C}}- \right]$ with the exception of polyethylene oxalate saturated aliphatic polyesters which have relatively low melting points, for example poly (ethylene adipate) melts at 54 °C. Therefore, they were used as plastizing agent segments (internal plastization) of elastic fibers or as secondary polymer plasticizers for poly (vinyl chloride). Poly (ethylene adipate) also serves as a non-oily ointment base and masking leather non-perimable because of its water repellent action[44]. Also glycols are reacted with adipic acid to form a linear polymer and as follows[30]:

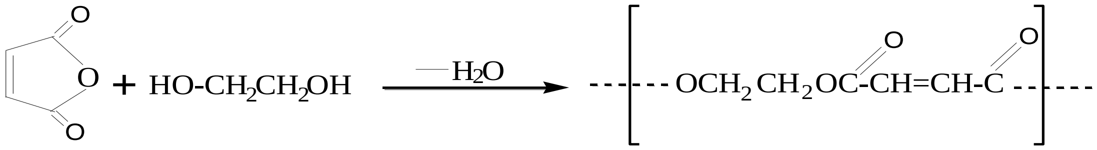


Equation (1): Synthesis of poly (ethyleneadipate)

1.2 Aliphatic unsaturated polyesters

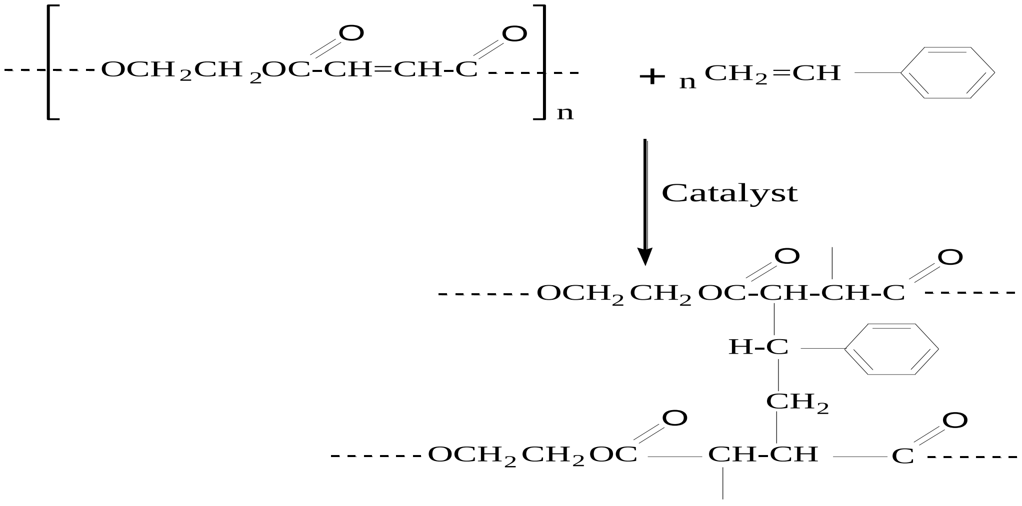
The unsaturated aliphatic polyester of commercial importance known as unsaturated polyester resin was prepared by free radical copolymerization with, for example , styrene or methylmethacrylate [31]. Unsaturated polyester resins are generally reinforced with glass fibers and have many applications, from transparent building construction elements to boat hulls [32].

Their application is facilitated by the use of what are known as sheet molding compounds (SMCs) which are formulated mixtures of unsaturated polyesters, vinyl monomers, initiators and glass fibers supplied as a sandwich between two polyethylene films. The properties of these types include the lower molecular weight, water resistance and the transparency to X- rays [33], For example :



Equation (2):the synthesis of unsaturated polyester

The unsaturated polyester is typically a solid dissolved in styrene, A number of peroxide curing agents are available for initiating polyesters resins[34] . Methylethylketone peroxide (MEKP) is normally used for room temperatures curing (cold curing) for unsaturated polyesters resin. Activation can be accomplished at room temperature by using a small amount of cobaltoctoate or other activators[35], the equation below represent the reaction between styrene and unsaturated polyester to give cross- linked polyester resin.



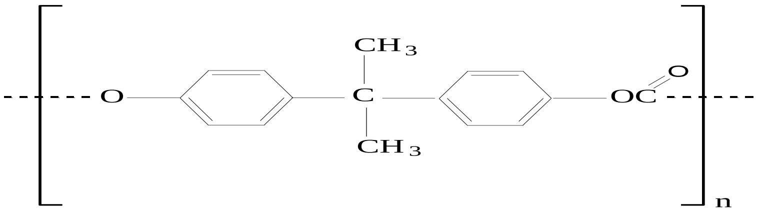
(Cross - Linked polyester resin)

Equation (3): Cross linking of unsaturated polyester

2. Aromatic Polyesters

2.1 Polycarbonates[36]

As carbonic esters, polycarbonates, Figure (1-1), are the simplest aromatic polyesters, only those polycarbonates with bisphenol-A their repeat unit have a commercial significance polycarbonates possess a low water absorption, moderately good thermal stability (TG ~ 150 °C), good electrical insulation properties, and excellent impact strength.

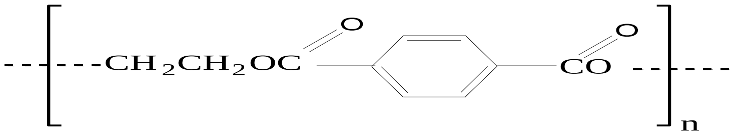


Poly[2,2-diphenylpropane-bis(4-phenyl)carbonate]

Figure (1-1): Cross linking of polycarbonate

2.2 Poly (ethylene terephthalate)[37]

Poly(ethyleneterephthalate) or PETP,Figure (1-2), is polyester made by the reaction of terephthalic acid and ethyleneglycol. Most of the produced poly (ethyleneterephthalate) is mainly melt- spun fibers. A smaller quantity is used for very thin films for the electrical industry. Tape recorder ribbons are produced also from PETP.



Poly(ethyleneterphthalate)

Figure (1-2): Poly (ethyleneterephthalate)

Construction components of (PETP) absorb practically no moisture. These components are hard and rigid. They exhibit very little wear and tear and show very little creep, and tolerant high mechanical loads. These physical properties, together with the very small linear coefficient of expansion make PETP ideal for high precision cog wheels and for moring comports in, for example, sewing machines.

3. Alkyd Resins

Alkyd resins occur through the conversion of alcohols (glycerin or trimethylol propane) and maleic acid at a temperature between 200 C◦ and 250 C◦. The first conversion is taken as far as products are still soluble with cross- linking agent after application e.g., as Lacquer resins[55]. Alkyd resin technology is still largely empirical because of its good mechanical and chemical properties and it was suitable as plastic and coating materials [38].

In the early 1970, a spate of poly (butylenes- terephthalate) plastics were introduced primarily as molding [39] materials because of their resistance to chemical stress cracking [38].

1.4 Graft polymers

Graft polymers are segmented copolymers with a linear backbone of one composite and randomly distributed branches of another composite. The figure (1-3) labeled "graft polymer" shows how grafted chains of species B are covalently bonded to polymer species A[40]. Although the side chains are structurally distinct from the main chain, the individual grafted chains may be homo-polymers or copolymers. Graft polymers have been synthesized for many decades and are especially used as impact resistant materials, thermoplastic elastomers, compatibilizers, or emulsifiers for the preparation of stable blends or alloys. One of the more well-known examples of a graft polymer is high impact polystyrene, which consists of a polystyrene backbone with polybutadiene grafted chains [41].

Graft copolymers are a branched copolymer where the components of the side chain are structurally different from that of the main chain. Graft copolymers containing a larger quantity of side chains are capable of wormlike conformation, compact molecular dimension, and notable chain end effects due to their confined and tight fit structures.[42] The preparation of graft copolymers has been around for decades. All synthesis methods can be employed to create general physical properties of graft copolymers. They can be used for materials that have impact resistant, and are often used as thermoplastics elastomers, compatibilizers or emulsifiers for the preparation of stable blends or alloys [43].

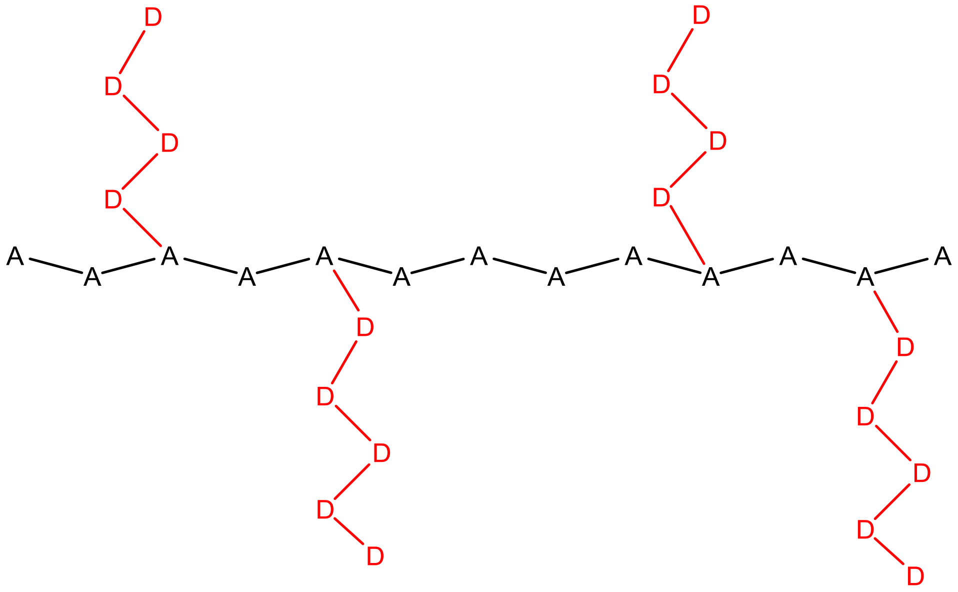
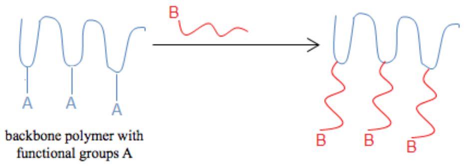
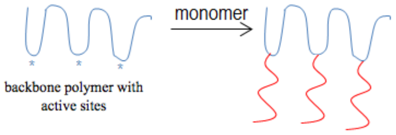


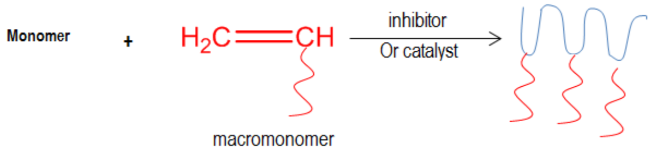
Figure (1-3): Graft polymer

Generally, grafting methods for copolymer synthesis results in materials that are more thermo-stable than their homo-polymer counterparts [44]. There are three methods of synthesis, grafting to, grafting from, and grafting through, that are used to construct a graft polymer. There are many different approaches to synthesizing graft co-polymers [43].

The grafting to method involves the use of a backbone chain with functional groups A that are distributed randomly along the chain [45]. The formation of the graft copolymer originates from the coupling reaction between the functional backbone and the end-groups of the branches that are reactive. These coupling reactions are made possible by modifying the backbone chemically [46].







Common reaction mechanisms used to synthesize these copolymers include free-radical polymerization, anionic polymerization, atom-transfer radical-polymerization, and living polymerization techniques[47].

Copolymers that are prepared with the grafting-to method often utilize anionic polymerization techniques. This method uses a coupling reaction of the electrophilic groups of the backbone polymer and the propagation site of an anionic living polymer [48]. This method would not be possible without the generating of a backbone polymer that has reactive groups. This method has become more popular with the rise of click chemistry. A high yield chemical reaction called atom transfer nitroxide radical coupling chemistry is for the grafting-to method for polymerization [49]. In the grafting-from method, the macromolecular backbone is chemically modified in order to introduce active sites capable of initiating functionality. The initiating sites can be incorporated by copolymerization, can be incorporated in a post-polymerization reaction, or can already be a part of the polymer[46]. If the number of active sites along the backbone participates in the formation of one branch, then the number of chains grafted to the macromolecule can be controlled by the number of active sites. Even though the number of grafted chains can be controlled, there may be a difference in the lengths of each grafted chain due to kinetic and steric hindrance effects. Grafting from reactions has been conducted from polyethylene, polyvinylchloride, and polyisobutylene [47]. Different techniques such as anionic grafting, cationic grafting, atom-transfer radical polymerization, and free-radical polymerization have been used in the synthesis of grafting from copolymers. Graft copolymers that are employed with the grafting-from method are often synthesized with ATRP reactions and anionic and cationic grafting techniques [50].

The grafting through, also known as the macro-monomer method, is one of the simpler ways of synthesizing a graft polymer with well-defined side chains. Typically a monomer of a lower molecular weight is copolymerized with free radicals with an acrylate functionalized macro-monomer. The ratio of monomer to macro-monomer molar concentrations as well as their copolymerization behavior determines the number of chains that are grafted [51]. As the reaction proceeds, the concentrations of monomer to macro-monomer change causing random placement of branches and formation of graft copolymers with different number of branches. This method allows for branches to be added heterogeneously or homogeneously based on the reactivity ratio of the terminal functional group on the macromolecular to the monomer. The difference in distribution of grafts has significant effects on the physical properties of the grafted copolymer. Polyethylene, polysiloxanes and poly(ethyleneoxide) are all macro-monomers that have been incorporated in a polystyrene or poly(methylacrylate) backbone. The macro-monomer (grafting through) method can be employed using any known polymerization technique[50]. Living polymerizations give special control over the molecular weight, molecular weight distribution, and chain-end functionalization [51].

Graft copolymers became widely studied due to their increased number of applications due to their unique structures relative to other copolymers such as alternating, periodic, statistical, and block copolymers which generally linear chains. Some common applications of graft copolymers include; Membranes for the separation of gases or liquids; Hydrogels; Drug deliverys; Thermoplastic elastomers; Compatibilizers for polymer blends; Polymeric emulsifiers and Impact resistant plastics[52].

By grafting polymers onto polymer backbones, the final grafted copolymers gain new properties from their parent polymers. Specifically, cellulose graft copolymers have various different applications that are dependent on the structure of the polymer grafted onto the cellulose[53]. Some of the new properties that cellulose gains from different monomers grafted onto it include; Absorption of water; Improved elasticity; Hydrophilic/Hydrophobic character; Ion-exchange; Dye adsorption capabilities; Heat Resistance; Thermo sensitivity; pH sensitivity and Antibacterial effect[54].

These properties give new application to the un-grafted cellulose polymers that include: Medical body fluid absorbent materials; Enhanced moisture absorbing ability in fabrics; Perm selective membranes; Stronger nucleating properties than un-grafted cellulose, and adsorption of hazardous contaminants like heavy metal ions or dyes from aqueous solutions by temperature swing adsorption; Sensors and optical materials and Reducing agents for various carbonyl compounds [55].

1.5 Rate of reaction

The reaction rate or rate of reaction is the speed at which reactants are converted into products. For example, the oxidative rusting of iron under Earth's atmosphere is a slow reaction that can take many years, but the combustion of cellulose in a fire is a reaction that takes place in fractions of a second. For most reactions, the rate decreases as the reaction proceeds. Chemical kinetics is the part of physical chemistry that studies reaction rates. The concepts of chemical kinetics are applied in many disciplines [56]. Formal definition, consider a typical chemical reaction:

$$a\,A + b\,B \rightarrow p\,P + q\,Q$$

The lowercase letters (a, b, p and q) represent stoichiometric coefficients, while the capital letters represent the reactants (A and B) and the products (P and Q).According to IUPAC's Gold Book definition[1] the reaction rater for a chemical reaction occurring in a closed system under isochoric conditions, without a build-up of reaction intermediates, is defined as and the reaction rate usually has the units of mol L^{-1} s^{-1}[57].

$$r = -\frac{1}{a}\frac{d(A)}{dt} = -\frac{1}{b}\frac{d(B)}{dt} = \frac{1}{p}\frac{d(P)}{dt} = \frac{1}{q}\frac{d(Q)}{dt}$$

The rate of a reaction is always positive. A negative sign is present to indicate that the reactant concentration is decreasing. The IUPAC recommends that the unit of time should always be the second.

The rate of reaction differs from the rate of increase of concentration of a product P by a constant factor (the reciprocal of its stoichiometric number) and for a reactant A by minus the reciprocal of the stoichiometric number. The stoichiometric numbers are included so that the defined rate is independent of which reactant or product species is chosen for measurement [58].

The above definition is only valid for a single reaction, in a closed system of constant volume, an assumption which should be stated explicitly in the definition. If water is added to a pot containing salty water, the concentration of salt decreases, although there is no chemical reaction [56].

1.5.1 Influencing factors on the reaction rate [57- 59]

1-The nature of the reaction: Some reactions are naturally faster than others. The number of reacting species, their physical state (the particles that form solids move much more slowly than those of gases or those in solution), the complexity of the reaction and other factors can greatly influence the rate of a reaction.

2-Concentration: Reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.

3-Pressure: The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas.The reaction rate increases in the direction where there are fewer moles of gas and decreases in the reverse direction. For condensed-phase reactions, the pressure dependence is weak.

4-Order: The order of the reaction controls how the reactant concentration (or pressure) affects reaction rate.

5-Temperature: Usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason that temperature increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants). The influence of temperature is described by the Arrhenius equation.

Reaction rates can be independent of temperature (non-Arrhenius) or decrease with increasing temperature (anti-Arrhenius). Reactions without an activation barrier (e.g., some radical reactions) tend to have anti Arrhenius temperature dependence: the rate constant decreases with increasing temperature.

All the factors that affect a reaction rate, except for concentration and reaction order, are taken into account in the reaction rate coefficient (the coefficient in the rate equation of the reaction)[58].

1.5.2 Rate equation [60, 61]

For a chemical reaction a A + b B → p P + q Q, the rate equation or rate law is a mathematical expression used in chemical kinetics to link the rate of a reaction to the concentration of each reactant. It is often of the type:

$$r = k(T)[A]^n[B]^m$$

For gas phase reaction the rate is often alternatively expressed by partial pressures. In these equations k(T) is the reaction rate coefficient or rate constant, although it is not really a constant, because it includes all the parameters that affect reaction rate, except for concentration, which is explicitly taken into account. Of all the parameters influencing reaction rates, temperature is normally the most important one and is accounted for by the Arrhenius equation. The exponent's n and m are called reaction orders and depend on the reaction mechanism. For elementary (single-step) reactions the order with respect to each reactant is equal to its stoichiometric coefficient. For complex (multistep) reactions, however, this is often not true and the rate equation is determined by the detailed mechanism. By using the mass balance for the system in which the reaction occurs, an expression for the rate of change in concentration can be derived. For a closed system with constant volume, such expression can look like

$$\frac{d[p]}{dt} = k(T)[A]^n[B]^m$$

1.5.3 Temperature dependence [62]

Each reaction rate coefficient k has a temperature dependency, which is usually given by the Arrhenius equation:

$$k = Ae^{-\frac{Ea}{RT}}$$

E_a is the activation energy and R is the gas constant. Since at temperature T the molecules have energies given by a Boltzmann distribution, one can expect the number of collisions with energy greater than E_a to be proportional to $e^{-Ea/RT}$. A is the pre-exponential factor or frequency factor. The values for A and E_a are dependent on the reaction. There are also more complex equations possible, which describe temperature dependence of other rate constants that do not follow this pattern. A chemical reaction takes place only when the reacting particles collide. However, not all collisions are effective in causing the reaction. Products are formed only when the colliding particles possess a certain minimum energy called threshold energy. As a rule of thumb, reaction rates for many reactions double for every 10 degrees Celsius increase in temperature,[4] For a given reaction, the ratio of its rate constant at a higher temperature to its rate constant at a lower temperature is known as its temperature coefficient (Q). Q_{10} is commonly used as the ratio of rate constants that are 10 °C apart.

1.5.4 Pressure dependence[63]

The pressure dependence of the rate constant for condensed-phase reactions (i.e., when reactants and products are solids or liquid) is usually sufficiently weak in the range of pressures normally encountered in industry that it is neglected in practice.

1.6 Activation energy [64, 65]

In chemistry, activation energy is the energy which must be available to a chemical system with potential reactants to result in a chemical reaction. Activation energy may also be defined as the minimum energy required starting a chemical reaction. The activation energy of a reaction is usually denoted by E_a and is expressed as kilojoules per mole (kJ/mol) or rarely kilocalories per mole (kcal/mol)

Activation energy can be thought of as the height of the potential barrier (sometimes called the energy barrier) separating two minima of potential energy (of the reactants and products of a reaction). For a chemical reaction to proceed at a reasonable rate there should exist an appreciable number of molecules with translational energy equal to or greater than the activation energy.The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.At a more advanced level, the net Arrhenius activation energy term from the Arrhenius equation is best regarded as an experimentally determined parameter that indicates the sensitivity of the reaction rate to temperature. There are two objections to associating this activation energy with the threshold barrier for an elementary reaction. First, it is often unclear as to whether or not reaction does proceed in one step; threshold barriers that are averaged out over all elementary steps have little theoretical value. Second, even if the reaction being studied is elementary, a spectrum of individual collisions contributes to rate constants obtained from bulk ('bulb') experiments involving billions of molecules, with many different reactant collision geometries and angles, different translational and (possibly) vibrational energies-all of which may lead to different microscopic reaction rates. In the Arrhenius equation, the term activation energy (E_a) is used to describe the energy required the transition. Likewise, the Eyring equation is a similar equation that also describes the rate of a reaction.

1.7 Swelling phenomena

A hydrogel has two phases: a permanent solid phase consisting of a polymer network, and an aqueous phase which varies according to the environment. The swelling phenomena can be explained thermodynamically in terms of the chemical potential of water [66].Before the equilibrium swelling is achieved, the chemical potential outside (water) the gel μ^0_1 is higher than that of (water) inside μ_1.Thus the water is absorbed by the gel. In other words the water is imbibed osmotically into the gel network. In doing so the chemical potential of water is lowered. The swelling process distends the polymer networks[65]. The stretched networks with their elastic contractibilityexert a pressure, which will raise μ_1;when the chemical potentials of water on both sides are equal, equilibrium is reached[67].At equilibrium these two forces, viz. the osmotic pressure which causes the gel to imbibe water by lowering $\mu^0{}_1$ and the elastic contractibility of the network which raises μ_1 are equal[68].

When macromolecules are added, $\mu^0{}_1$ alone is lowered since macromolecules cannot penetrate the gel networks. The higher μ_1 will force out some of the water. The networks contract and thus equalize the chemical potential of water both sides [69].

1.7.1 Factors affecting the process of swelling

The factors which influence the swelling of hydrogels can be divided into two groups; those which are favorable to the entrance of water into the polymer structure and those which resist or inhibit the water influx[70]; Some of these factors are summarized in Table (1-1) below. If a piece of polymer is placed in water, there will be an osmotic driving force for the water to enter the water free region within the polymer [71]. Strong positive interactions between chemical structures on the polymer and water (e.g. hydrogen bonding) will further increase the driving force for swelling [72].As water enters the polymer, the polymer chains which are (in most cases) in an equilibrium configuration are extended. This is illustrated schematically in figure (1-3). Figure (1-3a) represents the most entropically favorable configuration given the mechanical constraints of the polymer chain. The entrance of water into the system will necessitate its expansion and a consequent ordering of the polymer chain, figure

(1-3b).Since the chains will be elongated into less entropically desirable configurations, they exert the resistive force. When the osmotic force driving water into the system is balanced by the force exerted by the polymer chains in resisting expansion, at that point the equilibrium degree of swelling will have been achieved (the thermodynamic activity of the solvent (H_2O) in the gel will change until it is equal to its activity in the pure solvent). Increased cross-link density, (a shorter distance between cross-link points) will have the effect of increasing the resistive force to chain elongation. Consequently, more highly cross-linked systems demonstrate a lower degree of equilibrium swelling[71]. If the polymer chains are inflexible, swelling will also be inhibited due to increased resistance to deformation from their equilibrium configurations. Finally, if the free volume in the polymer is sufficiently low, bulk water may be unable to penetrate into the polymer matrix to initiate the swelling process [73]. A quantitative description of swelling in cross-linked polymers formed in the swollen state has been developed [74] and applied to hydrogel system [75].

