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Synthesis a novel nano graft co-polymer and studying the swelling behaviors using different molar ratios of acrylic acid monomer

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Keyword: nanoparticle, nanoparticle polymer; nanoparticle co-polymer; solubilization process; , Interpenetrating polymer network, Swelling, Swelling of polymer, Swelling of nanoparticle, Swelling of co-polymer, Swelling of nanoparticle co-polymer.

Abstract

In this work, the nanoparticle graft co-polymer was prepared, by using glycerol as material containing the three alcoholic groups, and that reacted with terphthalic acid which have two carboxylic group as a first step, and then added 0.5 mole of fumaric acid to prepared graft co-polymer, as a second step by solubilization process. The acrylic acid monomer was added to the nano graft co-polymer in different number of moles (1.5, 2.0 & 2.5 mole). The swelling ratio measurements of the graft co-polymer, in three different buffer solution (2.2, 7.0 and 8.0), in the constant temperature at 310 K. The results showed that the increases of number of the moles of the acrylic acid monomer, Leads to increase of swelling ratio.

Introduction

Copolymerization is the joint polymerization of two or more monomer species. High–molecular mass compounds obtained by copolymerization are called copolymers [1] . The molecular chain of a copolymer is composed of different units, in accordance with the number of initial monomers [2]. If the reactants of a polycondensation have several different monomers, the result will be a copolymer [3]. The reaction of co-polycondensation has acquired great technical importance in recent years and is now widely used for the synthesis of various mixed polyesters and polyamides (e.g. containing ester and amide bonds simultaneously) and other copolymers. For instance co-polycondensation of hexamethylenediamine, adipic acid and terephthalic acid [4]; Polymers may be classified as hydrophobic or hydrophilic, according to whether or not they dissolve or swell in water. The polymers which contain hydrophobic groups (e.g. C_2H_5) are water insoluble. The polymers which contain a hydrophilic group (e.g. OH), are water soluble, in the case of linear polymers or swellable in the case of cross linked polymers. In other words, the hydrogel can be defined as a polymeric material which will swell in solvent and it contains a significant fraction of water (usually more than 20%) within its structure. The term xerogel is given to the polymer network alone (dry state) **[5]**, thus:

Xerogel + Water → Hydrogel

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Hydrogels, are a coherent system rich in water; they are made up of two principal components; a constant solid component consisting of a polymer network, and a variable liquid component, either water or an aqueous solution. The aqueous component can undergo exchange with the environment by diffusion or evaporation [6, 7]. For getting materials combining biocompatibility with a good mechanical strength, two methods are used [8,9]: Copolymerization of hydrophilic monomers with hydrophobic monomers or with cross-linking agent or grafting of hydrophilic monomers on stronger polymer supports [10, 11, 12] .

Experimental

1. Chemicals

All chemicals were used in this work analytical grade, imported from different companies.

2. Preparation of nano graft co-polymer [13, 14]

The first step; In a 200 ml two-necked round bottom flask, (2.0 mole, 332gm) of terphthalic acid and (50 ml) of DMSO, were mixed together, this flask was equipped with a thermometer. The mixture warmed carefully with a hot plate magnetic stirrer to 40 ^{o}C until clear liquor is formed and added (1.0 mole, 92gm) of glycerol to the solution. The mixture warmed carefully to 120 ^{o}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 esterification 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 50 ^{o}C. **The second step**; About (0.5mole, 58gm) of fumaric acid, was dissolved in 10 ml of DMSO at 40 ^{o}C, and added to the mixture (which prepared in the first step 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 prepared of nano 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 gm.) 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, 0.147gm) of hydroquinone was added to the reactants with stirred by mechanical stirrer.

3. Preparation of polymeric specimens

The specimens of polymeric material containing different number of moles of the acrylic acid monomer were prepared by using Methylethylketone peroxide (MEKP) as a hardener and cutting as a disc in dimensions (thickness=3mm & diameter=10mm) and the weighted of the xerogel discs was exactly 0.4 gm of all specimens were used in the swelling study.