Table (1-1): Some of the factors which influence the swelling of hydrogel at room temperature

Favorable to swelling	**Inhibit swelling**
- Osmotic potential	- Weak interactions with H_2O
- Strong interactions with H_2O	- Low free volume
- High free volume	- Low chain flexibility
- High chain flexibility	- High cross-linking density
- Low cross-linking density	

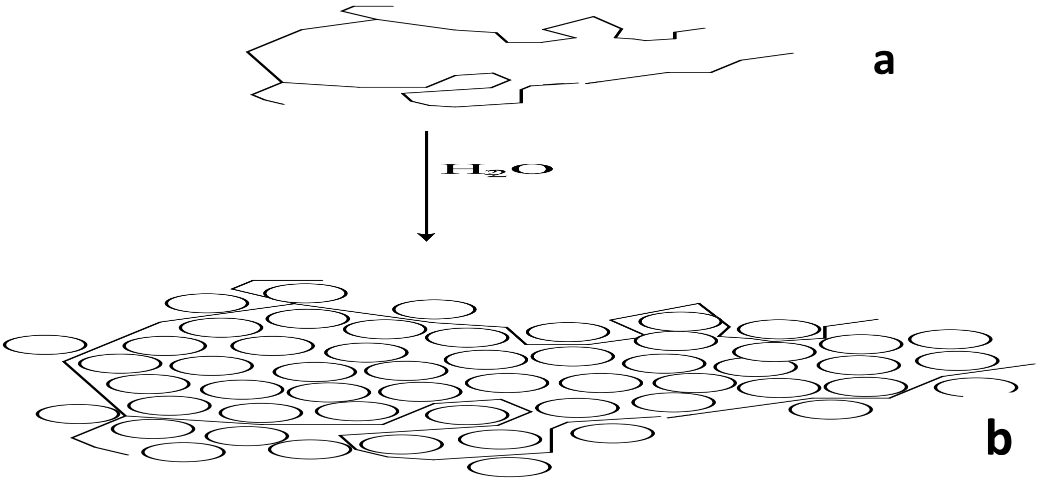
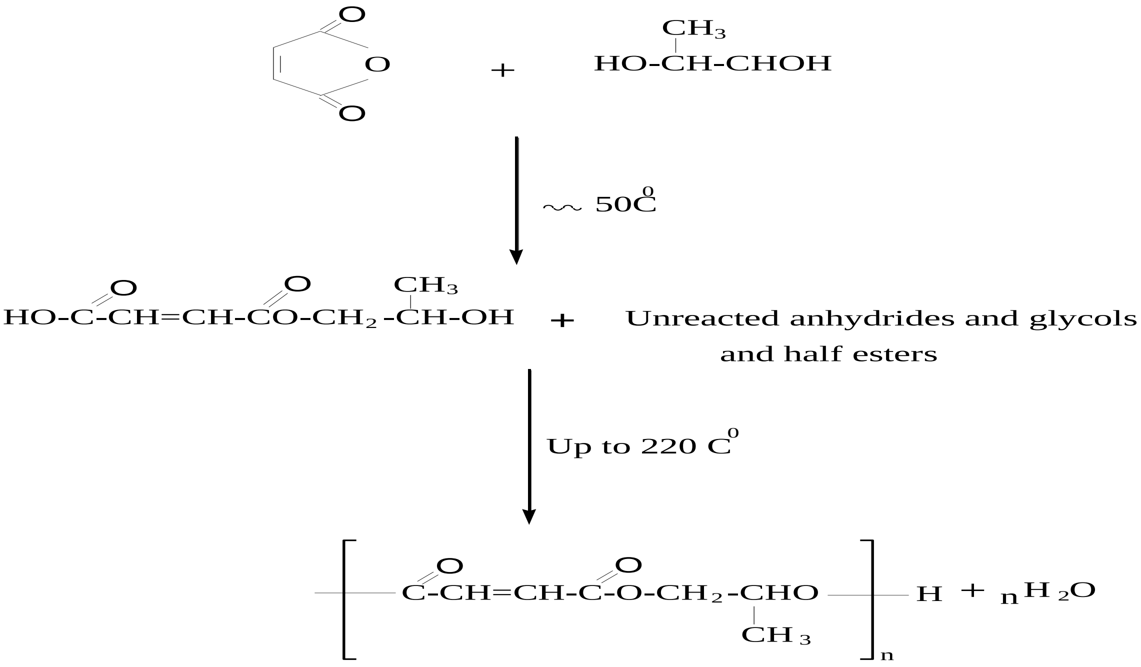


Figure (1-3): Water entrance into a single, idealized hydrogel chain segment

1.8 Manufacture of unsaturated polyester resin processes

1.8.1 Fusion process [76, 77]

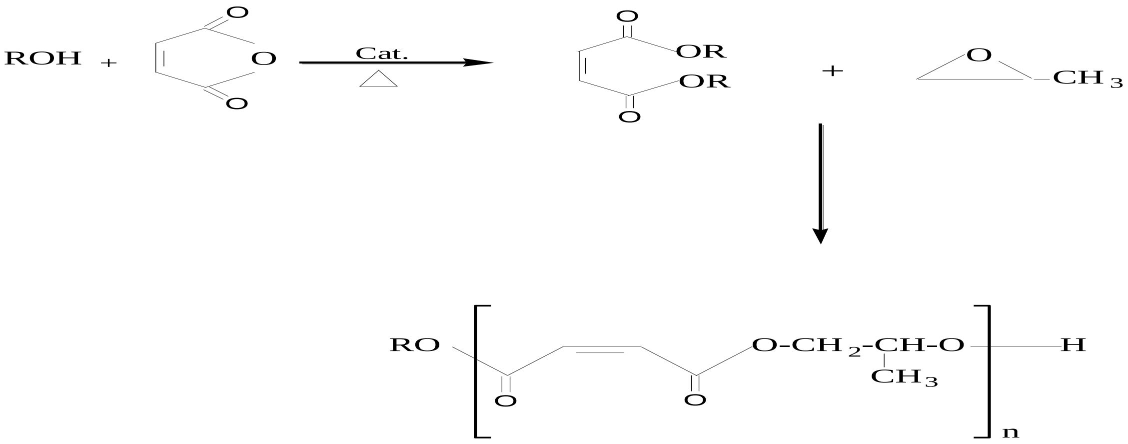
Most unsaturated polyester is made by the polycondensation of carboxylic acids or anhydrides with glycols to result in linear polymers. The common feature of this chemistry is the generation of water that needs to remove from the reactor. The scheme(1-1) uses maleic anhydride and propylene glycol. In reality with these reactant ratios, the resin is never completely capped with glycols and some carboxylic acid functionality remains unconverted to ester. The addition reaction of maleic anhydride and the primary hydroxyl of propylene glycol proceeds readily at very low temperatures due to the high acidity of the anhydride. This type of addition also occurs with other anhydrides, though higher temperatures are required to attain an equal reaction rate. The reaction continues as the temperature is increased and water is removed from the reactor. This produces higher molecular weight materials from the reaction of the half ester carboxyl groups with primary and secondary hydroxyls of other half ester groups. The cook end point may be determined by viscosity or acid value or both. The majority of unsaturated polyester production involves the fusion process but there is a wide variability of component selection within the acids, anhydrides and glycols.



scheme (1-1)

1.8.2 Oxide Process [78, 79]

The preparation of unsaturated polyesters from anhydrides and propylene oxide is a well-known technology that has received little commercial attention. The chemistry of this process is shown in reaction (1-2). The reaction temperature is usually in the range of (30-150)C^{o}. Reaction pressure is variable but generally less than 150 Psi in a batch reactor Catalysts of a wide range serve to promote the anhydride – alkylene oxide reaction, which is sluggish in their absence. The catalysts of interest include alkaline earth metals and tertiary amines. The best results have been obtained with lithium chloride which is active at a concentration as low as (0.03%) by weight. This reaction scheme shows reaction initiation with water or an organic hydroxyl compound and the use of propylene oxide and maleic anhydride. There is no reaction by products during ester formation.



Scheme (1-2)

1.8.3 Solubilization Process [80, 81]

Solubilization is the process of incorporating the solubilizate (the component that undergoes solubilization) into or onto micelles.

Solubilization may occur in a system consisting of a solvent, an association colloid (a colloid that forms micelles), and at least one other solubilizate. Solubilization is distinct from dissolution because the resulting fluid is a colloidal dispersion involving an association colloid. This suspension is distinct from a true solution, and the amount of the solubilizate in the micellar system can be different (often higher) from the regular solubility of the solubilizate in the solvent. In non-chemical literature and in everyday language, the term "solubilization" is sometimes used in a broader meaning as "to bring to a solution or (non-sedimenting) suspension" by any means, e.g., leaching by a reaction with an acid. Micellar solubilization is widely utilized, e.g.

in laundry washing using detergents, in the pharmaceutical industry, for formulations of poorly soluble drugs in solution form and in cleanup of oil spills using dispersants. Literature distinguishes two major mechanisms of solubilization process of oil by surfactant micelles, affecting the kinetics of solubilization:[3] surface reaction, i.e., by transient adsorption of micelles at the water-oil interface, and bulk reaction, whereby the surfactant micelles capture dissolved oil molecules.

1.9 Nanotechnology [82- 84]

The term nanotechnology was first used by Norio Taniguchi, a professor of the University of Tokyo, using the word to describe tools that use nanoparticles. Nanotechnology is defined as the ability to monitor, measure, process and manufacture nano-materials, and the nanometer-nm is part per a billion of a meter, which is very small.

Nanotechnology is used to describe materials, with new and greatly improved compositions and components. These improvements include biophysical and chemical properties and nanotechnology has become almost the word spoken these days or at least some terms with a nano-scale, such as nano-scale, nano-materials, nano-particles.

Nano-materials have many properties, including two-dimensional or so-called nano-sheets, which have attracted considerable attention due to their unique physical and chemical properties, including the excellent handling of 2D, providing new opportunities for the development of different materials in dimensions. This type of compounds offers a variety of applications to this technique in industries and environment as well as in medical and biological sciences through ion exchange, stimulation, packaging and other qualities.

Nanotechnology or Nano-scale materials are materials that have crystals of a fraction of a Part per a billion of a meter. (NP) is used to describe one or more components that have at least one dimension in a range of 1-100 nm. NP atoms are characterized by having large surface properties, and the surface of any of these materials has many reactions, Because of the large surface size of the NP, surface activity is very high, and these materials are likely to be used in much smaller quantities than normal and large surface area, allowing them to react quickly with less time, so many properties of different materials can be changed on the nano-meter, here lies the strength of nanotechnology.

1.10 Aim of the work

The objective of the work is:

1 - Preparation of the graft co-polymer in two processes, fusion and solubilization.

2. Calculate the rate of polymerization and activation energy of the polymerization processes of linear co-polymer which prepared in fusion process.

3 - Calculate the swelling of the graft co-polymer which prepared by the two processes (fusion and solubilization) in three different buffer solutions (2.2, 7.0 and 8.0) at a constant temperature of 310 K.

2. Experimental Part

2.1 Chemical and Techniques

2.1.1Chemicals

The following table (Table 2-1) showed all solid and liquid chemical materials which used in this study

Table (2-1): The solid and liquid chemical materials

Materials	Purities	Company
Acrylic acid Monomer }	Were purified by vacuum distillation [85]	FLUKA
Borax	99%	BDH
Cobalt octoate(6 %)	96.8%	BDH
Dimethylsulphoxide (DMSO)		
Ethanol	99.9%	FLUKA
Fumaric acid	98.5%	MERCK
Glycerol	99.5%	MERCK
Hydrochloric acid	37%	BDH
Hydroquion	98%	MERCK
KCl	99%	BDH
Methylethylketoneperoxide	98%	BDH
Ortho xylene	99%	MERCK
Sodium hydroxide	99%	FLUKA
Terphthalic acid	99%	MERCK
Toluene	99%	GCC

2.1.2 Techniques

1. Fourier Transformer Infra-Red Spectroscopy. FT-IR spectra in range 500-4000 cm^{-1} were obtained by using potassium bromide disc on FT-IR–instrument model (8400 s) Shimadzu spectrophotometer /Japan. University of Kufa / College of Pharmacy

2. ^{1}HNMR Spectroscopy. Bruker spectrometer,400 MHz, Switzerland, France with DMSO d_6, University of Osmania / Hyderabad / India.

3. ^{1}HNMR Spectroscopy. Bruker spectrometer, 400 MHz, Switzerland, France with DMSO d_6, University of AL-albayt / Jordon

4. Atomic Force Microscope (AFM), Oxford, USA / Department of Chemistry/ Baghdad University.

5. Brookfild digital viscometer, model (RVDVE230), Brookfild engineering laboratories, INC/USA. Department of Chemistry/Kerbala University

6. Fourier Transformer Infra-Red Spectroscopy. FT-IR spectra in range 400-4000 cm-1 were obtained by using potassium bromide disc on FT-IR–instrument model (8400 s) Bruker spectrophotometer /Germany. University of Babylon / College of since .

2.2 Preparation of co-polymer

Two processes were used to prepare the graft co- polymer, these are Fusion and Solubilization processes; where the method of preparing each of them is described as shown below:

2.2.1 Using fusion process

2.2.1.1 Preparation of a linear co-polymer[86]

In a 500 ml three-necked round bottom flask, (2.0 mole, 332g) of Terphthalic acid and (1.0 mole, 92g) of glycerol were mixed together, the flask was equipped with a thermometer and a mechanical stirrer. The mixture warmed carefully with an electric heating mantle to 270 ^{0}C until a clear liquor is formed and then about 25 ml of xylene was added carefully to the reaction flask, in the form of batch (two drops in each batch), Withdrawal of water formed in the esterfication process, and the flask was gently heated. Heating was stopped after 150 min. at 325 ^{0}C, until no more water came off.

2.2.1.2 Preparation of a graft co-polymer [86]

The reaction flask was allowed to cool to 110 ^{0}C, and (0.5mole, 58g) of fumaric acid, was added carefully to the reaction flask, and the flask was gently rise heated, after melting material, added the drops of xylene in the form of batch (two drops in each batch), until no more water came off at 275 ^{0}C and 125 min. to prepare a new graft co-polymer.

The flask was allowed to cool to 50 ^{0}C and (1.0, 1.5 and 2.5 mole) about (36, 72 and 108g), respectively of acrylic acid monomer, was added to the graft co-polymer and stirred by mechanical stirrer, until a pourable syrup was formed, and (1.36×10^{-3}mole, 0.147g) of hydroquinone was added to the reaction flask, with stirred by mechanical stirrer.

The viscosity and density of the prepared co-polymer were calculated using Brookfild digital viscometer instrument and Hydrometer instrument respectively, and the average number of molecular weight ($\overline{Mn}$) was determined using end group analysis method; the procedure of this method as follows [86]:

About 1 gm of resin sample are weighted accurately into a beaker, 10 ml of xylene solvent were added to the resin sample. The resin was allowed to dissolve in the solvent, with careful warming in a water bath and then addition two drops of phenolphthalein as indicator. The solution was titrated with 1N of sodium hydroxide solution until a faint pink color. The volume of sodium hydroxide solution used was noted. The average number molecular weight ($\overline{Mn}$) of the resin is then calculated as follows:

$$\overline{\mathbf{Mn}} = \mathbf{r \cdot q \cdot w / g}$$

Where, r is the number of reactive groups per molecule, q is the equivalent weight of the reagent, w is the weight of resin sample and g is the number of grams of reagent.

2.2.2 Using solubilization process

2.2.2.1 Preparation of a linear co-polymer

In 200 ml two-necked round bottom flask, (2.0 mole, 332g) of terphthalic acid and (50 ml) of DMSO, were mixed together. This flask was equipped with a thermometer. The mixture warmed carefully with ahot plate magnetic stirrer to 40 ^{0}C untilclear liquor is formed and added (1.0 mole, 92g) of glycerol to the solution. The mixture warmed carefully to 120 ^{0}C,then about 25 ml of xylene was added carefully to the reaction flask, in the form of batch (two drops in each batch), withdrawal of water formed by the esterfication process, and the flask was gently heated.

Heating was stopped after 80 min. at 145 ^{o}C, until no more water came off. Leave the reaction flask to cool to about 50C^{o}.

2.2.2.2 Preparation of a graft co-polymer

About (0.5mole, 58g) of fumaric acid, was dissolved in 10 ml of DMSO at 40 ^{o}C, and added to the mixture (the flask contents which prepared in 2.2.2.1 above).The flask was gently rise heated to 100 ^{o}C, added the drops of xylene in the form of batch (two drops in each batch), until no more water came off at 115 ^{o}C after 45 min. to prepare graft co-polymer.

Leave the reaction flask to cool to the laboratory temperature, and then add the distilled water, where the suspension solution is form, then leave the suspension solution to precipitate and then filtered and washed with distilled water and leaves to dry. About (1.0, 1.5 and 2.5 moles) which equal (36, 72 and 108 g) respectively of acrylic acid monomer was added to the graft co-polymer and stirred by mechanical stirrer, until pourable syrup was formed. About (1.36×10^{-3}mole, 0.147g) of hydroquinone was added to the reactants with stirred by mechanical stirrer.

2.3 Rate of polymerization and activation energy

The rate of polymerization in different times (Min.) at a constant temperature was calculated by measuring the acid value (The acid value of a resin is defined as the number of mg of sodium hydroxide required to neutralize 1.0 gm of resin). The procedure of this method as follows [86]:

About 1.0 gm of resin sample are weighted accurately into a beaker, 10 ml of xylene solvent were added to the resin sample. The resin was allowed to dissolve in the solvent, with careful warming in a water bath and then addition two drops of phenolphthalein as indicator. The solution was titrated with 1.0 N of sodium hydroxide solution until a faint pink color. The volume of sodium hydroxide solution used was noted and the acid value of the resin is then calculated as follows:

$$\text{Acid value} = \frac{\text{Volume of sodium hydroxide}}{\text{Weight of sample}} \times 56$$

The slope of a plot of acid value(A.V.) versus time (Min.) represents the rate of polymerization. The activation energy (Ea) of polymerization of the modified unsaturated polyester resin was calculated from Arrhenius equation. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate of polymerization, at which a reaction proceeds. From the equation, the activation energy can be found through the relation [56] :

$$\boldsymbol{K = Ae^{-Ea/(RT)}}$$

Where A, is the frequency factor for the reaction, R, is the universal gas constant, T is the absolute temperature (usually in Kelvin's), and k, is the reaction rate coefficient. Even without knowing A and Ea, can be evaluated from the variation in reaction rate coefficients as a function of temperature (within the validity of the Arrhenius equation).

2.4 Determinations of the thermodynamic function[87]

By using Van Huff complementary equation, the thermodynamic functions were determination of the linear co-polymer. The relationships below were used to calculate these functions.

$$\ln K = -\,(\Delta H / RT) + \text{constant} \ldots\ldots (1)$$

$$\Delta G = -RT.\ \ln K \ldots\ldots (2)$$

$$\Delta S = (\Delta H - \Delta G) / T \ldots\ldots (3)$$

2.5 Swelling [88- 91]

The known weight and diameter of dried discs were put in sample vials. The swelling time was counted when the solvent was added into the sample vials. At regular time intervals the swollen discs were taken out using tweezers and the excess water on the surface of the discs was removed by wiping with the edge of whatman no.1 qualitative filter paper. They were weighed and returned to the vials immediately. All the weighing of the discs (hydrogel or xerogel), was carried out in a stopperweighing bottle. The diameter of the hydrogel and xerogel discs, were measured with calipers. The thickness of the hydrogel and xerogel discs was measured with a micrometer. The solvent contents of the hydrogel were calculated according to the following equations:

$$\text{Water content \%} = \frac{\text{Wt. of hydrogel} - \text{Wt. of xerogel}}{\text{Wt. of hydrogel}} \times 100$$

The swelling of the discs that was carried out at 310 K, the swelling behavior in two different buffer solutions, pH equal 2.2, 7.0 and 8.0 respectively is to show the effect of the change of pH on the sample disc.

The procedures of swelling discs, the solution contents that same were explain of in 2.5 above, and the methods of prepared buffer solutions was:

1- pH = 2.2

This solution was prepared, by mixing 50 ml of 0.2 M of KCl and 7.8 ml of 0.2 M of HCl.

2- pH = 8.0

This solution was prepared, by mixing 100 ml of 0.025 M of Borax and 41 ml of 0.1 M of HCl.

3. RESULTS & DISCUSSION

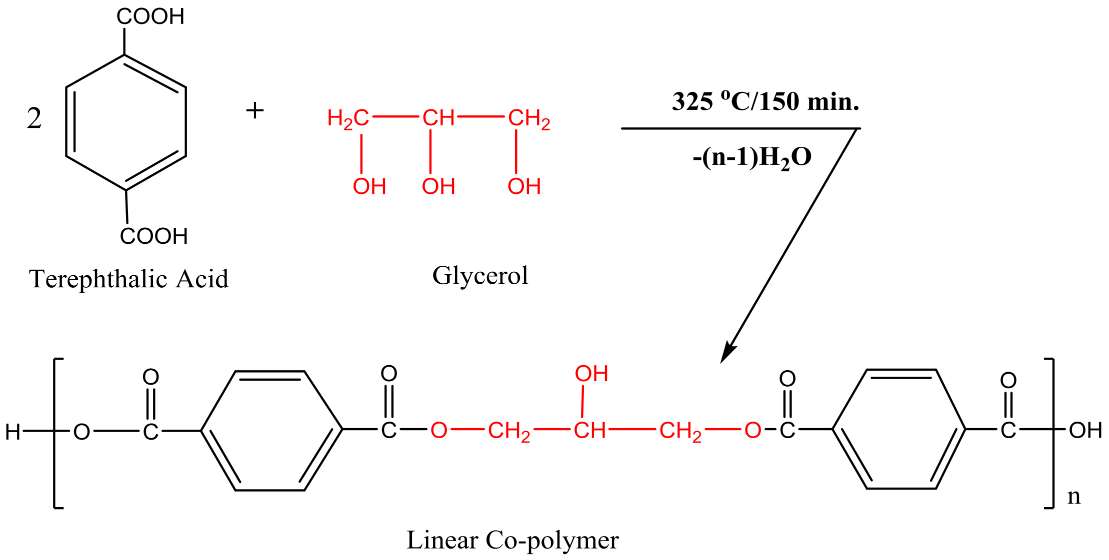
3.1 Preparation of graft co-polymer

The graft co-polymer was synthesized by two processes:

3.1.1 Using fusion process

3.1.1.1 Preparation of linear co-polymer

The linear co-polymer was synthesized by reacting of terphthalic acid with glycerol by esterfication process in 150 Min. at 325 ^{o}C, as shown in equation (3-1). The negative test of $NaHCO_3$ solution proves that the whole terphthelic acid was reacted. Table (3-1), represents the physical properties of the linear co-polymer.



Equation (3-1): Synthesis of linear co-polymer.

Table (3-1): The physical properties of the linear co-polymer

Physical properties	Value
Molecular Weight ($\overline{Mn}$)	2200gm/mole
Acid Value	28
Density	1.2 (gm / cm^3)

Figure (3-1) represents the FT–IR spectrum [92]of the linear co-polymer. It showed the appearance ofa strong broad band at about3423 cm^{-1} for stretching alcoholic (-OH) with stretching (H–bond), and also showed a weak band at about 2902cm^{-1} due to the -OH for Carboxylic acid, the C-H sp^{3}and sp^2 hybridization absorption at about 2544 cm^{-1}, 2654 cm^{-1}respectively. The spectrum also showed a strong band at about1726 cm^{-1} assigned to a stretching band C=O for ester group. The spectrum appearance is a weak sharp bands at about 1597cm^{-1}, 1581 cm^{-1} due to C=C for conjugated system of benzene ring and also showed a bands at about 1284 – 1259cm^{-1} assigned to C-O absorption band.

Figure (3-2), The spectrum of ^{1}HNMR[93] showed, which explain the singlet signal at 13.24 ppm characteristic of proton in carboxylic acid group. Furthermore, the multiples in the region 7.53- 8.10 ppm back to all protons in aromatic ring, the signals at 6.27-6. 46 ppm for four protons of methylene in the structure of co-polymer, the multiples at 4.24- 4.50 ppm of methyl protons, but the triplet signal in 3.44- 3.62 ppm due to the proton of aliphatic alcohol so this spectrum was confirmed the structure of our target polymer.

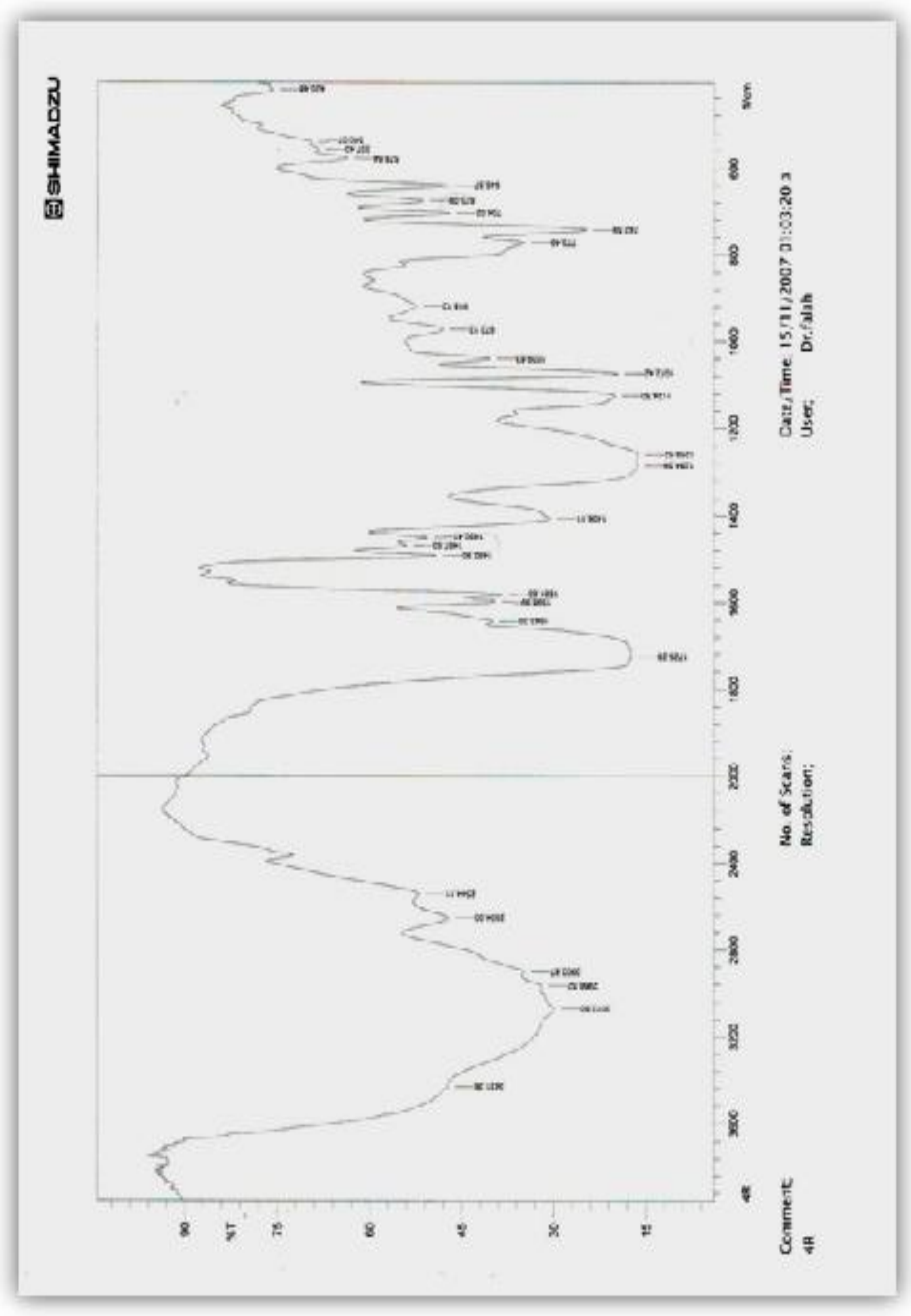


Figure (3-1): The FT-IR spectrum of linear co-polymer.

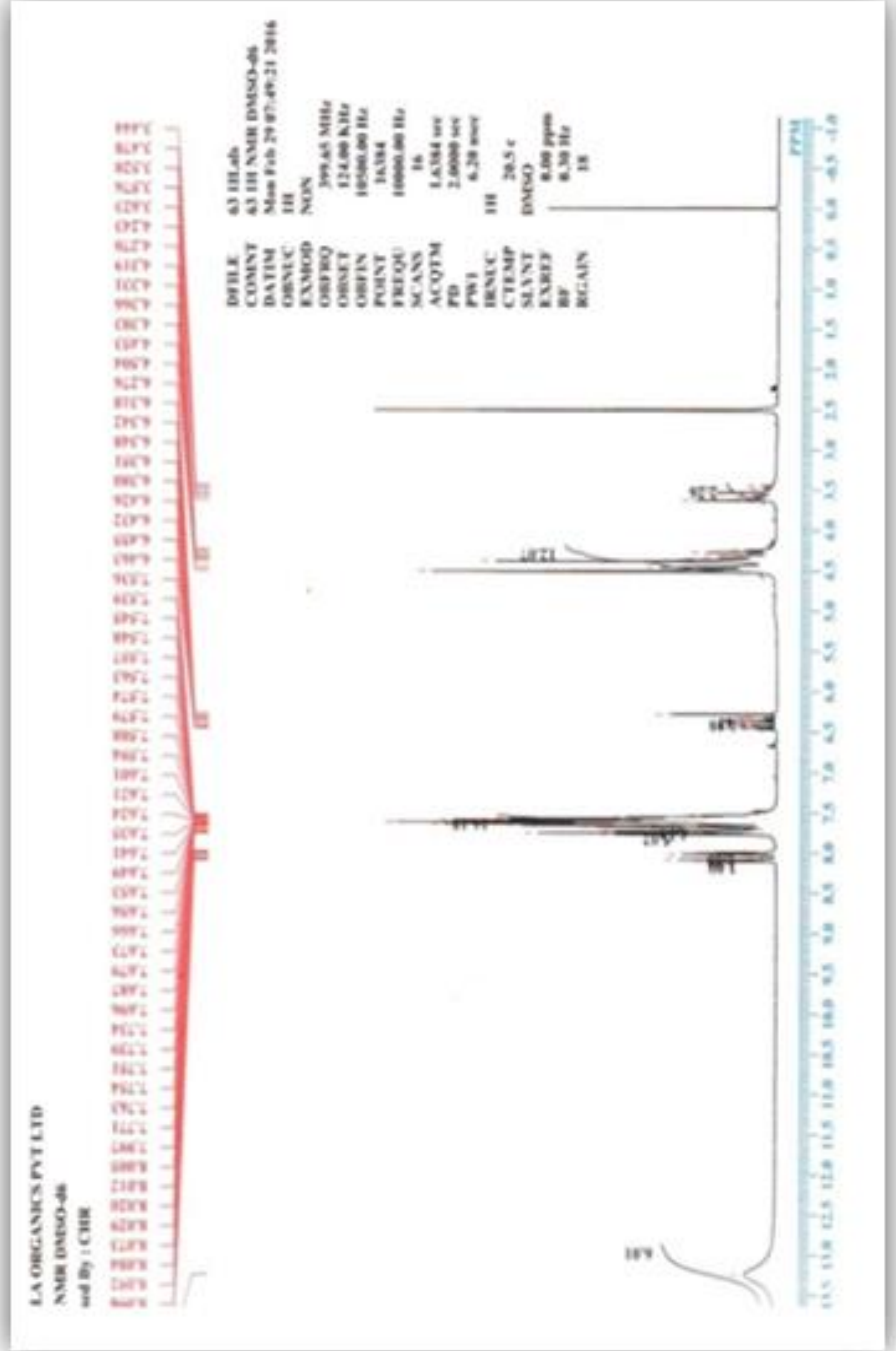
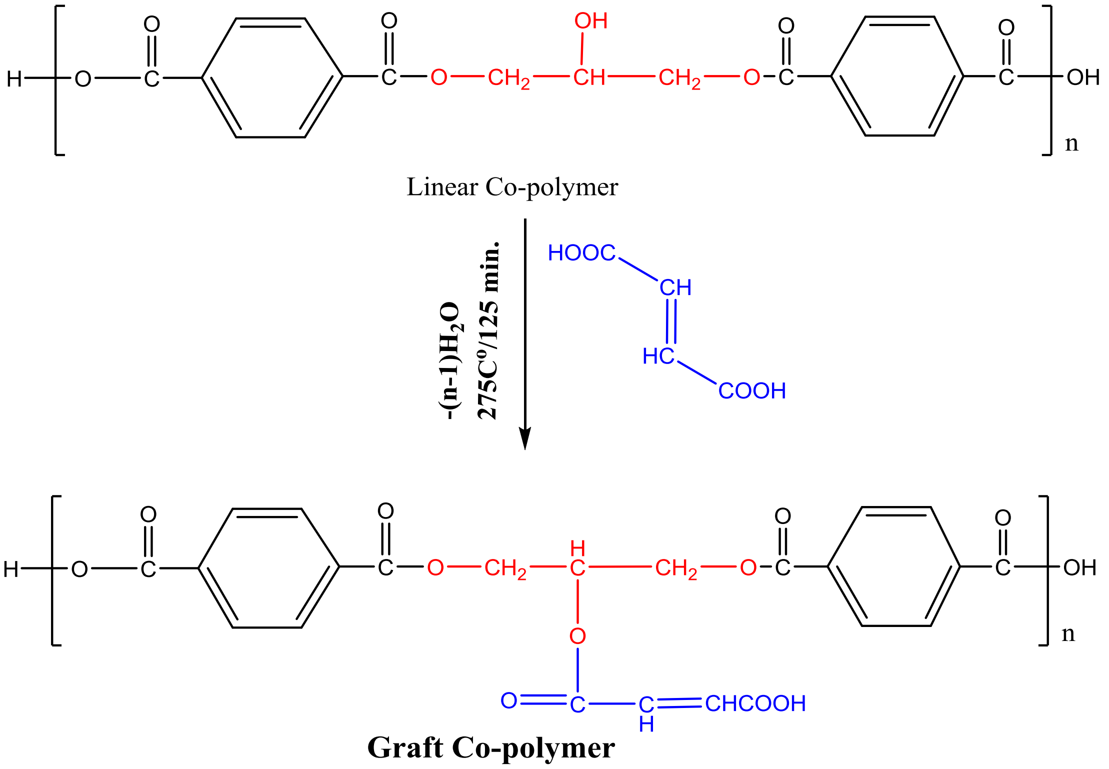


Figure (3-2): The ^{1}HNMR spectrum of linear co-polymer.

3.1.1.2 Preparation of graft co-polymer

The graft co-polymer was synthesized by reacting the linear co-polymer (which prepared in 3.1.1.1), with 0.5mole of fumaric acid to produce graft co-polymer at 275 C^0,and 125Min., as shown in equation (3-2). The negative test of $NaHCO_3$ solution proves that the prepared graft co-polymer doesn't contain any un-reacted acid. Table (3-3) represents the physical properties of the graft co-polymer. Three different numbers of moles (1.0, 1.5 and 2.5 mole) respectively of acrylic acid monomer were added to the graft co-polymer to prepare three different graft co-polymer.



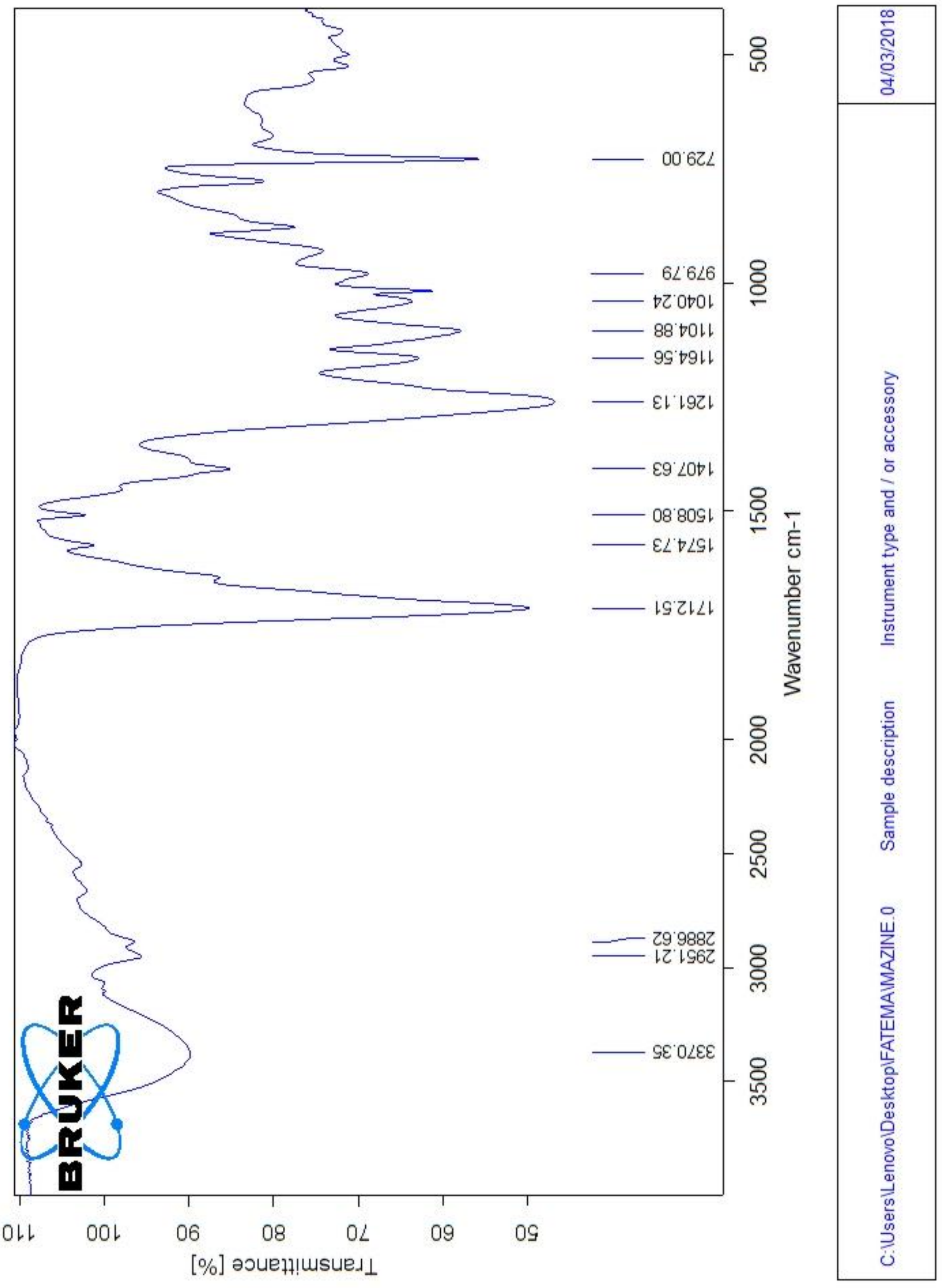
Equation (3-2): Synthesis of graft co-polymer.

Figure(3-3) showed the FT – IR spectrum of the graft co-polymer, it's showed the appearance of a strong broad band at 3370 cm^{-1} for stretching alcoholic(-OH) with stretching (H–bond) and the spectrum also showed the aliphatic (C-H), aromatic (=C-H) and alkenes (=C–H) at approximately at 2951 cm^{-1} , 2886 cm^{-1} and 3050 cm^{-1} respectively, and the spectrum also showed a strong sharp band at 1712 cm^{-1} and 1261 cm^{-1} for a stretching band (C=O) ester and (C-O) ester respectively.

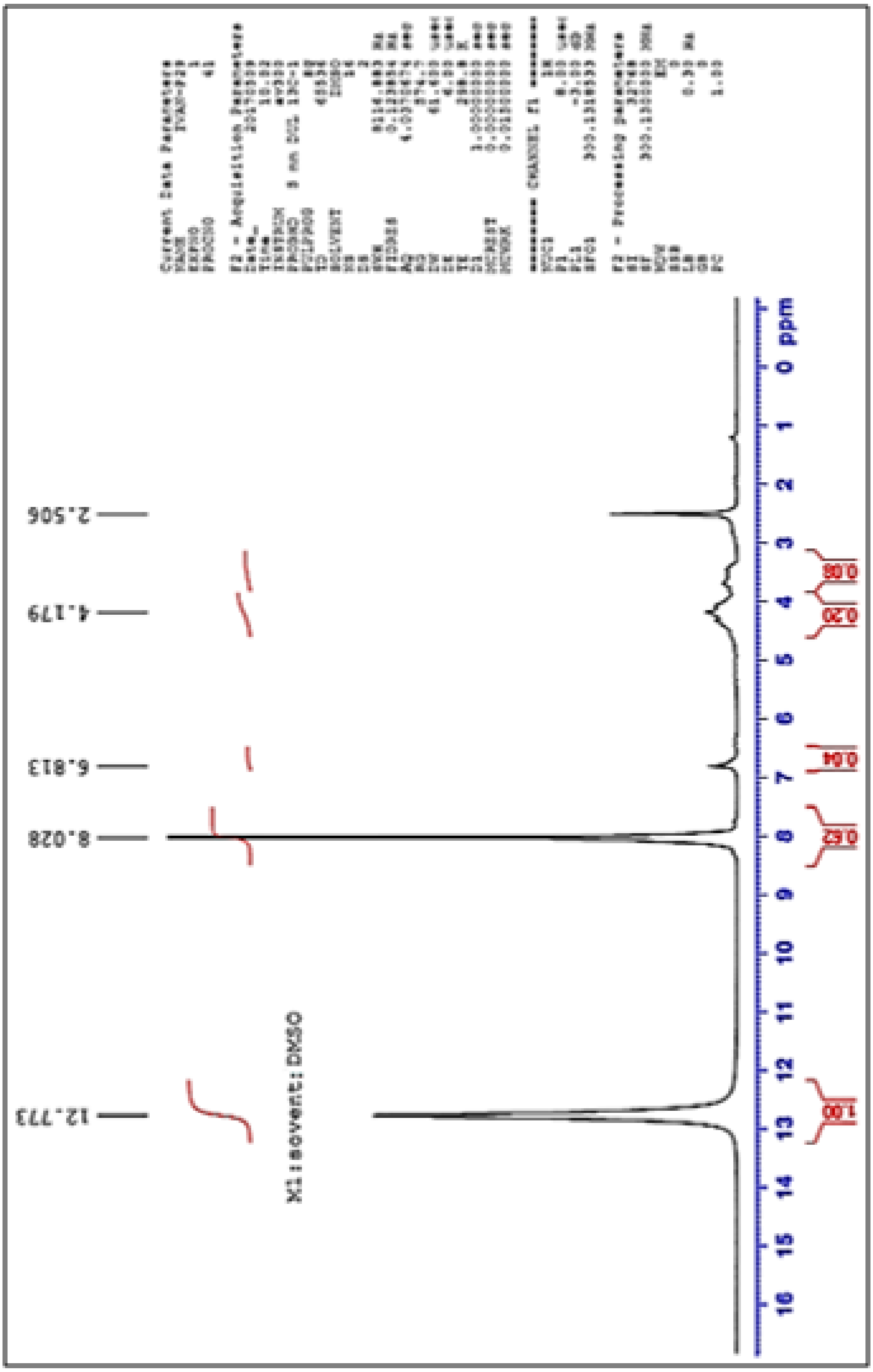
Figure (3-4) showed the ^{1}HMNR spectrum of the graft co-polymer, its showed the appearancea single signal at 2.5 ppm for DMSO , multi signal at range 3.5-4.8 ppm which can be attributed to [CH_2-O-C=O , -CH=CH-] groups,aromatic protons signal observed as doublet signal at 6.81-8.02 ppm in addition to single signal at 12.77 ppm for carboxylic acid protons.

Table (3-3):Physical properties of the graft co-polymer

Physical properties	**Value**
Molecular Weight ($\overline{Mn}$)	Around 2800 gm/mole
Solid content	61 %
Viscosity	23 poise
Gel time	15-20 min at 25C^{0}
Acid Value	26
Density	1.5 (gm/cm^{3})



Figure(3-3): The FT-IR spectrum of the graft co-polymer.

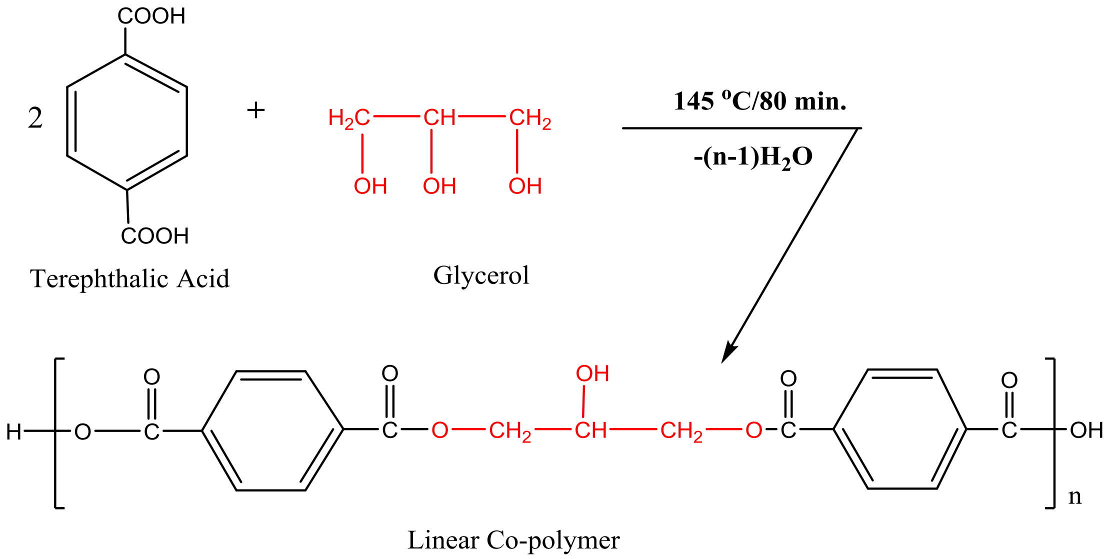


Figure(3-4): The ^{1}HMNR spectrum of the graft co-polymer

3.1.2 Using solubilization process

3.1.2.1 Preparation of linear co-polymer

The linear co-polymer was synthesized by dissolved theterphthalicacid in amount of DMSO at 40^{o}C and added the glycerol and warmed the mixture carefully by esterfication process in 80 min. at 145 C^{o} as shown in equation (3-3). It was observed that the FT-IR and ^{1}HMNR spectrum of the prepared polymer in this process is similar to that of the fusion process.

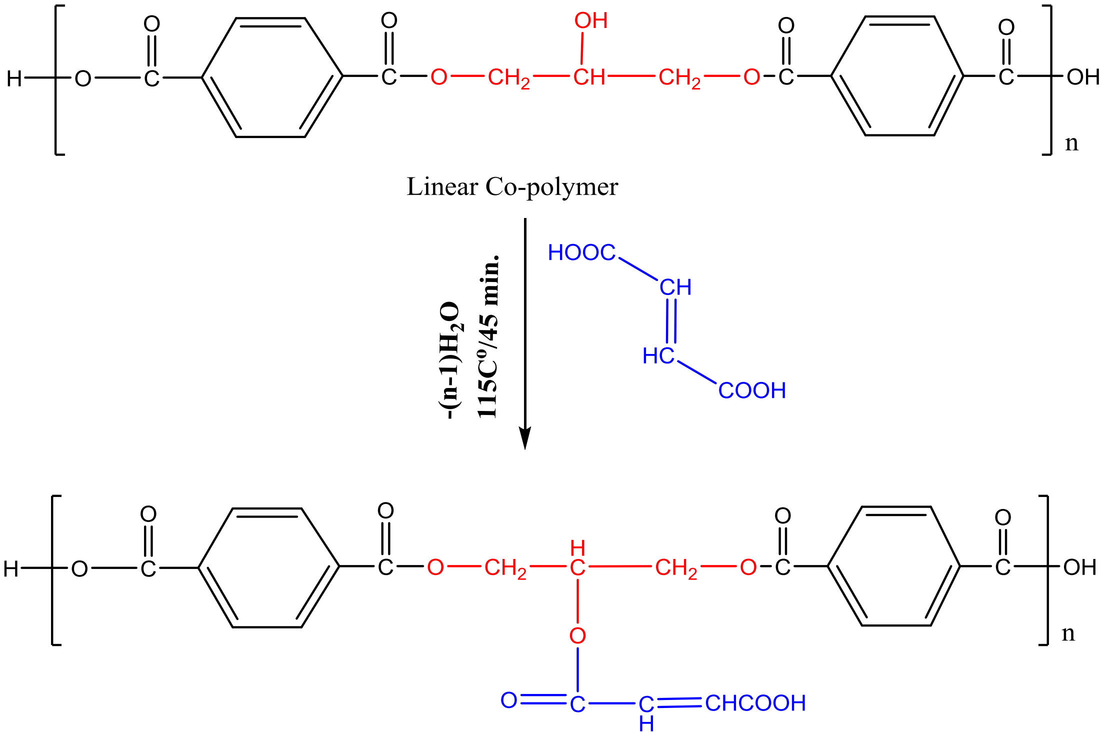


Equation (3-3): Synthesis of linear co-polymer

3.1.2.2 Preparation of a graft co-polymer

The graft co-polymer was synthesized by dissolved 0.5mole of fumaric acid in DMSO and added to the linear co-polymer (which prepared in 3.1.2.1) to produce graft co-polymer at 115 C^{o} after 45 min., as shown in equation (3-4). It was observed that the infrared spectrum of the prepared polymer in this process is similar to that of the fusion process.

Three different numbers of moles (1.5, 2.0 and 2.5 mole) respectively of acrylic acid monomer were added to the graft co-polymer to prepare three different graft co-polymers.



Graft Co-polymer

Equation (3-4): Synthesis of graft co-polymer.

3.2 Atomic Force Microscopic (AFM) measurements

The size of particles of the linear and graft co-polymers which prepared by using solubilization process was measured by the atomic force microscope (AFM). The results showed that the co-polymersare nanoparticles co-polymers, as shown below:

Figure (3-5 a, b &c) shows the outer surface of the nanoparticles of linear co-polymer. The roughness of this surface and the square root square are calculated according to the coefficient:

$$Rm = \sqrt{\sum_{i=1}^{n} \frac{(Zi - Zav)^2}{N}}$$

Where N, Z = the number of measured points

The roughness coefficient of a linear co-polymer surface was 1.19 nm and the square root square was equal to 1.37 nm. This indicates that the bold size of the nanoparticles plays an important role in the roughness of the surface, its uniform crystalline system, and the surface homogeneity. Also, the average of height of the particles was equal to 4.80 nm, as observed in figure (3-5 a).

Table (3-4) represents the total rate of the particle sizes of the common linear nanoparticle and the different proportions of these volumes. The results indicate that the molecular size of the linear co-polymer nanoparticle was 94.09 nm and figure (3-6) represents the distribution of the different proportions of particle sizes of the linear co-polymer nanoparticle.

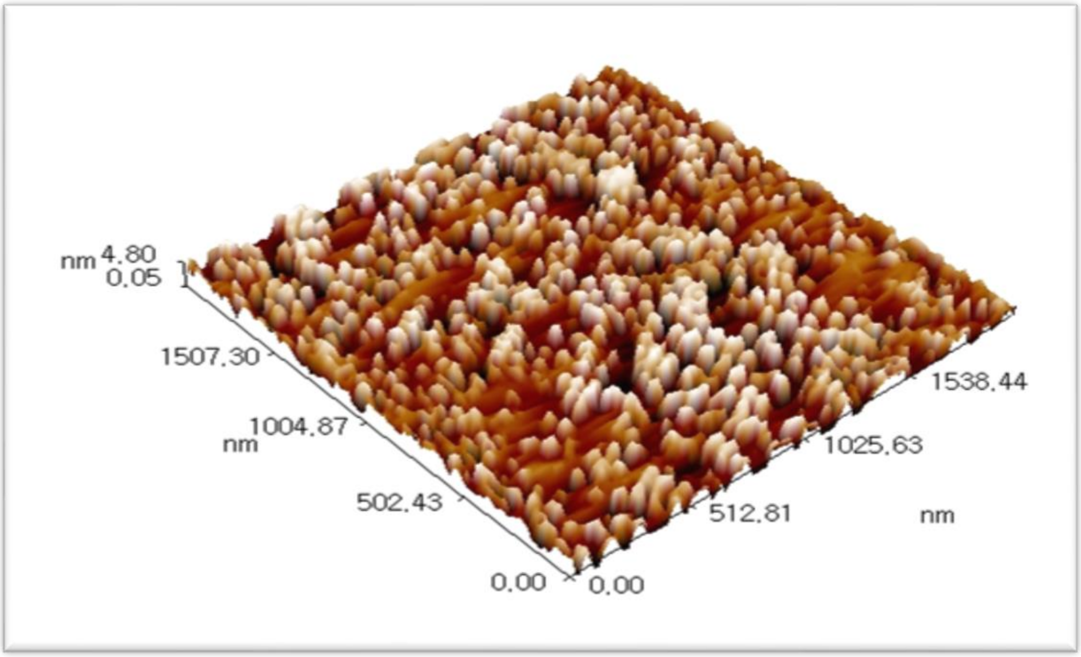


Figure (3-5 a): Image of Atomic Force Microscope for linear co-polymer shows 3D Image.

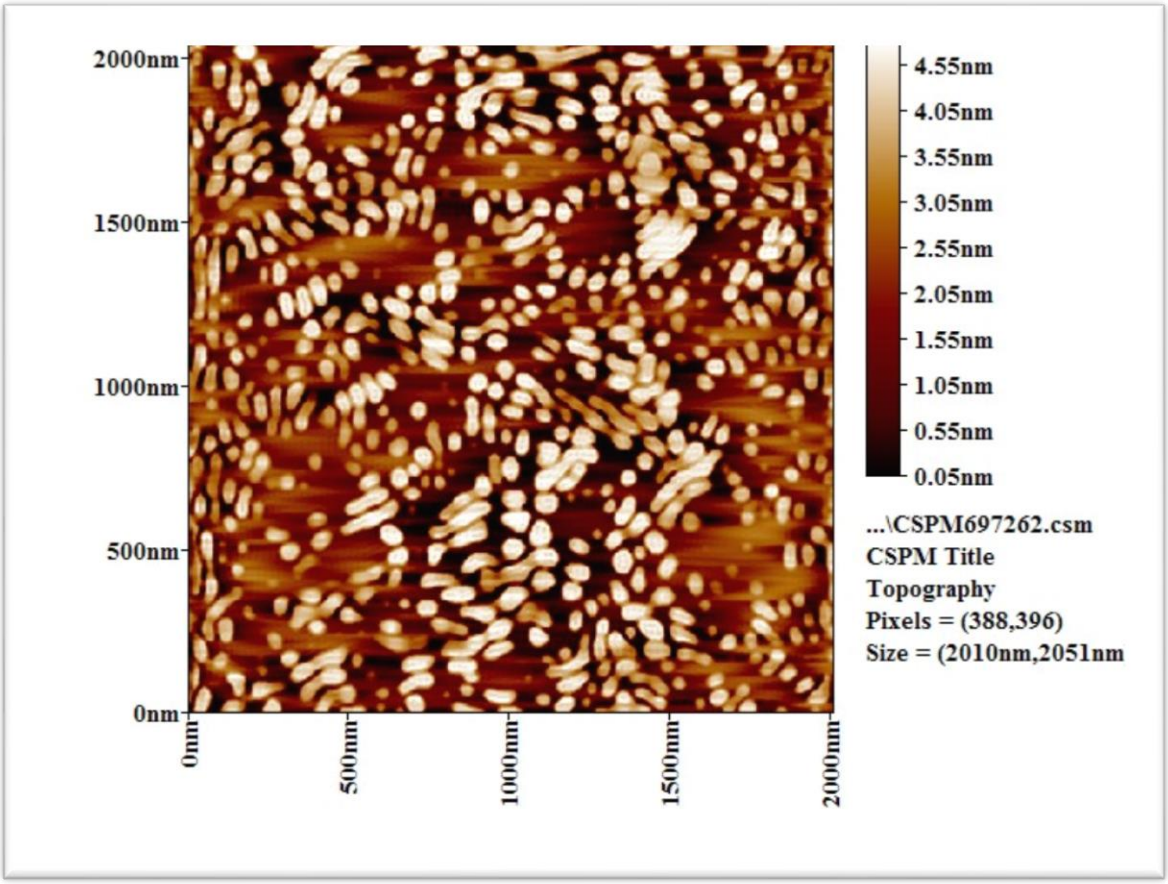
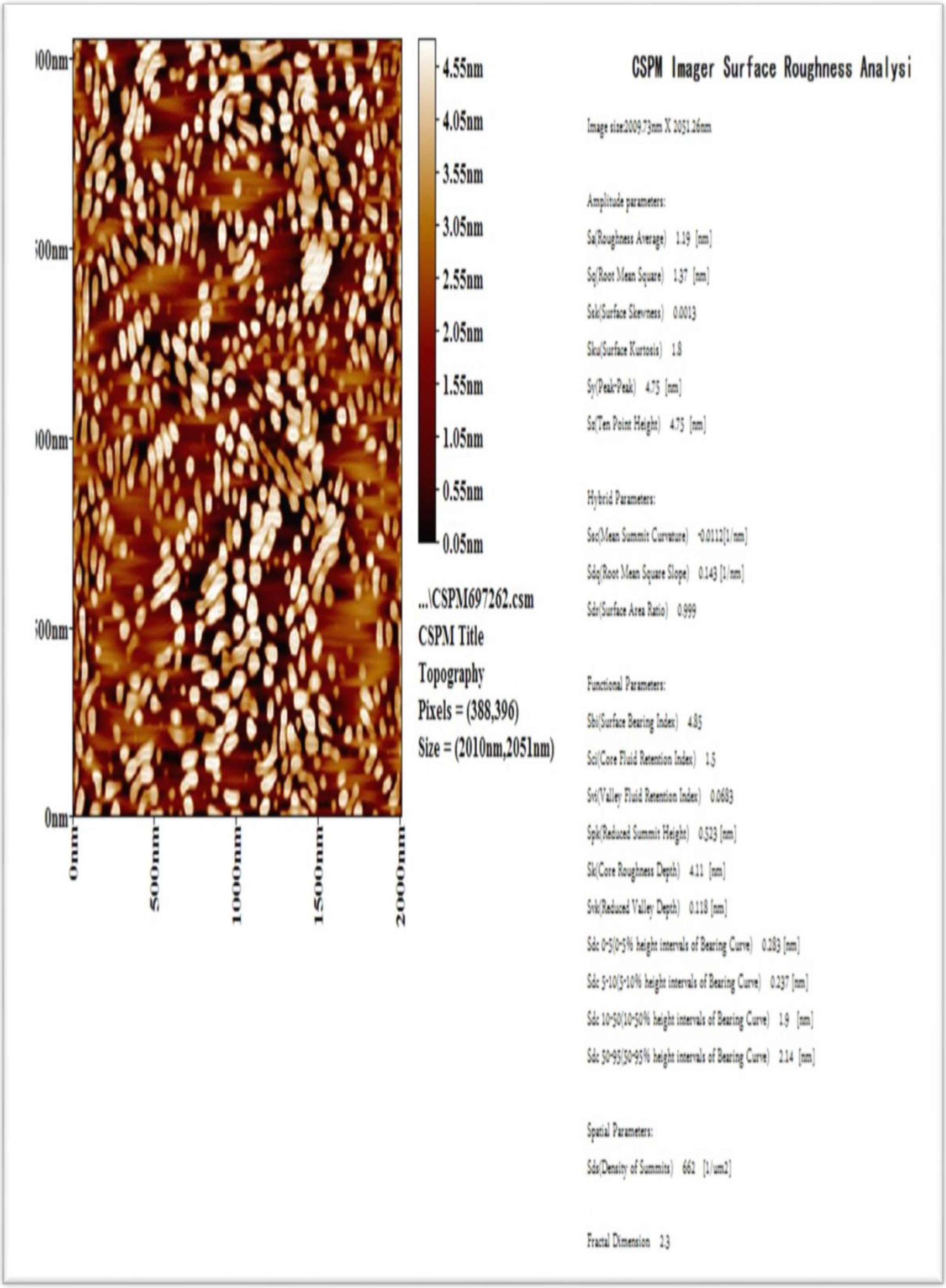


Figure (3-5 b): Image of Atomic Force Microscope for linear co-polymer shows 2D Image.



...\CSPM697262.csm
CSPM Title
Topography
Pixels = (388,396)
Size = (2010nm,2051nm)

CSPM Imager Surface Roughness Analysi

Image size:2009.73nm X 2051.26nm

Amplitude parameters:
Sa(Roughness Average) 1.19 [nm]
Sq(Root Mean Square) 1.37 [nm]
Ssk(Surface Skewness) 0.0013
Sku(Surface Kurtosis) 1.8
Sy(Peak-Peak) 4.75 [nm]
Sz(Ten Point Height) 4.75 [nm]

Hybrid Parameters:
Ssc(Mean Summit Curvature) -0.0112[1/nm]
Sdq(Root Mean Square Slope) 0.143 [1/nm]
Sdr(Surface Area Ratio) 0.999

Functional Parameters:
Sbi(Surface Bearing Index) 4.85
Sci(Core Fluid Retention Index) 1.5
Svi(Valley Fluid Retention Index) 0.0683
Spk(Reduced Summit Height) 0.523 [nm]
Sk(Core Roughness Depth) 4.11 [nm]
Svk(Reduced Valley Depth) 0.118 [nm]
Sdc 0-5(0-5% height intervals of Bearing Curve) 0.283 [nm]
Sdc 5-10(5-10% height intervals of Bearing Curve) 0.237 [nm]
Sdc 10-50(10-50% height intervals of Bearing Curve) 1.9 [nm]
Sdc 50-95(50-95% height intervals of Bearing Curve) 2.14 [nm]

Spatial Parameters:
Sds(Density of Summits) 662 [1/um2]

Fractal Dimension 2.3

Figure (3-5 c): Image of Atomic Force Microscope for linear co-polymer shows 2D Image and showing all details of particles

Table (3-4): The total diameter of the particle sizes of the linear co-polymer nanoparticle and the different proportions of these volumes

Sample:1	**Code:**Sample Code
Line No.:lineno	**Grain No.:**139
Instrument:CSPM	**Date:**2018-04-23

Avg. Diameter:94.09 nm	**<=10% Diameter:75.00 nm**
<=50% Diameter:90.00 nm	**<=90% Diameter:115.00 nm**

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
75.00	7.19	7.19	100.00	8.63	68.35	125.00	1.44	93.53
80.00	12.95	20.14	105.00	7.19	75.54	130.00	5.76	99.28
85.00	16.55	36.69	110.00	7.19	82.73	145.00	0.72	100.00
90.00	11.51	48.20	115.00	5.04	87.77			
95.00	11.51	59.71	120.00	4.32	92.09			

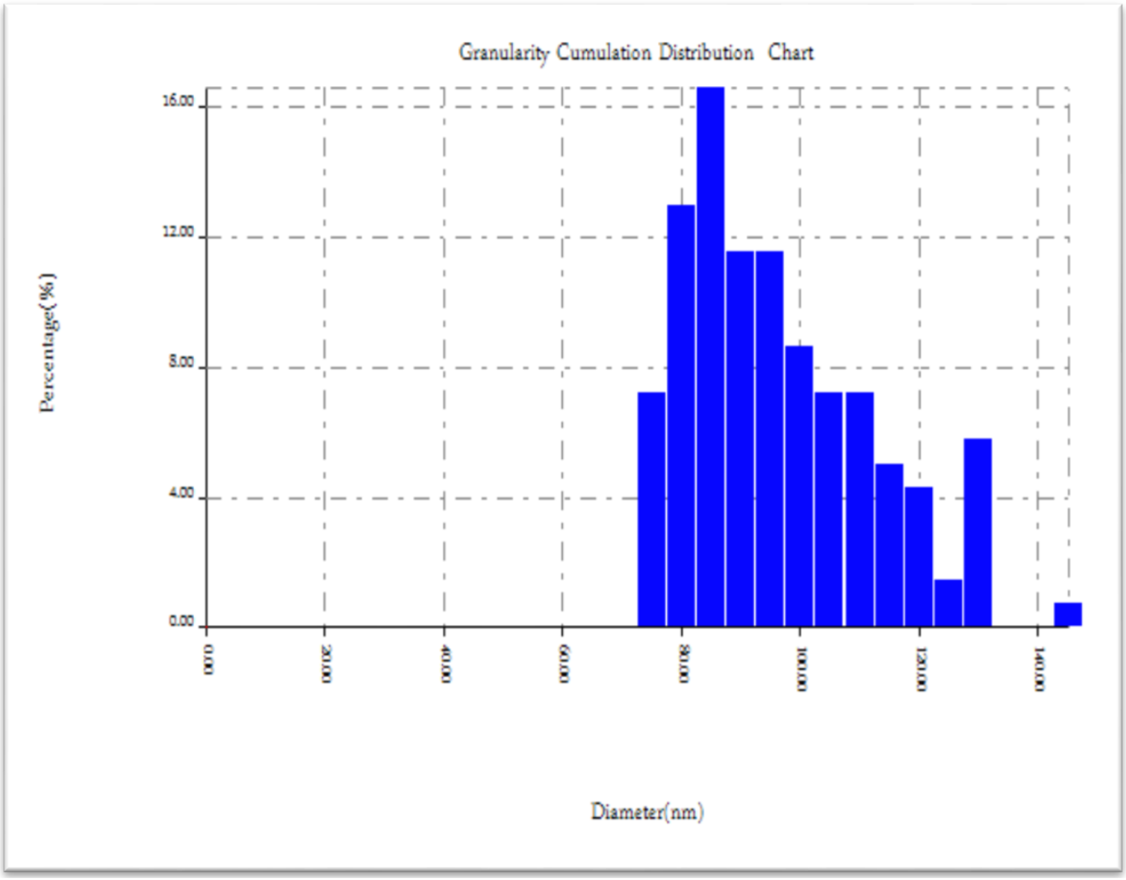


Figure (3-6): Distribution of the different proportions of particle sizes of the linear co-polymer nanoparticle.

On the other hand, figure (3-7 a, b &c) shows the outer surface of the nanoparticles of graft co-polymer. The roughness coefficient of a graft co-polymer surface was 1.68 nm and the square root was equal to 1.96 nm. This indicates that the bold size of the nanoparticles plays an important role in the roughness of the surface, its uniform crystalline system, and the surface homogeneity, Also, the average of height of the particles was equal to 7.2 nm, as observed in figure(3-7 a).

Table (3-5) represents the total diameter of the particle sizes of the graft co-polymer nanoparticle and the different proportions of these volumes; The results indicate that the molecular size of the graft co-polymer nanoparticle was 56.80nm and figure (3-8) represents the distribution of the different proportions of particle sizes of the graft co-polymer nanoparticle.

Table (3-5): The total diameter of the particle sizes of the graft co-polymer nanoparticle and the different proportions of these volumes

Sample:M4 **Line No.:**lineno **Instrument:**CSPM	**Code:**Sample Code **Grain No.:**259 **Date:**2018-04-23
Avg. Diameter:56.80 nm **<=50% Diameter:50.00 nm**	**<=10% Diameter:0 nm** **<=90% Diameter:70.00 nm**

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	26.64	26.64	65.00	11.58	81.08	80.00	3.47	99.23
55.00	26.64	53.28	70.00	8.88	89.96	95.00	0.77	100.00
60.00	16.22	69.50	75.00	5.79	95.75			

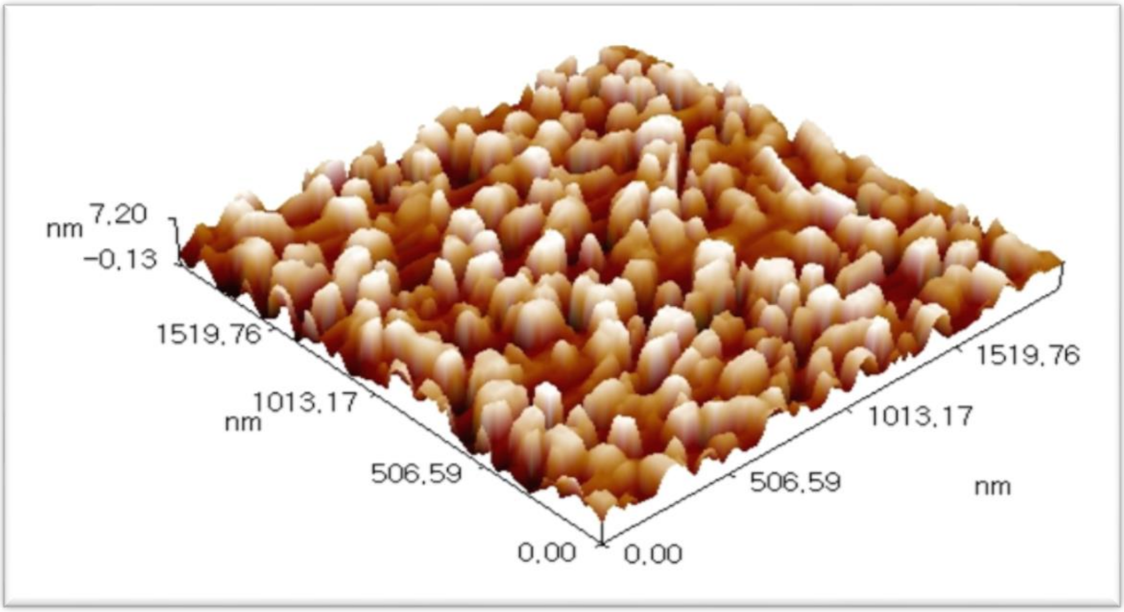


Figure (3-7a): Image of Atomic Force Microscope for graft co-polymer shows 3D Image.

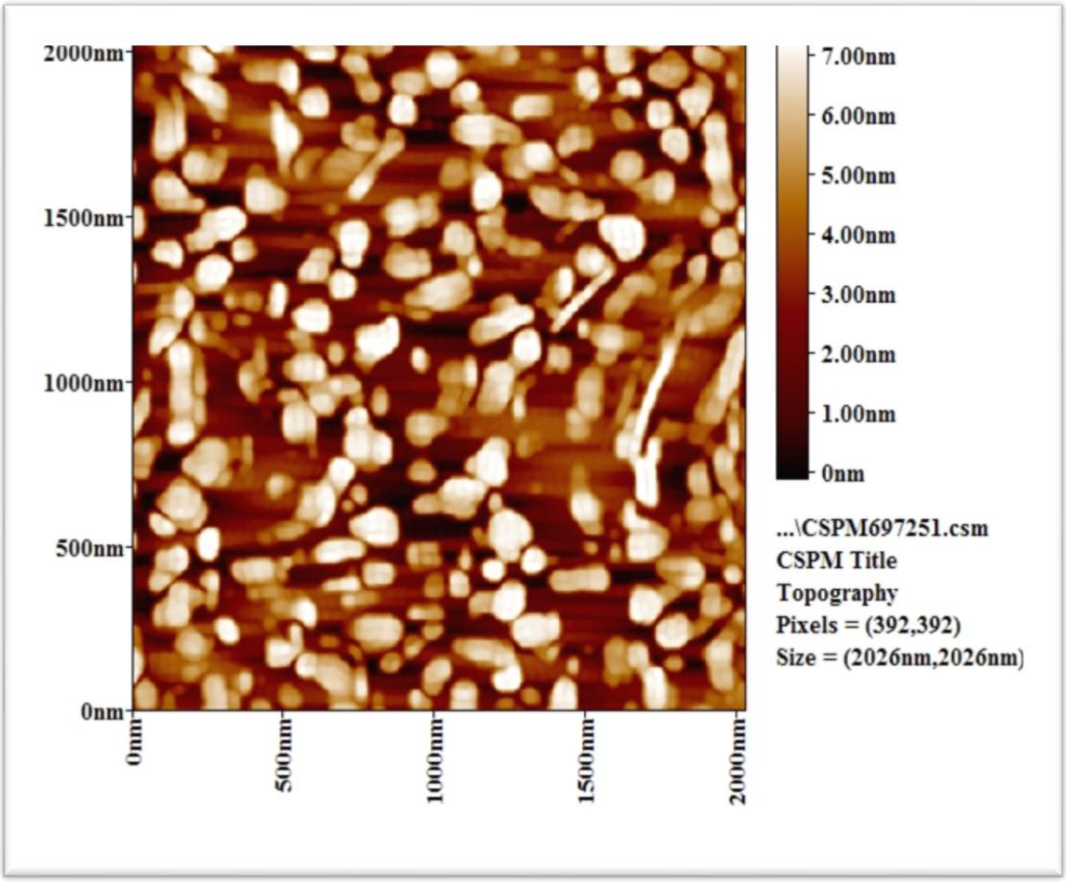
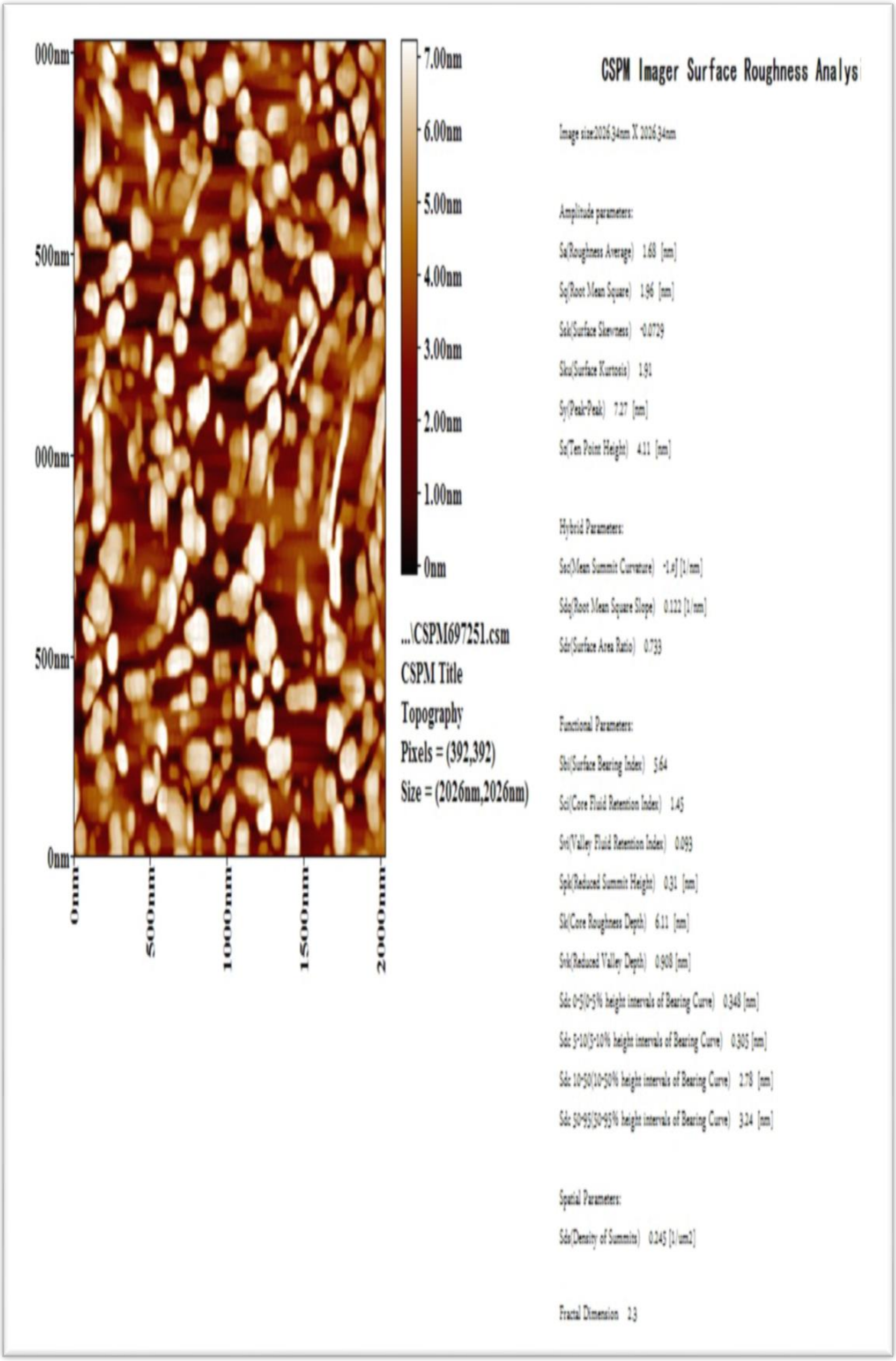


Figure (3-7 b): Image of Atomic Force Microscope for graft co-polymer shows 2D Image.



...\CSPM697251.csm
CSPM Title
Topography
Pixels = (392,392)
Size = (2026nm,2026nm)

CSPM Imager Surface Roughness Analys

Image size:2026.34nm X 2026.34nm

Amplitude parameters:
Sa(Roughness Average) 1.68 [nm]
Sq(Root Mean Square) 1.96 [nm]
Ssk(Surface Skewness) -0.0729
Sku(Surface Kurtosis) 1.91
Sy(Peak-Peak) 7.27 [nm]
Sz(Ten Point Height) 4.11 [nm]

Hybrid Parameters:
Ssc(Mean Summit Curvature) -1.#J [1/nm]
Sdq(Root Mean Square Slope) 0.122 [1/nm]
Sdr(Surface Area Ratio) 0.733

Functional Parameters:
Sbi(Surface Bearing Index) 5.64
Sci(Core Fluid Retention Index) 1.45
Svi(Valley Fluid Retention Index) 0.093
Spk(Reduced Summit Height) 0.31 [nm]
Sk(Core Roughness Depth) 6.11 [nm]
Svk(Reduced Valley Depth) 0.908 [nm]
Sdc 0-5(0-5% height intervals of Bearing Curve) 0.348 [nm]
Sdc 5-10(5-10% height intervals of Bearing Curve) 0.305 [nm]
Sdc 10-50(10-50% height intervals of Bearing Curve) 2.78 [nm]
Sdc 50-95(50-95% height intervals of Bearing Curve) 3.24 [nm]

Spatial Parameters:
Sds(Density of Summits) 0.245 [1/um2]

Fractal Dimension 2.3

Figure (3-7 c): Image of Atomic Force Microscope for graft co-polymer shows 2D Image and showing all details of particles

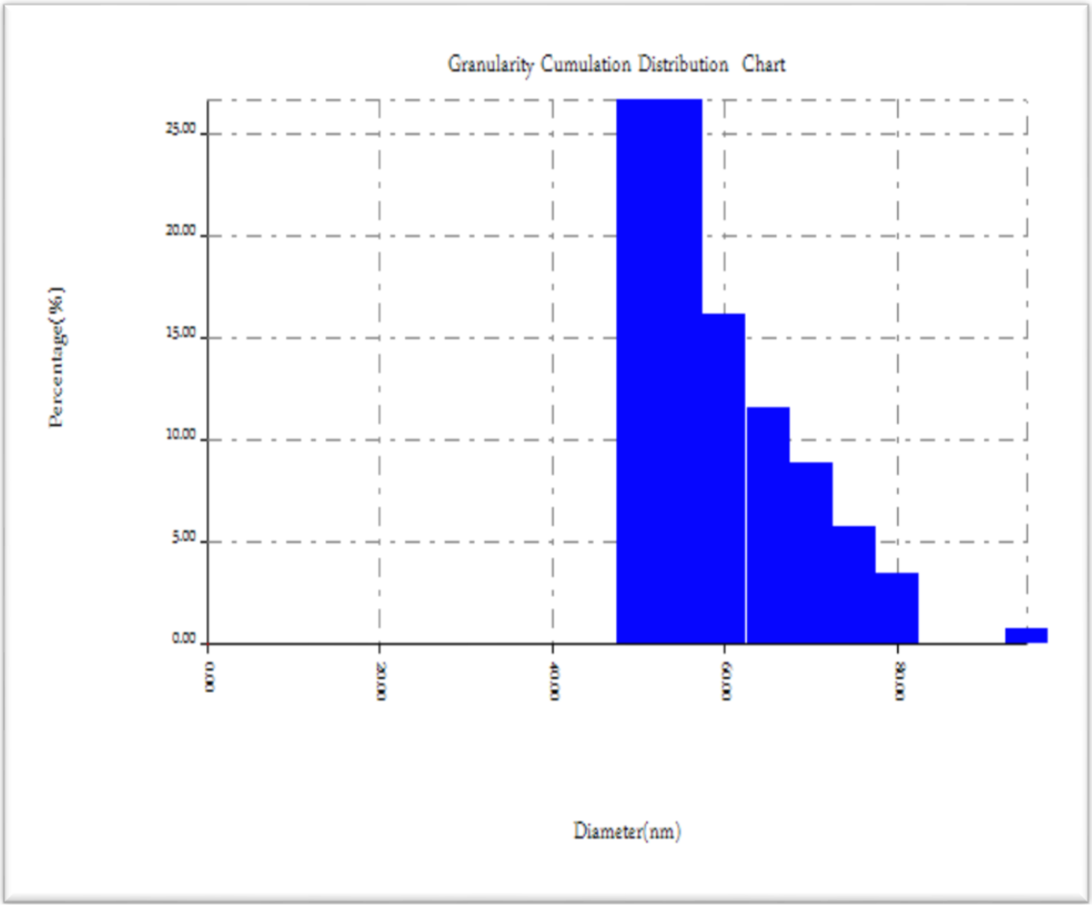


Figure (3-8): Distribution of the different proportions of particle sizes of the graft co-polymer nanoparticle.

3.3 Determination of the rate of polymerization

The rate of polymerization in different times (Sec.) at a constant temperature was calculated by measuring the acid value. The slope of a plot of acid value (A.V.) versus time (Sec.) represents the rate of polymerization. Table (3- 6) shows the acid value in different times at different temperatures. Figure (3-9) represents the plot of acid value versus time (Sec.). The rate of polymerization of the linear co-polymer was (120 Sec.$^{-1}$) at a constant temperature in 583 K. The activation energy (Ea) of polymerization of the co-polymer was calculated from

Arrhenius equation [156], and it was found (242.3531 J/mole) at a constant temperature in 583K.

Table (3-6): Represent the acid value in different times at different temperatures.

Time (Sec.)	Acid Value	Slope	Temp. (K)
120 240 360 480	240.0 220.0 198.8 182.0	-0.1722	563
120 240 360 480	176.4 162.4 147.0 135.0	-0.1101	568
120 240 360 480	126.0 114.6 103.6 92.4	-0.0833	573
120 240 360 480	81.2 73.0 64.4 57.4	-0.0676	578
120 240 360 480	47.9 42.8 37.0 30.0	-0.0497	583

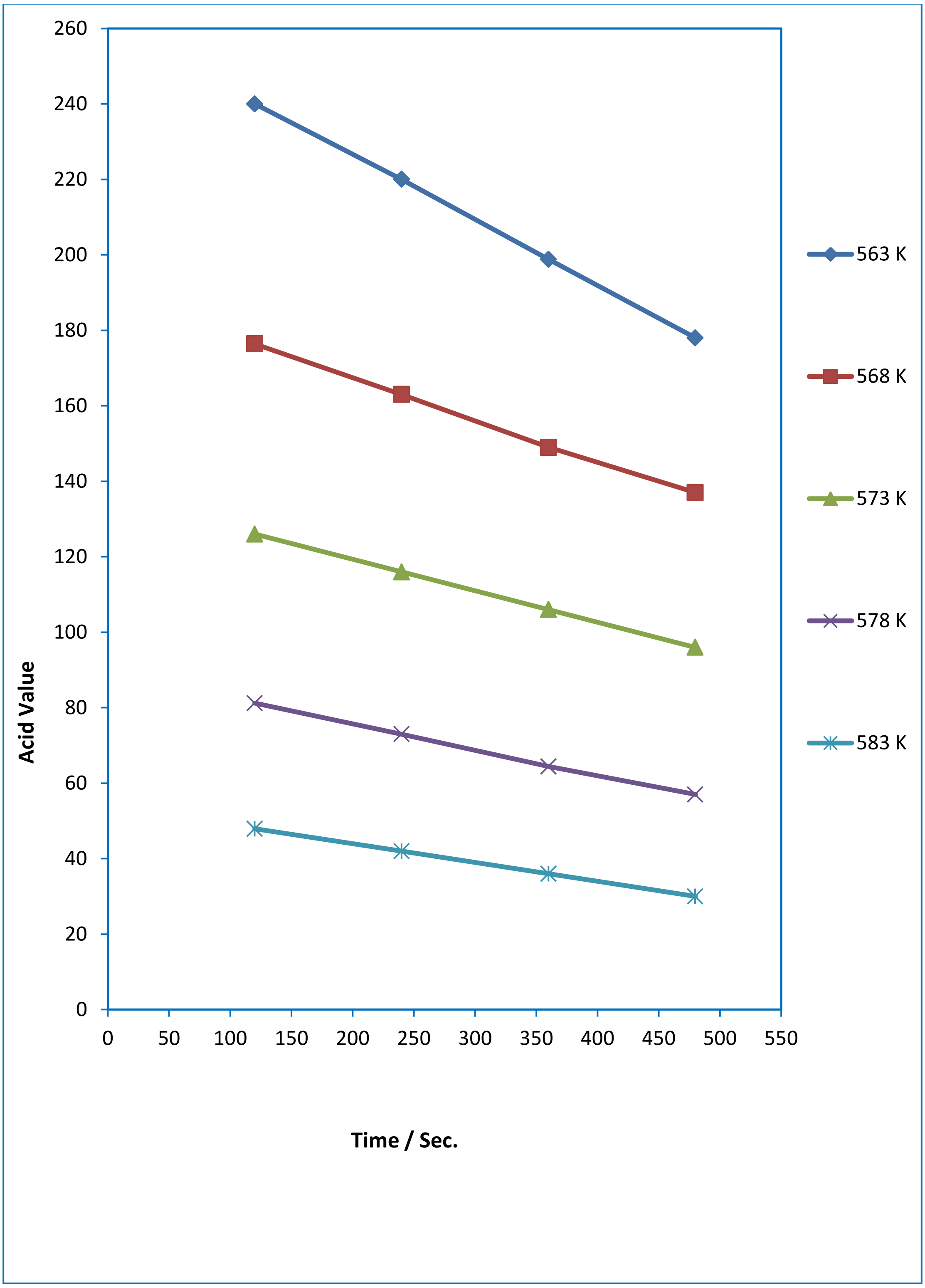


Figure (3-9): The plot of Acid value Vs. Time (Sec.) in different temperatures

3.4 Determinations of the thermodynamic function

By using Van Huff complementary equation, the thermodynamic functions were determination of the linear co-polymer. Table (3-7) shows the thermodynamic functions. Figure (3-10) represents the plot of Ln K vis. 1/T.

Table (3-7): The thermodynamic functions of the linear co-polymer.

no	**T (K^o)**	**1/T**	**lnK**	**ΔH (KJ/mol)**	**ΔG (KJ/mol)**	**ΔS (KJ/mol.K)**
1	563	1.776×10^{-3}	-0.1003	2.9×10^{3}	0.469	5.150
2	568	1.7605×10^{-3}	-9.2992		43.914	5.097
3	573	1.7452×10^{-3}	-10.733		51.131	4.971
4	878	1.7301×10^{-3}	-15.232		73.197	4.890
5	583	1.7152×10^{-3}	-24.063		116.634	4.774

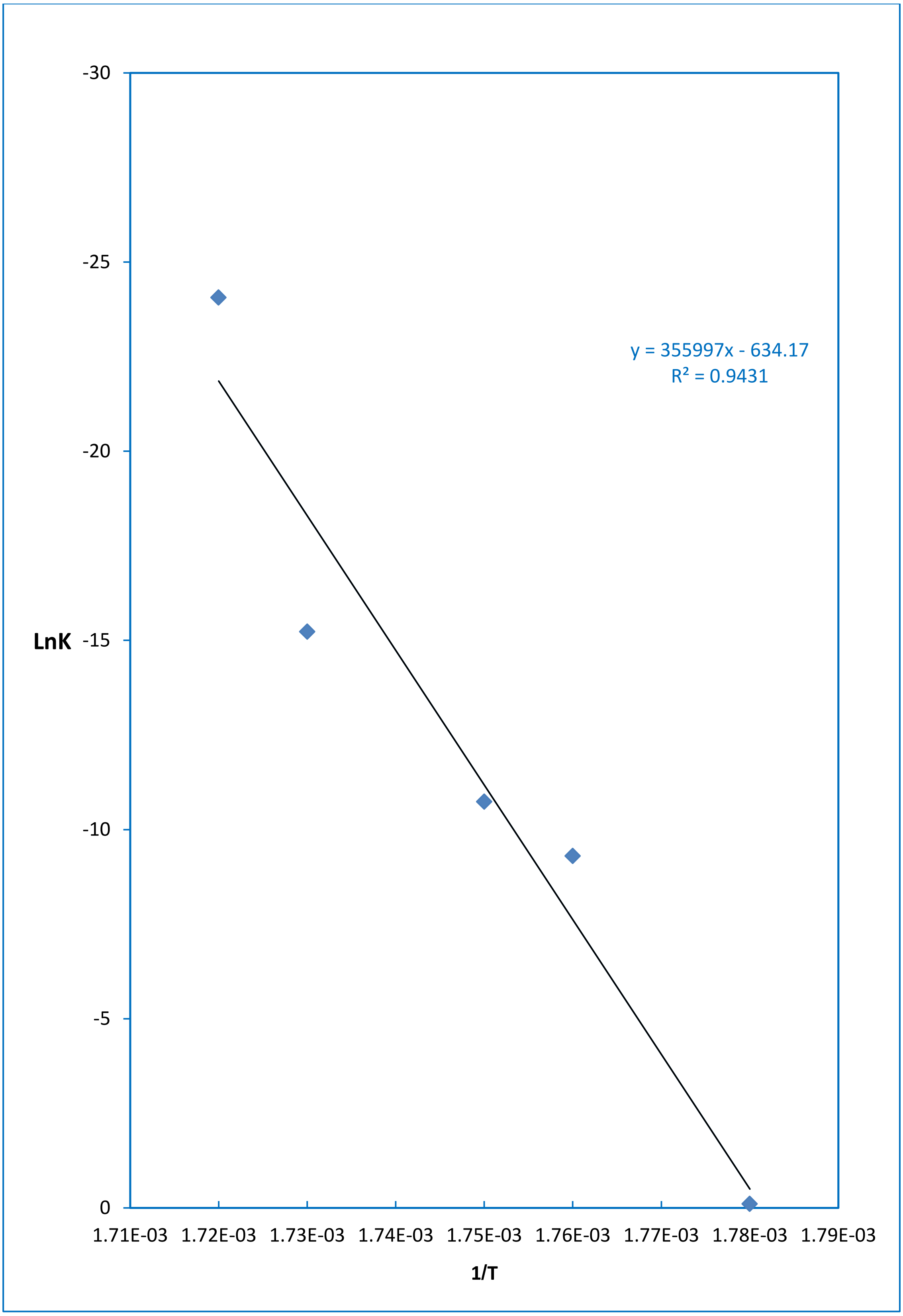


Figure (3-10): The plot of ln K vis. 1/T

3.5 Swelling

A chemically cross-linked polymer can increase its volume, figure(3-11), numerous folds by absorbing great a mount of solvent [95].The degree to which the volume increases depends on the degree to which the polymer "likes" the solvent and the degree of cross-linking. Solvents swell cross-linked polymer networks to a degree determined by both the solvent-polymer interactions and the polymer network structure [96].

According to the Flory–Renner theory[97], the swellings degree is a balance between the entropy of the polymer and liquid mixing, the entropy change caused by reduction in the number chain of polymer conformations upon swelling, and the heat of mixing of the polymer and liquid.

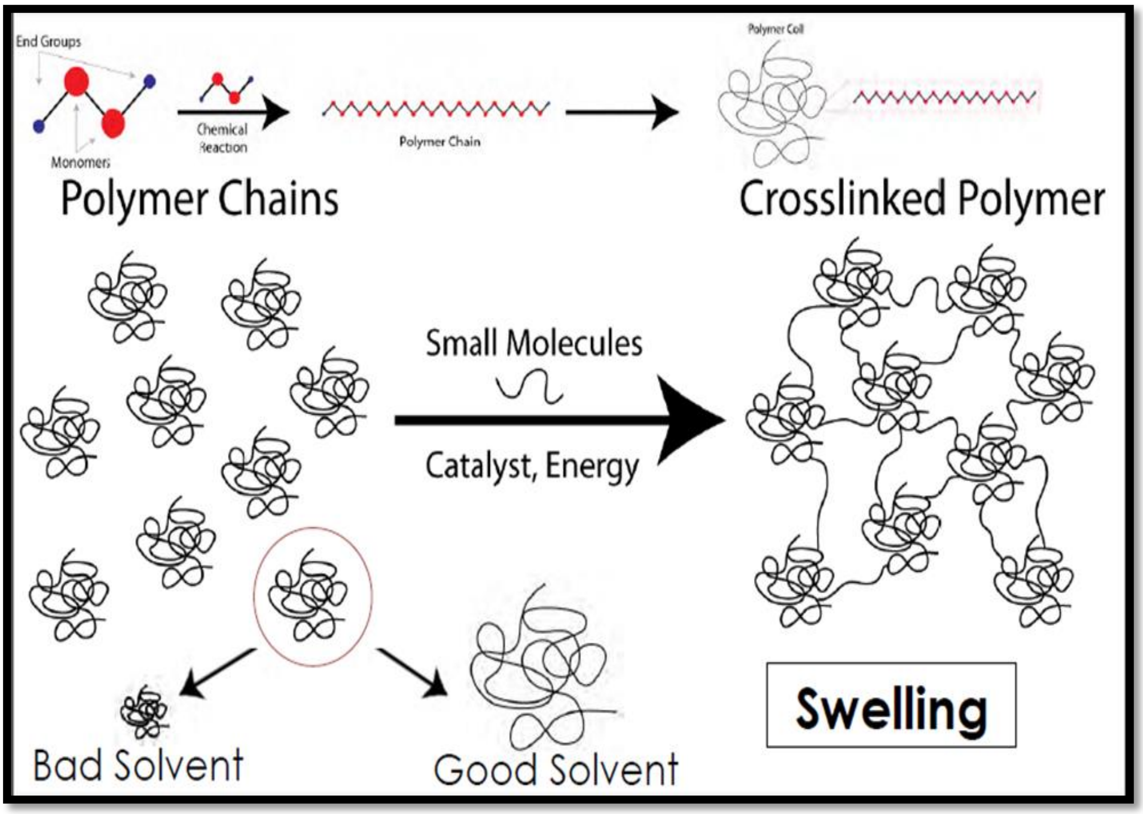


Figure (3-11): The swelling ofthe polymers

There are two types of swelling, limited swelling, when they are limited solubility of the polymer in solvents. When a solvent enters polymer and does not dissolve the polymer but swelly it [98]. The chains are in an entangled and relaxed conformation between two network junctions. However, when the solvent enters the polymer, the liquid molecules move the network junctions away from each other (as the polymer swells in the solvent). As the network junctions move away [99], the polymeric chains do not separate completely from each other, figure (3-12).Thus, two phases are formed, one separated from the solute in the swelling polymer and the other from the pure solute [100], and unlimited swelling . It is that process which leads to spontaneous dissolution. The liquids that possess a high to a certain polymer and known as good solvents to penetrate through the chain to give this type of swelling that led lastly to polymeric dissolution [98]. Several factors controlled of polymers swelling, including the nature of the solvent, molecular weight of the polymer, the structural reformation, the number of links, , the degree of the surrounding medium heat [101] .

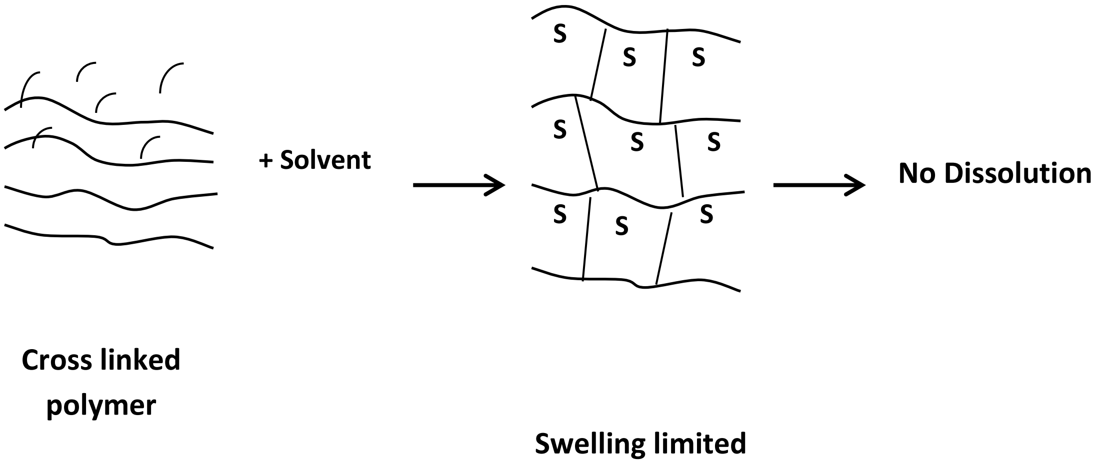


Figure (3-12): Swelling limited for certain polymers

3.5.1 Fusion process

1- Swelling of the graft co-polymers which prepared by fusion process was measured by using three different pH (2.2, 7.0 and 8.0) respectively. The swelling curves showed a plot of water content for different compositions against swelling time (Min.). The initial swelling rate was medium, the maximum being reached within the first few hours of the swelling. The shape of the swelling curves indicated that water–soluble molecules were being released from the xerogel upon swelling. The thicker discs required longer time to attain maximum equilibrium.

2- In this work the thickness of the dry discs (xerogel) was exactly 3.0mm and the diameter was exactly 10.0mm and the weighted was exactly 0.5 gm of all samples were used in the swelling study at 310 K.

3- A plot of water content versus time showed the curves of graft co-polymer for three different numbers of moles from acrylic acid monomer ranging from 1.5, 2.0 and 2.5 mole, against swelling time (Min.) at constant temperatures 310 K, as shown in tables (3-8) to (3-10) and figures (3-12) to (3-17) respectively.

4- As clearly shown in these figures increasing the time (Min.) with increasing of the water content (%), This behavior can be explained due to, the structure of co-polymers,i.e., present of the hydrophilic groups in the xerogel, number of mole from acrylic acid monomer and nature of the buffer solution. All these factors will increase the water content (%) with the increasing of time, and an increase in the number of moles of acrylic acid monomer leads to an increase in swelling, because of the increase in the number of hydrophilic groups in the back bone of monomer; On the other hand, the low values of swelling process were affected by low degree of cross linking, i.e., in the graft co-polymer with 1.5 mole of acrylic acid monomer, the values will be low comparing with the values in the graft co-polymer with 2.5 moles of acrylic acid monomer.

Table (3-8): Swelling ratio (%) in different times of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

Time (hour)	Swelling ratio (%)		
	Number of moles acrylic acid monomers		
	1.5 moles	2.0 moles	2.5 moles
1	5.0111	5.1241	5.2356
2	5.0433	5.1468	5.2582
3	5.0660	5.1695	5.2708
4	5.0887	5.1822	5.2930
5	5.1114	5.2149	5.3156
(day)			
1	6.0165	6.1600	6.2875
2	6.0580	6.1855	6.3130
3	6.0835	6.2110	6.3385
4	6.1090	6.2365	6.3640
5	6.1345	6.2620	6.3895

Table (3-9): Swelling ratio (%) in different times of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

Time (hour)	Swelling ratio (%)		
	Number of moles of acrylic acid monomers		
	1.5 mole	2.0 mole	2.5 mole
1	7.0160	7.2455	7.4555
2	7.0590	7.2890	7.5084
3	7.1035	7.3230	7.5421
4	7.1374	7.3640	7.5859
5	7.1692	7.4192	7.6299
6	7.2023	7.4325	7.6690
(day)			
1	8.0180	8.2526	8.4931
2	8.0571	8.2917	8.5381
3	8.0963	8.3308	8.5831
4	8.1323	8.3699	8.6281
5	8.1744	8.4090	8.6731
6	8.2135	8.4481	8.7181

Table (3-10): Swelling ratio (%) in different timesof graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

Time (hour)	Swelling ratio (%)		
	Number of moles acrylic acid monomers		
	1.5 moles	2.0 moles	2.5 moles
1	9.1011	9.2439	9.3854
2	9.1218	9.2642	9.4056
3	9.1423	9.2844	9.4258
4	9.1627	9.3046	9.4460
5	9.1831	9.3248	9.4662
6	9.2033	9.3450	9.4864
7	9.2236	9.3652	9.5066
(day)			
1	10.0190	10.6150	11.2185
2	10.1040	10.7010	11.3060
3	10.1890	10.7870	11.3935
4	10.2740	10.8730	11.4810
5	10.3590	10.9590	11.5685
6	10.4440	11.0450	11.6560
7	10.5290	11.1310	11.7435

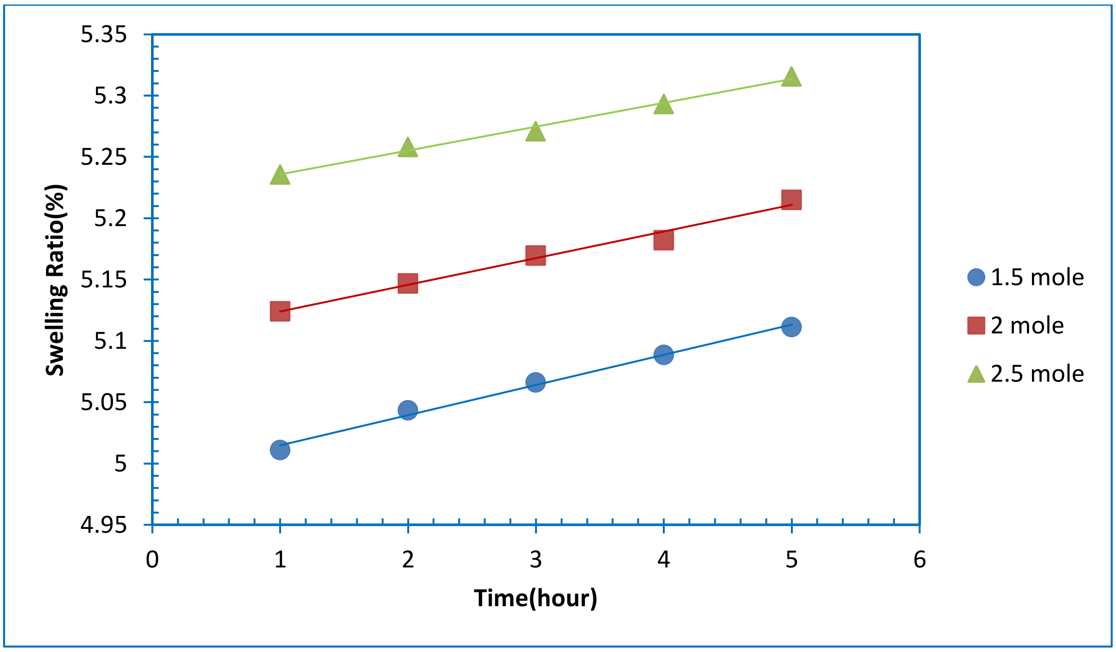


Figure (3-13):Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

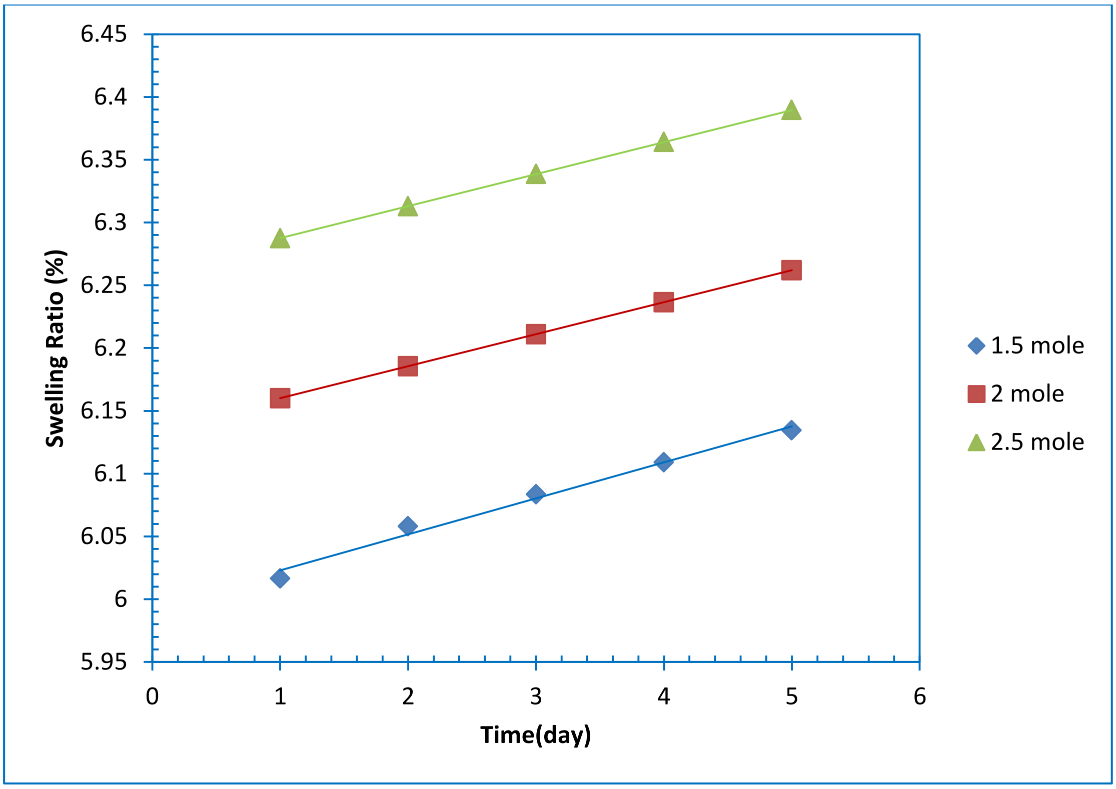


Figure (3-14): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

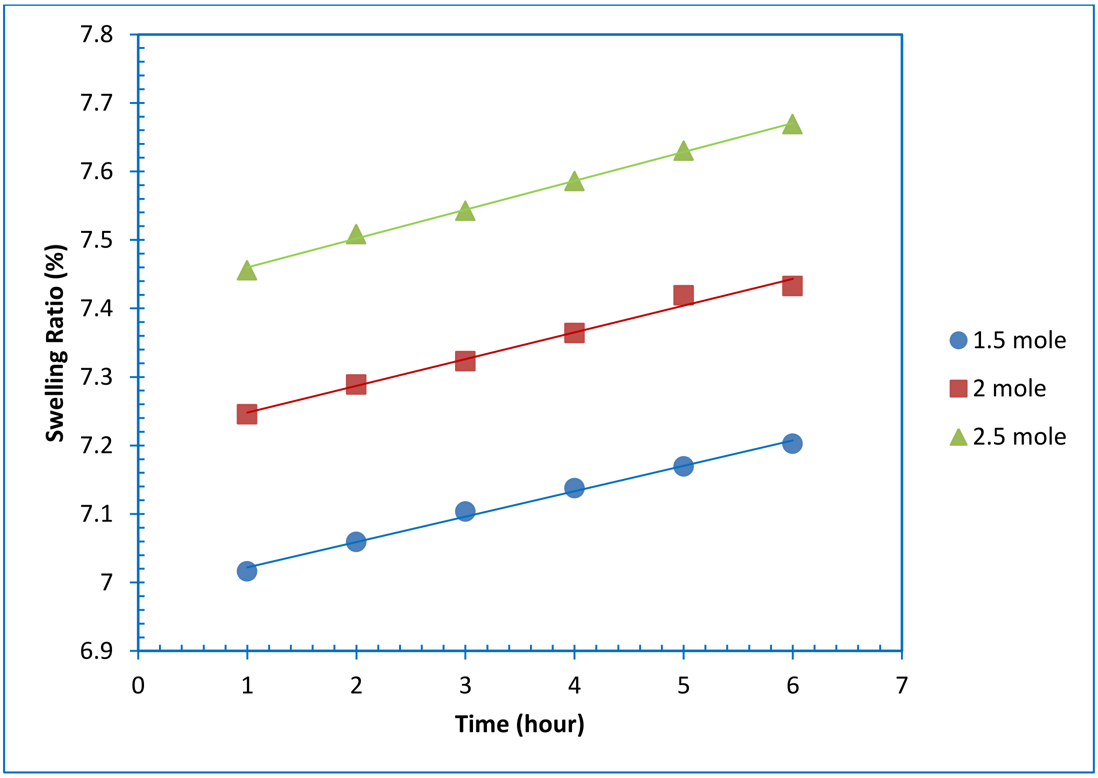


Figure (3-15):Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

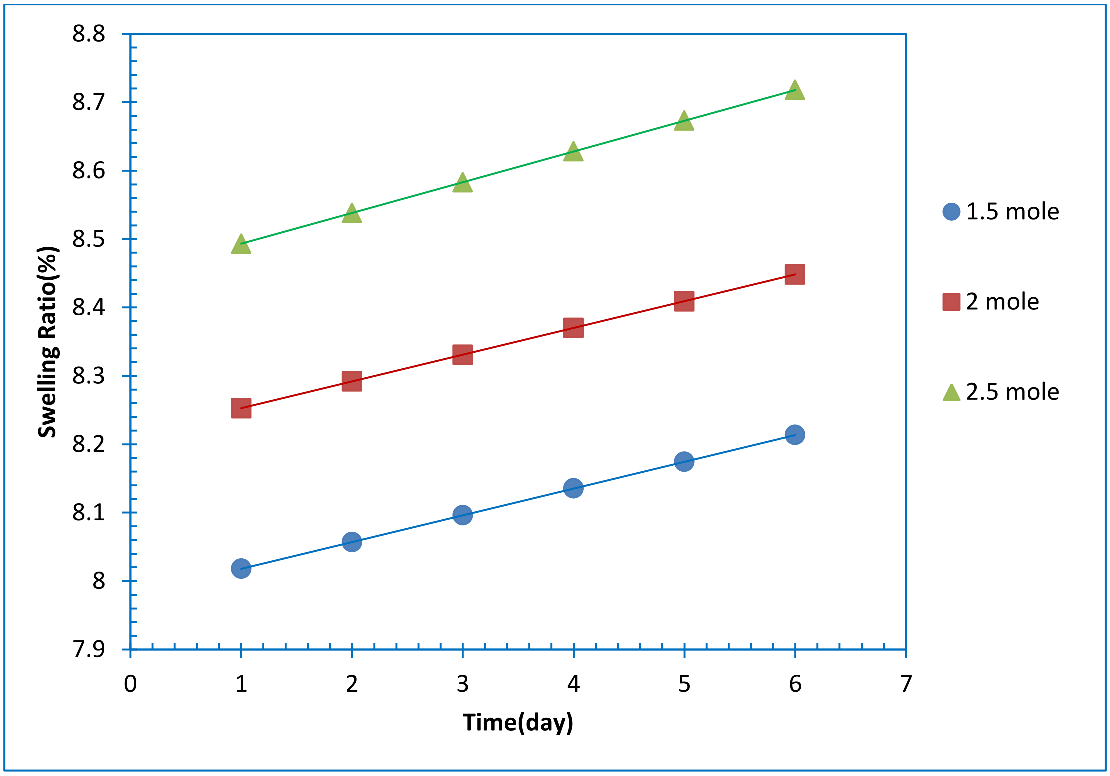


Figure (3-16):Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

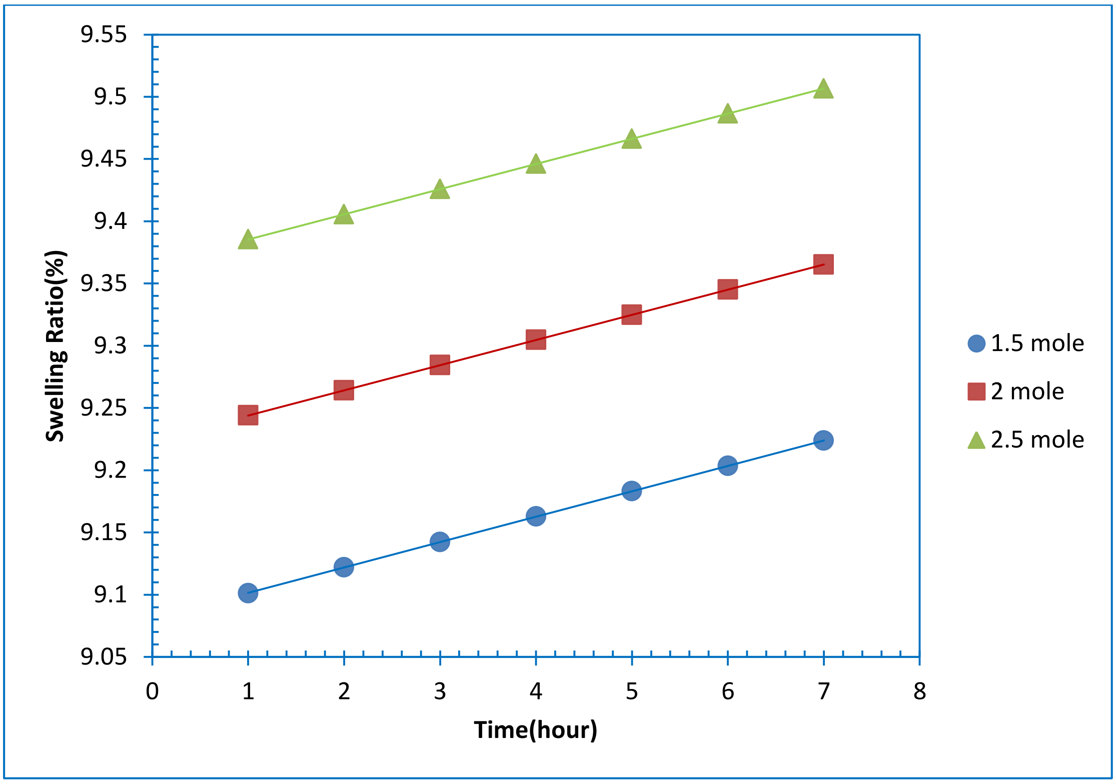


Figure (3-17):Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

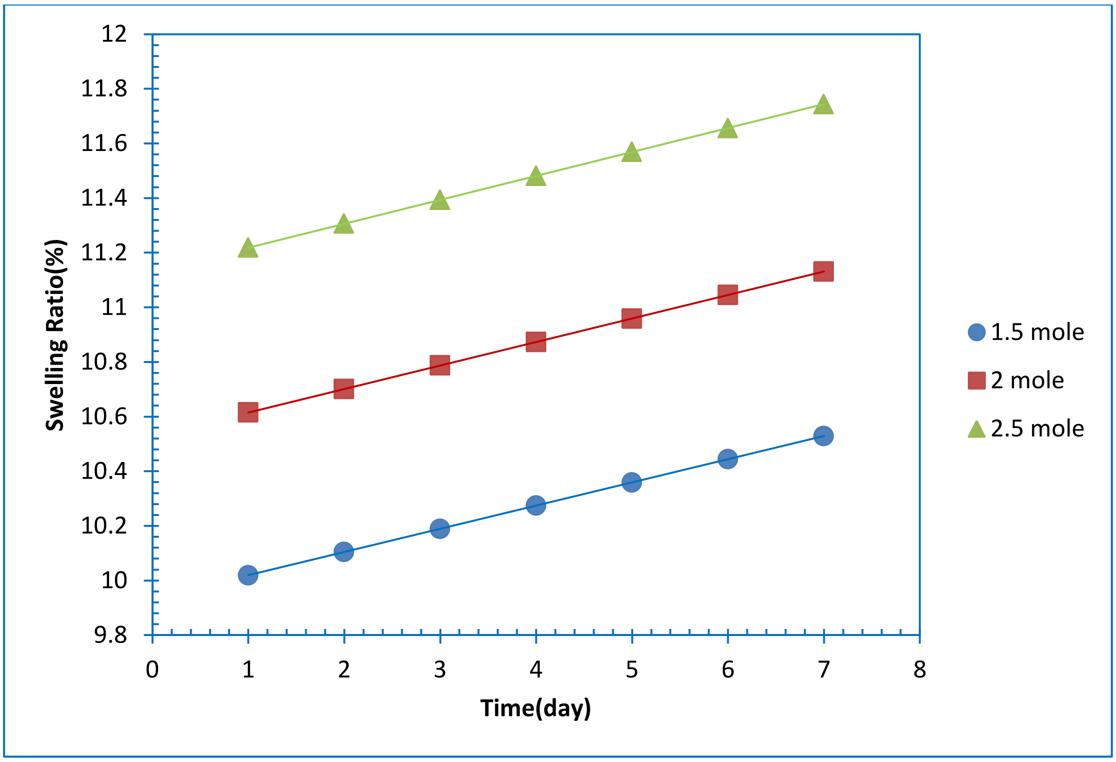


Figure (3-18): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

3.5.2 Solubilization process

Swelling of the graft co-polymers which prepared by solubilization process were measured by using three different pH (2.2, 7.0 and 8.0) respectively.

The method of calculation used was the same as for the swelling in (3.5.1). All the results are presented in tables (3-11) and (3-13) and the results obtained were plotted against temperature in figures (3-18) and (3-23) respectively. The increase of water content (%) with increasing time is an indication of polymeric network's ability to absorb solution significantly hampered due to the presence of cross linking in the hydrogel which depends largely on the surrounding medium acidic, where in the medium of a high pH becomes acidic ionic aggregates more gradually.

It has been observed that the time required for the swelling of the hydrogel increase with the increase in the number of moles of acrylic acid monomer and also has noted that the speed of the swelling of hydrogel increases dramatically in the solution with a high pH (8.0) compared with the solution with a low pH (2.2). For this reason, we found that the solution be further swelled when the pH=8 and that because of the increased hydrophilicity and the resulting increase hydrophilic groups so the hydrogel is because of it is ability to absorb solution in large quantities and gives swelled bigger.

Table (3-11): Swelling ratio (%) in different times, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310K

Time (hour)	Swelling ratio (%)		
	Number of moles acrylic acid monomers		
	1.5 moles	2.0 moles	2.5 moles
1	10.0459	19.6139	24.2050
2	12.2807	20.7439	25.2300
3	14.7242	21.1300	26.2550
4	16.2561	22.1550	27.2800
5	18.8750	23.1800	28.3050
(day)			
1	20.9663	25.0779	30.4717
2	22.5824	27.8120	31.5967
3	24.6787	29.9467	33.6888

Table (3-12): Swelling ratio (%) in different times, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

Time	Swelling ratio (%)		
	Number of moles of acrylic acid monomers		
(hour)	1.5 mole	2.0 mole	2.5 mole
1	17.8532	23.4303	30.0782
2	18.5206	26.2174	31.9392
3	19.6391	27.3431	33.1997
4	20.1065	28.6393	35.7601
5	21.1290	29.7749	36.8160
(day)			
1	19.1385	24.4877	29.6780
2	20.4919	25.6311	30.9519
3	21.7569	26.8490	31.7869
4	22.8969	27.9788	33.8219

Table (3-13): Swelling ratio (%) in different times, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

Time	Swelling ratio (%)		
	Number of moles acrylic acid monomers		
(hour)	1.5 moles	2.0 moles	2.5 moles
1	29.0780	38.5876	43.9414
2	31.7748	40.5203	44.6637
3	32.7826	41.5537	45.8605
4	33.7601	42.5787	46.7676
5	35.6821	43.6037	47.1303
6	36.7420	44.9870	48.3456
7	37.5812	45.2731	49.6302
(day)			
1	44.0756	49.4606	54.9496
2	45.1306	50.5156	56.1049
3	46.1856	51.5706	57.2044
4	47.2406	52.6556	58.3034
5	48.2956	53.7106	59.3884
6	49.3506	54.7956	60.4684
7	50.4056	55.8506	61.5434

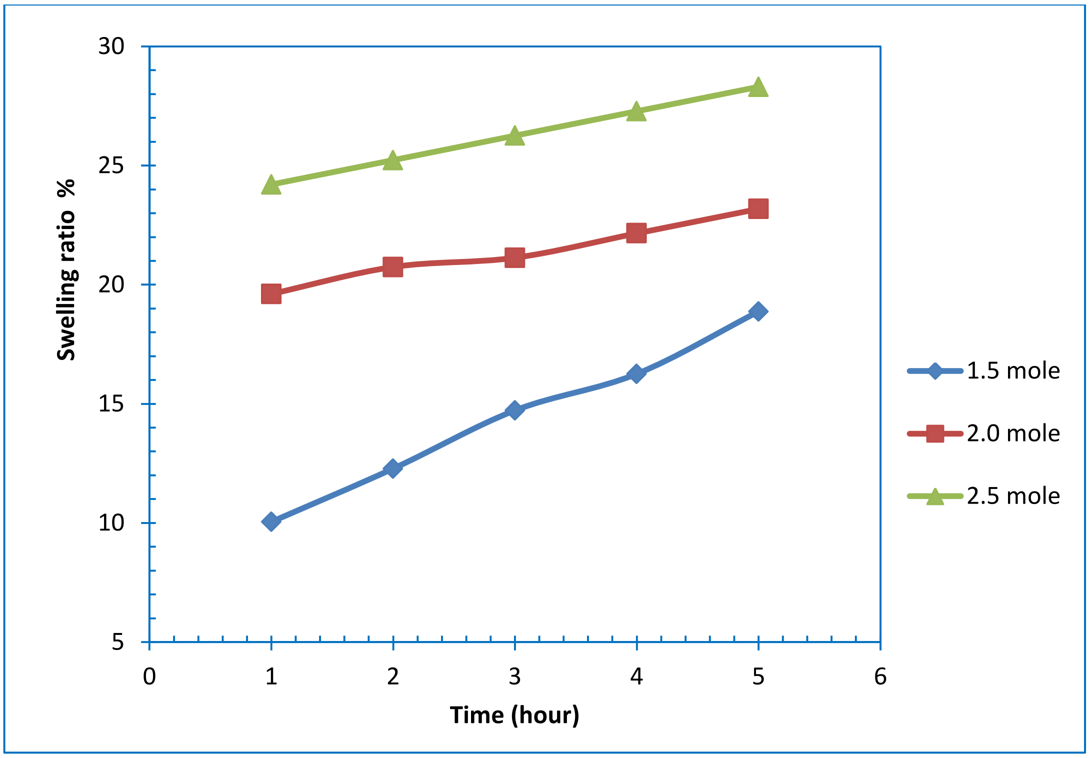


Figure (3-19): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

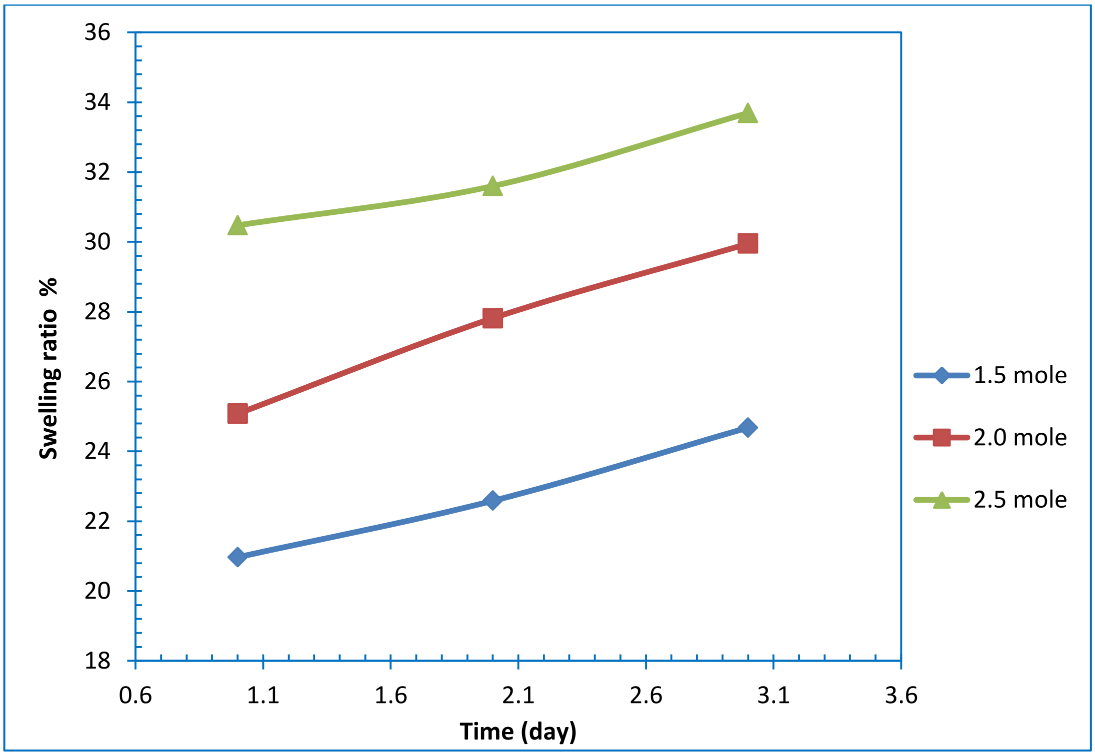


Figure (3-20): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

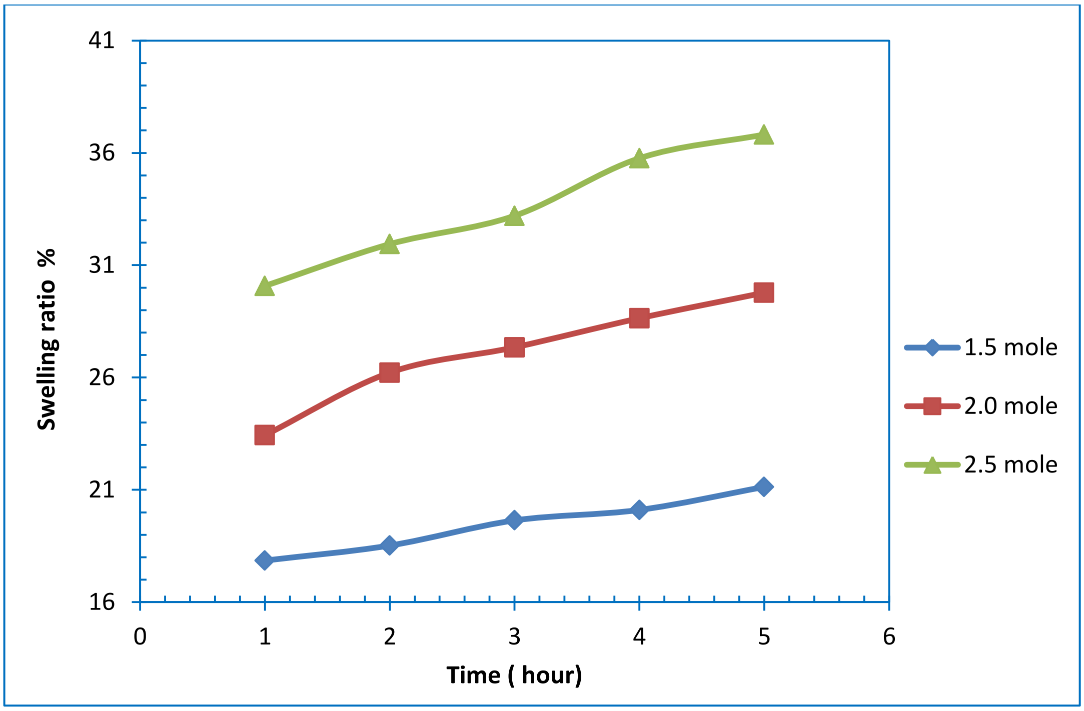


Figure (3-21): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

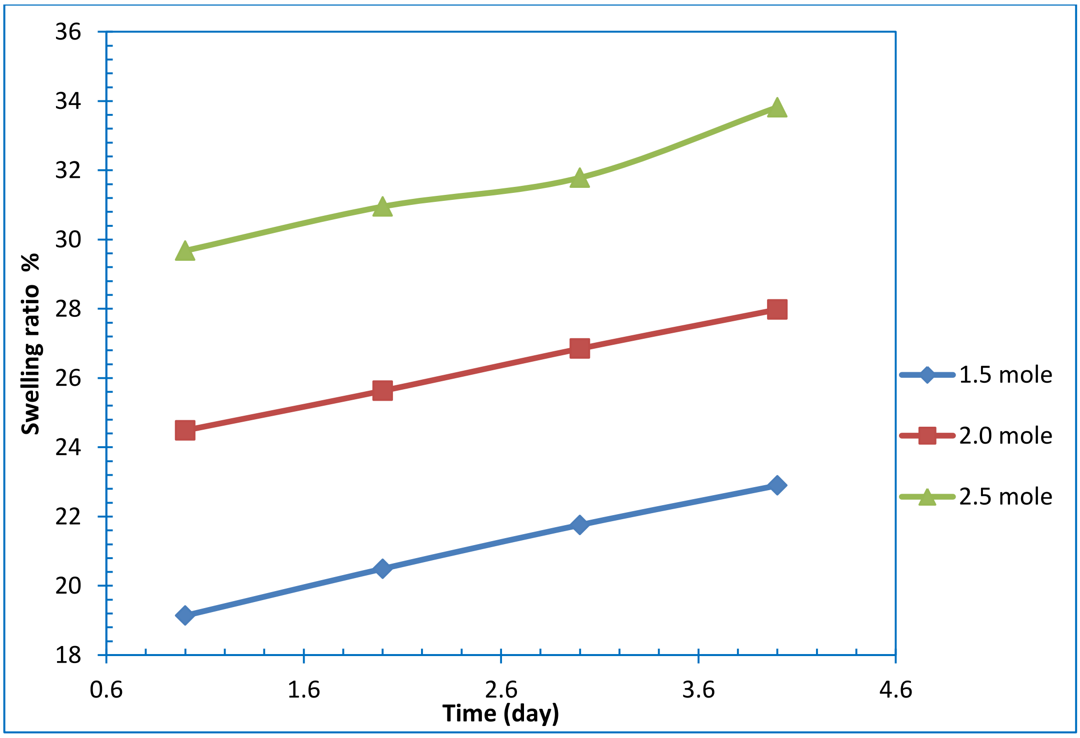


Figure (3-22): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

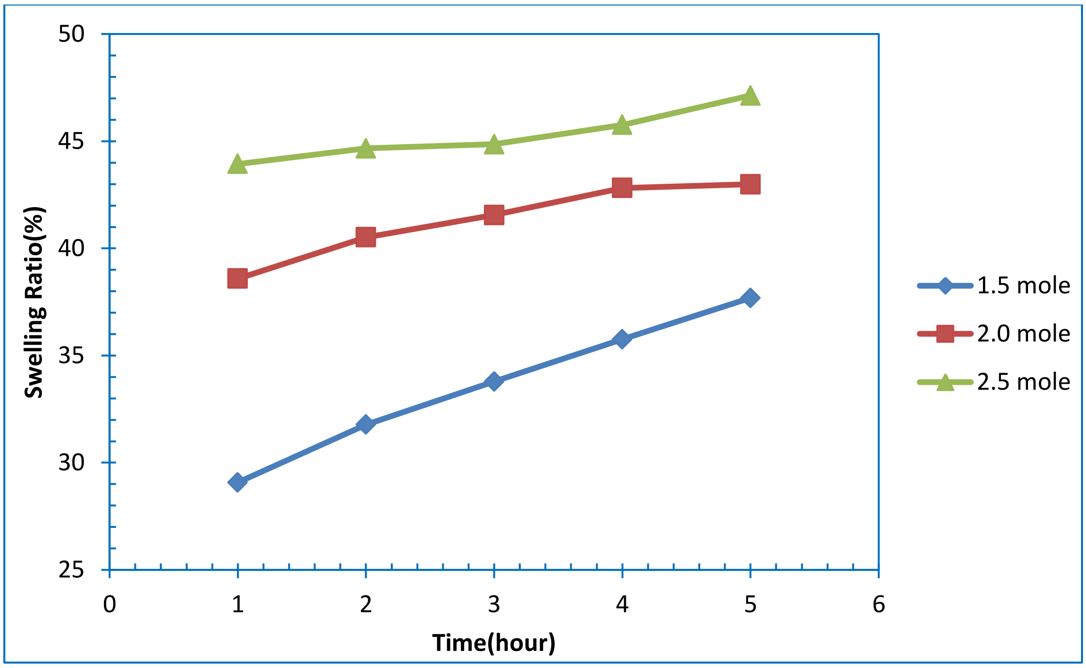


Figure (3-23): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

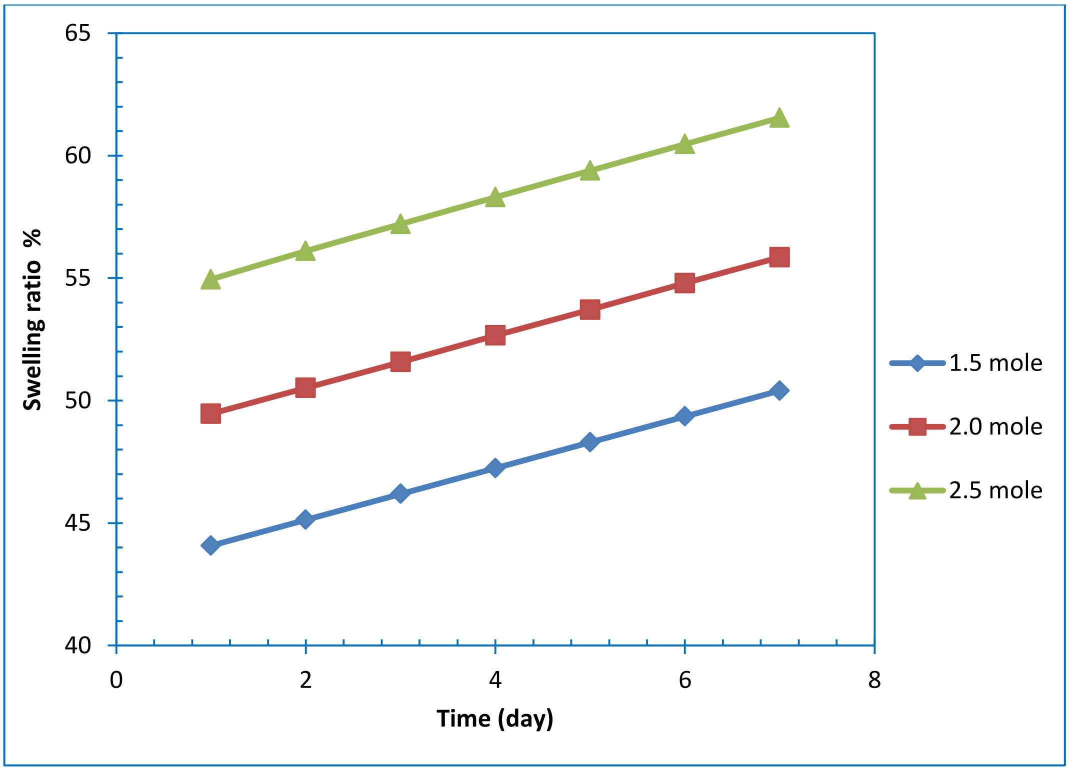


Figure (3-24): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

Conclusion and Future Work

1. Conclusion

Preparation of graft co-polymer by reaction of one mole of glycerol which has three hydroxyl groups, with two moles of terphthalic acid monomer, which have two groups from carboxylic acid. This reaction will give one point of hydroxyl group that can react with fumaric acid to form graft co-polymer which can make cross-linking with the added monomer. When adding three different monomers, we will get three types of graft co- polymers that differ in the number of points of correlation. Thus, they will differ in the number of hydrophilic groups and differ in the swelling ratio.

As clearly shown in the results, the increasing time (hour and day) increases the buffer solution content (%). This behavior can be explained in that compound of solvent and the structure of polymer, i.e., present of the hydrophilic groups in the xerogel, concentration and pH of buffer solution. All these factors will increase the buffer solution content (%) with the increased time. This corresponds with the findings of earlier research and the low values of swelling process were affected by high chain flexibility and the degree of cross linking, i.e., in the graftco-polymer with 0.5 mole of acrylic acids. The values are low comparing with the values in the graft co-polymer with 1.5 mole of acrylic acid monomer [102, 103].

2. Future Work

We can propose the following:

1-Calculate the rate of reaction and the activation energy of the graft co- polymer.

2 - Use of other types of hydroxyl compounds to provide a greater number of points of joint with carboxylic acids.

3 - Use of other types of monomers to form a three-dimensional network

4- Use of polymer joint nanotechnology measurements in medical applications.

Reference

[1]. Patel HB; Patel HL; Shah ZHandModasiya MK.; Am J Pharm Res.; 1: 19-38;(2011)

[2]. Caló E. and Khutoryanskiy V.V.; European Polymer Journal; Vol. 65; pp.252-267;(2015)

[3]. Alge D.L.; Azagarsamy M.A.; Donohue D.F. and Anseth K.S.; Biomacromolecules ; 14; 949-953; (2013)

[4]. Swarbrick J.; Encyclopedia of Pharmaceutics; 4thedition ;Vol .I I ; D-F; 6000 Broken Sound Parkway NW; Suite300; Boca Raton; FL 33487-2742; Taylor & Francis Group; (2013)

[5]. Jeong U. ;Teng X. ;Wang Y.;Yang H. and Xia Y; Adv.Mater.; 19,33;(2007)

[6]. Illum.L; J. Pharm.Sci.; 96(3) ; 473-483; (2007)

[7]. Xiao Cand Yang M.; Carbohydrate Polymers.; 64: 37-40;(2006)

[8]. GhazizadehY;MirzadehH;AmanpourS;Ahmadi H and RabbaniSh; Iran Polym J.;15;821-828; (2006)

[9]. Li L.; Wang Y.; Pan L.; Shi Y.; Cheng W.; Shi Y.; Yu G. ;Nano Lett.; 15 ; 1146–1151;(2015)

[10]. Thakur V.K. and Kessler M.R; Polymer ;69; 369-383; (2015)

[11]. Crescenzi V; Cornelio L; Di MeoC;Nardecchia S and Lamanna R. ;Bio-macromolecules ;8; 1844 - 1855 ; (2007)

[12]. Li Z. and Guan J. ; Expert opinion on drug delivery.; 8: 991-1007; (2011)

[13]. Hoare T.R. and Kohane D.S. ; Polymer; Vol.49;Issue8;1993-2007;(2008)

[14]. Khan, I.U.; Serra , C.A.; Anton , N. and Vandamme, T.;. Int. J. Pharm.; v.441;n.1-2;809-817;(2013)

[15]. Mathot F. et al.; J. Control. Release ;111; p.47–55;(2006)

[16]. Ganji F and Vasheghani-Farahani E.; Iran Polym J.; 18: 63-88;(2009)

[17]. Berger J.; Reist M.; Mayer J.M.; Felt O.; Peppas N.A. and Gurny R.; Eur .J.Pharm. Biopharm.;57;1;(2004)

[18]. Flory P.J. , Principles of polymer chemistry , Cornel University Press , Ithaca; NewYork; P.88;(1953).

[19]. Garima S.; Alka L. and Shiv Sankar B.; J.funda.andpharma. Rese.; 2:35-48;(2014)

[20]. Robinson J. and Lee V.; Controlled Drug Delivery ; Fundamentals and Applications, second edition; New York;52 Vanderbuilt Avenue; Informa Healthcare USA; Inc; (2009)

[21]. Hoffman A.S.; Intelligent Polymers; in: K. Park (Ed.); Controlled Drug Delivery: Challenge and Strategies;Ameri-can Chemical Society; Washington; DC;1997; 485–497

[22]. Bae H.Y; Stimuli-Sensitive Drug Delivery, in: K. Park (Ed.), Controlled Drug Delivery: Challenge and Strategies, Ameri- can Chemical Society, Washington, DC, 1997, 147–160

[23]. Zhu J; Biomaterials.; 31;4639-4656; (2010)

[24]. Masaki T ; Matsuura T ; Ohkawa K ; Miyamura T ; Okazaki l ; Watanabe T and Suzuki T.; The Biochemical Journal.;397(2); 345-53 ;(2006)

[25]. Lutolf MP; Nat Mater . ;8(6); 451–453;(2009)

[26]. Chung HK and Park TG; Nano Today ;4(5);429–437;(2009)

[27]. Oh JK.; Can J Chem.; 88(3) ; 173–184;(2010)

[28]. Tabata Y. ; J. R. Soc .Interf.; 6:S311–24;(2009)

[29]. Ahmed E.M. ; Journal of advanced research; Vol. 6 ; Issue 2;105–121;

(2015)

[30]. Wen Zhao;XingJin;YangCong;Yuying Liu and Jun Fu .; J ChemTechnol Bio. technol;88(3);327-39 ;(2013)

[31]. CovielloT;GrassiM;RamboneG;Alhaique F, A; Biomaterials;22;1899-1909;(2001)

[32]. Garcia Y;CollighanR;Griffin M and Pandit A;J Mater Sci Mater Med;18;1991-2001;(2007)

[33]. IizawaT;TaketaH;MarutaM;IshidoT;GotohTandSakohara S.; Journal of applied polymer science; 104:842-850;(2007)

[34]. AalaieJ;Vasheghani-Farahani E; Semsarzadeh MA and Rahmatpour A.; J MacromolSci;Part B;47;1017-1027 ; (2008)

[35]. Takashi L;Hatsumi T; Makoto M; Takashi I;TakehikoGandShuji S.;. J ApplPolymSci.; 104: 842;(2007)

[36]. Yang L; Chu JSand Fix JA. ;Inte. J.Pharma.; 235;1-15;(2002)

[37]. Shaikh R.P. ;Pillay V. ;Choonara Y.E. ;Toit L.C.;Ndesendo V.M.K. ;BawaP.andCooppan S.; AAPS Pharmscitech.;2(1);441-459; (2010)

[38]. Banerjee S;SiddiquiL;BhattacharyaSS;KaityS;Ghosh A andChattopadhyay P; et al.;Inte.J. biologicalmacromolecules.; 50: 198-206;(2012)

[39]. Lipatov Y.S; Prog. Polym. Sci.; 27: 1721-1801; (2002)

[40]. DeligkarisK;TadeleTS;Olthuis Wand van den Berg A.; Sensors and Actuators B: Chemical.;147:765-774;(2010)

[41]. StenekesRJ;Talsma Hand Hennink WE; Biomaterials; 22, 1891-1898; (2001)

[42]. Hennink W; Van Nostrum CF.;Advanced drug delivery reviews.; 64: 223-236;(2012)

[43]. Ahmed E. M .; . Journal of AdvancedResearch.;14;78-82;(2013)

[44]. De Jong . S; Van Eerdenbrugh , B van; Nostrum C. V; Kettenes-van den. Bosch, J and Hennink. W. ;J.Contro. Rele.;71: 261-275; (2001)

[45]. Siepmann J and Peppas N.; Advanced drug delivery reviews.; 64: 163-174; (2012)

[46] Ganji F; VasheghaniFarahaniSandVasheghaniFarahaniE. ;Iranian Poly.J. ;19: 375-398; (2010)

[47]. Mourya V.;InamdarN;Tiwari. A;. Advanced Materials Letters.; 1: 11-33;(2010)

[48]. Zhang R; Tang M; Bowyer A;Eisenthal Rand Hubble J.; Biomaterials; Volume 26 ;4677–83; (2005)

[49]. Sato A; Choi SW; Hirai M;Yamayoshi A; Moriyama R and YamanoT;etal.; J Control Release.;122:209–316; (2007)

[50]. Das N.; Inte. J. Pharmacy and Pharmaceutical Sci. ; Vol. 5; Issue 3;112-117;(2013)

[51]. Iwai K;Hanasaki K and Yamamoto M.; JLuminescence; 1289: 87-89;(2000)

[52]. Lee J;CuddihyMJandKotov NA.; Tissue Eng Part B.;14(1); 61-68;(2008)

[53]. Chang C;DuanB;CaiJand Zhang L.;EurPolym J.;21:92–100; (2010)

[54]. Bode S.; Bose R.; Matthes S.; Ehrhardt M.; Seifert A.; Schacher F.; Paulus R.; Stumpf S.; Sandmann B . andVitz J.; Polym. Chem. ; 4; 4966–4973; (2013)

[55]. Mukherjee S.; Hill M.R. and Sumerlin B.S.; Soft Matter ; 11; 6152–6161;(2015)

[56]. LimF.and Sun A.M.; Science ;210;908-910;(1980)

[57]. Magnin D.; Lefebvre J.;Chornet E. and Dumitriu S. Carbohydrate Polymers; 55; 437-453;(2004)

[58]. Amiri S. and Rahimi A.; Iran Polym. J. ; 25;pp.559-577; (2016)

[59]. Sung HW; Huang DM ;Chang WH ; Huang RN and Hus JC; J Biomed Mater Res.;46;520-530;(1999)

[60]. WeberLM ;Lopez CG and Anseth KS.; J Biomed Mater Res A;90;720-729; (2009)

[61]. Bryant SJ;Nuttelm an CRandAnseth KS.; J Biomater Sci. Polym. Ed.; 11;439-457; (2000)

[62]. Yin H; Gong C; Shi S; Liu X; Wei YandQian Z.; J Biomed Mater Res B.; 92: 129-137; (2010)

[63]. DankersPYW;Boomker JM; Huizinga-van der Vlag A; Smedts FMM; HarmsenMC;vanLuyn MJA.; MacromolecBiosci; 10(11);1345-54;(2010)

[64]. Peppas N.A. and Merrill E.W.; J. Polym. Sci. A Polym . Chem. ; 14; 441–457;(1976)

[65]. Matanović M.R. ; Kristl J. and Grabnar P.A; Int. J. Pharm. ;472;262–275;(2014)

[66]. Peppas N.A. and Mongia N.K.; Eur. J. Pharm. Biopharm.; 43;51–58;(1997)

[67]. Hamidi M . ; Azadi A. and Refiei P. ; Adv. Drug Deliv. Rev.; 60;1638-1649;(2008)

[68]. CasadeiMA;PitarresiG;CalabreseR;PaolicelliPandGiammona G; Biomacro molecules, 9, 43-49, (2008)

[69]. Schmaljohann D; Adv Drug Delivery Rev; 58; 1655-1670;(2006)

[70]. Chiu HC; Wu ATand Lin YF; Polymer; 42;1471-1479;(2001)

[71]. PeppasN;BuresP;Leobandung Wand Ichikawa H. ;European journal of pharmaceutics and biopharmaceutics; 50;27-46; (2000)

[72]. Peppas NA.; J. bioactive and compatible poly. ; 6: 241-246; (1991)

[73]. Yoo MK; Sung YK; Lee YMand Cho CS.; Polymer;41:5713-5722;(2000)

[74]. Ebara M;YamatoM;HiroseM;Aoyagi T ;Kikuchi A .and Sakai K.;Biomacromolecules.;4;344 -353;(2003)

[75]. Liu SQ; Yang YY;Liu XM and Tong YW.;Biomacromolecules ;4;1784 -1793;(2003)

[76]. Bajpai A.K.; Shukla S.K.; Bhanu S. and Kankane, S .;Prog. Polym. Sci.; 33 ;1088–1118;(2008)

[77]. Guyton A.C. and Hall J.E.; Secretory functions of the alimentary tract. In Textbook of Medical Physiology (Guyton A.C. and Hall J.E. ; eds) ;815–832 ; W.B. Saunders Co.; (1998)

[78]. Deshpande A.A. ;et al.; Drug Dev. Ind . Pharm; 18;1225–1279;(1992)

[79]. Allen L and Ansel HC; Ansel's pharmaceutical dosage forms and drug delivery systems,Tablets in:10 thed.Lippincott Williams and Wilkins; 264-269; (2013).

[80]. Patel V.R. and AmijiM.M. ;Pharm. Res. ;13; 588–593;(1996)

[81]. Nguyen M.K. and Lee D.S. ;Macromol. Biosci.; 10; 563–579;(2010)

[82]. Shim W.S.; Yoo J.S.; Bae Y.H. and Lee D.S.;Biomacromolecules;6; 2930–2934;(2005)

[83]. Huynh D.P.; Nguyen M.K.; KimB.S. and Lee D.S.; Polymer; 50; 2565–2571;(2009)

[84]. Ito A. et al.; Jpn . J. Hosp.Pharm.;20;41-49 ;(1994)

[85]. Zaman M.; RasoolS.;Ali MY.; QureshiJ.;Adnan S.;Hanif M.; Sarfraz RM.;Ijaz H and Mahmood A.; Adv.Polym.Tech.;8;1157-1161 ;(2014)

[86]. Redfarn C.A. & Bedford J. , Experimental Plastics , Inrt-Science Publishers Inc. ,NewYork,P.30 & p. 51,(1960)

[87]. Grainger ST and El-Sayed MEH.; Stimuli-sensitive particles for drug

delivery biologically-responsive hybrid biomaterials: a reference for material scientists and bioengineers. World Scientific Publishing Co. Pte. Ltd., Danvers; 171-189; (2010)

[88]. Gil E.S. and Hudson S.M.; Prog. Polym. Sci.; 29(12):1173-1222;(2004)

[89]. P eppas N . A . ; Hilt J . Z . ; KhademhosseiniA.and Langer R. ;. Adv. Mater; v.18; n.11;1345-1360; (2006)

[90]. EntezamiA.A.andMassoumi B.; Iranian Polym. J.; vol.15; no.1;13-30;(2006)

[91]. De S.K ;Aluru N. ; Johnson B. ; Crone W. ; Beebe D.J .and Moore J. ; J.Microelectromech. Syst. ; 11; 544–555;(2002)

[92]. R. Silverstein, F. Webster and D. Kiemle; Spectrometric Identification of Organic Compounds; John-Wiley & Sons; 7th Ed.; 117; New York; (2005).

[93]. Pavia L., Lampman L., Kris S. &Vyvyan R.; Introduction to Spectrophotometer; 4 th Ed, (2009)

[94]. Dong L. and Jiang H.; Soft Matter;3;1223-1230;(2007)

[95]. Mukherjee S.; Hill M.R. and Sumerlin B.S.; Soft Matter ; 11; 6152–6161;(2015)

[96]. Deng G.; Li, F.; Yu, H.; Liu, F.; Liu, C.; Sun W.; Jiang H. and Chen Y.; ACS Macro Lett.; 1; 275–279; (2012)

[97]. Tuncaboylu D. C.; Sahin M.; Argun A.; Oppermann W. and Okay O.; Macromolecules; 45;1991; (2012)

[98]. Phadke A.; Zhang C.; Arman B.; Hsu C.-C.; Mashelkar A. ;Lele A. K.; Tauber M. J.; Arya G. and Varghese S.; Proc. Natl. Acad. Sci.; U.S.A. ; 109; 4383; (2012)

[99]. Hao X.; Liu H.; Lu Z.; Xie Y. and Yang H.; J. Mater. Chem. A.1;6920;

(2013)

[100]. Hufdi R. Z.; Abdulla N.N. and AL-Baiati M.N.; MSc. Thesis; University of Babylon; 32; (2016).

[101]. Ding R.; Yu X.; Wang P.; Zhang J.; Zhou Y.; Cao X.; Tang H.; Ayres N. and Zhang P.; RSC Adv.; 6 ; 20392–20398; (2016)

[102]. Zahraa M. & M. N. AL-Baiati;J. Global Pharma. Tech.; 12(9):50-56; (2017)

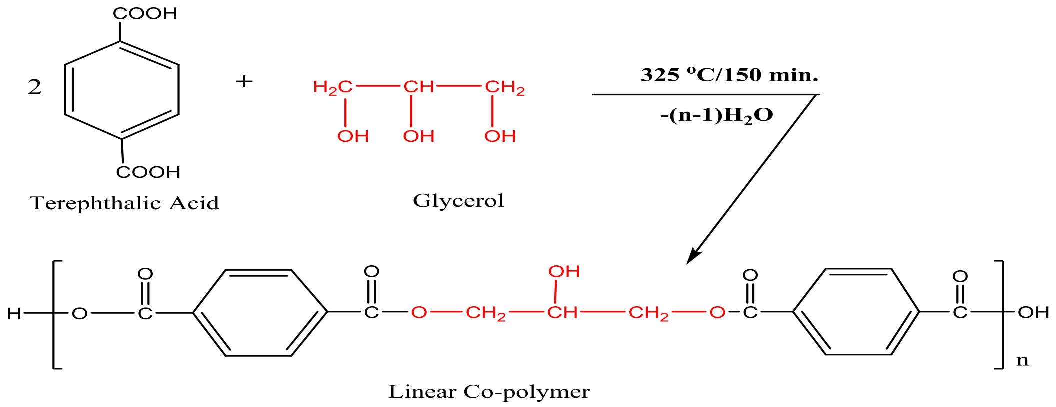
[103]. ZahraaMushtaqAbd Al-Aama& M. N. AL-Baiati; J. Pharm. Sci. & Res.; Vol. 10(4); 723-732; (2018)

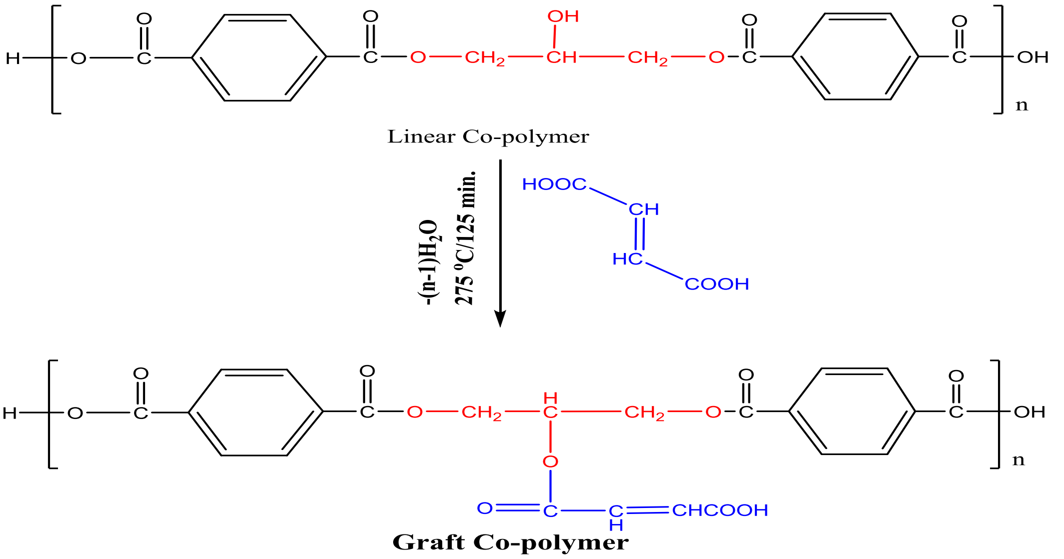
الخلاصة

في هذا العمل ، تم تحضير البوليمر المشترك المطعم ، بطريقتين (الانصهار و الإذابة) من تفاعل مول واحد من الكليسرول مع مولين من حامض الترفثاليك ، لتكوين البوليمر المشترك الخطي و البوليمر المشترك المطعم حضر من تفاعل البوليمر المشترك الخطي مع نصف مول من حامض الفيوماريك،

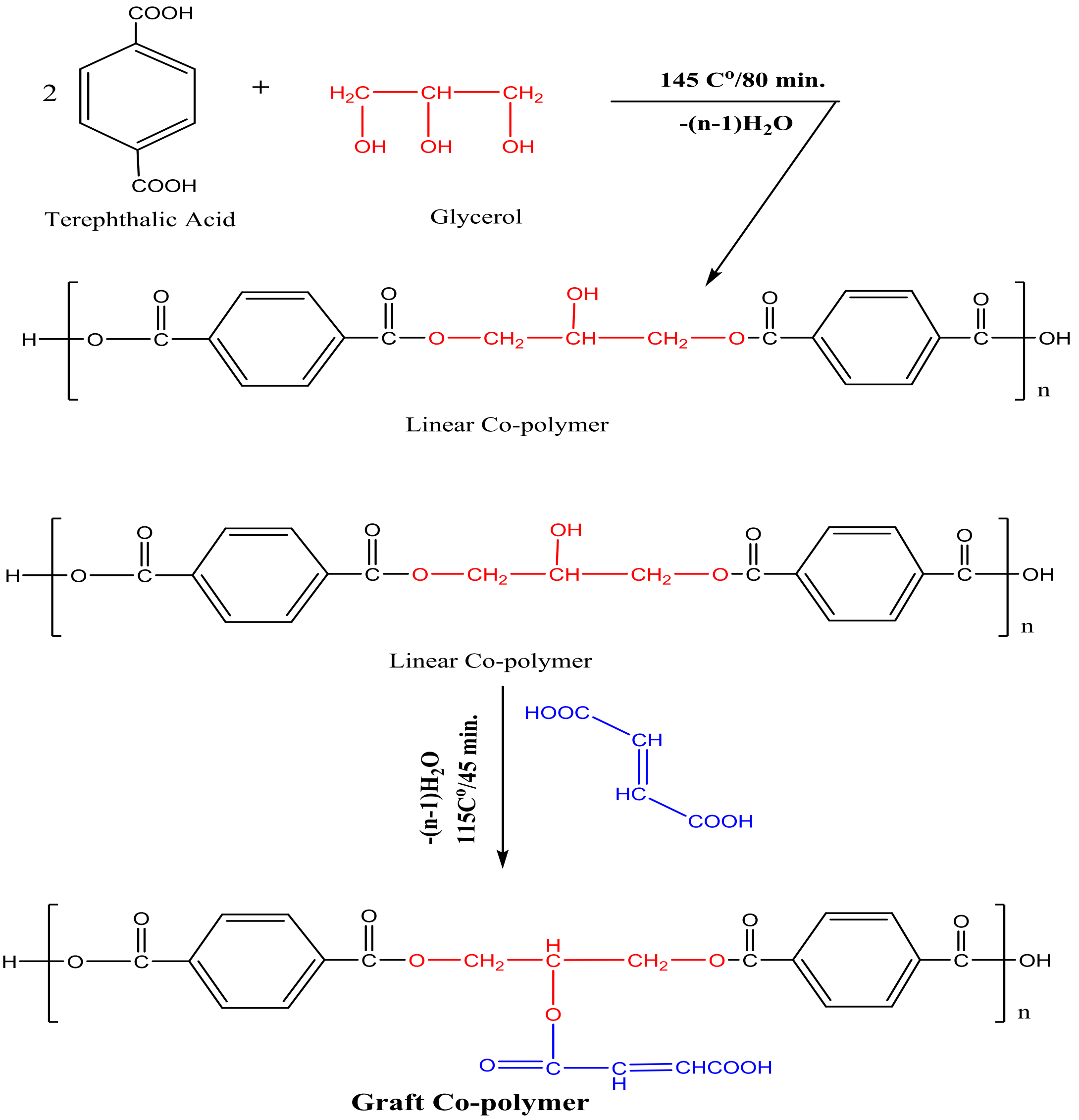
أولا: طريقة الانصهار

البوليمر المشترك الخطي في 150 Min. عند 325 C̊ و البوليمر المشترك المطعم عند 275C̊ و 125 Min. ، كما نلاحظ في المعادلات التالية، تم تشخيص الناتج بواسطة تقنية الأشعة ما تحت الحمراء و الرنين النووي المغناطيسي البروتوني .





ثانيا: طريقة الإذابة ، البوليمر المشترك الخطي حضر عند 80 min. و $145\ C^o$ اما المطعم فقد حضر في $115\ C^o$ و 45 Min. ، كما نلاحظ في المعادلات ادناه . تم اجراء الفحص بمجهر القوة الذرية (AFM) للجزيئات الناتجة من طريقة الإذابة ، و أظهر الفحص ان الجزيئات نانوية وان شدة الصلابة لسطح البوليمر المشترك الخطي مساوية الى 1.19 nm والجذر التربيعي المربع يساوي 1.37 nm وحجم الجزيئة النانوية البوليمر المشترك الخطي 94.09 nm ، اما شدة الصلابة لسطح البوليمر المشترك المطعم فكانت 1.68 nm والجذر التربيعي المربع يساوي 1.96 nm وحجم الجزيئة النانوية البوليمر المشترك المطعم 56.80nm



تم حساب سرعة البلمرة وطاقة التنشيط للبوليمر المشترك الخطي حيث وجد انه مساوي الى $120\ Sec.^{-1}$ و 242.3531 J/mole على التوالي.

تم حساب الدوال الثرموداينمك للبوليمر المشترك الخطي بدرجات حرارية مختلفة و كما موضح في الجداول أدناه:

no	**T (K^{0})**	**1/T**	**lnK**	**ΔH (KJ/mol)**	**ΔG (KJ/mol)**	**ΔS (KJ/molK)**
1	563	1.776×10^{-3}	-0.1003	2.9×10^{3}	0.469	5.150
2	568	1.7605×10^{-3}	-9.2992		43.914	5.097
3	573	1.7452×10^{-3}	-10.733		51.131	4.971
4	878	1.7301×10^{-3}	-15.232		73.197	4.890
5	583	1.7152×10^{-3}	-24.063		116.634	4.774

تم قياس نسبة الانتفاخية لكل نماذج hydrogel في ثلاثة دوال حامضية مختلفة (pH=7.0) (pH=2.2) و (pH=8.0) بثبات درجة الحرارة 310K كدالة للزمن ، وقد أظهرت النتائج التي تم الحصول عليها ان نسبة الانتفاخية في الوسط القاعدي اعلى من نسبتها في الوسط الحامضي و هذا يؤكد على ان البوليمر المشترك المطعم في الوسط القاعدي يكون انتقائيا في سلوكه ، في المقابل فأن نسبة الانتفاخية للبوليمر المشترك المطعم و المحضر بطريقة الاذابة اعلى من نسبتها للبوليمر المشترك المطعم المحضر بطريقة الانصهار .