4. Swelling

The known weight and diameter of dried discs (Xerogel) were put in sample vials. The swelling time was counted when the solvent was added into the sample vials [10, 11]. The buffer solution contents of the hydrogels were calculated according to the following equations [15]:

Buffer solution % = (Wt. of hydrogel - Wt. of xerogel / Wt. of hydrogel) × 100

Results and Discussion

1. Preparation of graft co-polymer

The first step; Figure (1), represent the FT–IR spectrum of the linear co-polymer, showed the appearance of a strong broad band at about 3423 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^2hybridization absorption at about 2544 cm^{-1}, 2654 cm^{-1}respectively, and the spectrum also showed a strong band at about1726 cm^{-1} assigned to a stretching band C=O for ester group. The spectrum appearance a weak sharp bands at about 1597cm^{-1},1581cm^{-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 [18] . Figure (2), The spectrum of ^{1}HNMR showed, which explain the singlet signal at 13.24 ppm characteristic ofproton 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 dueto the proton of aliphatic alcohol so this spectrum was confirmed the structure of our target polymer [19].

The second step; Figure(3), showed the FT – IR spectrum of the graft co-polymer, it's showed the appearance of a strong broad band at 3500 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 2880 cm^{-1} , 3140 cm^{-1} and 3050 cm^{-1} respectively, and the spectrum also showed a strong sharp band at 1740 cm^{-1} and 1250 cm^{-1} for a stretching band C=O ester and C-O ester respectively. Figure (4), The spectrum of ^{1}HNMR, its showed the appearance a 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.

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-polymers are nanoparticles co-polymers, as shown below:

Figure (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 observe in Figure (5 a). Table (1), 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 (6), represent the distribution of the different proportions of particle sizes of the linear co-polymer nanoparticle. On the other hand, figure (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 square 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 observe in Figure (7 a). Table (2) represents the total rate 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 56.80 nm and figure (8) represent the distribution of the different proportions of particle sizes of the graft co-polymer nanoparticle.

3. Measured of swelling

The swelling curves of graft co-polymer showed a plot of buffer solution content for different compositions against swelling time (hour and day). 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 buffer solution–soluble molecules were being released from the xerogel upon swelling. [14].

A plot of buffer solution content versus time showed hydration curves of graft co-polymer for three different numbers of moles from acrylic acid compositions ranging from 1.5, 2.0 and 2.5 mole, against swelling time at constant temperatures, as shown in Tables (3) to (5) and Figures (9) to (14) respectively.

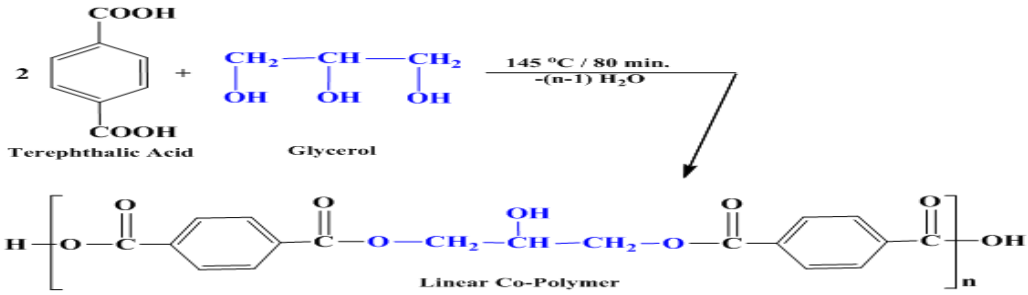
As clearly shown in these figures increasing the time with increases of the buffer solution content (%), this behavior can be explained due to, the pH of buffer solution and the structure of polymer, i.e., present of the hydrophilic groups in the xerogel, concentration and nature of the pH of buffer solution. All these factors will increase the buffer solution content (%) with the increased of time [14]. The low values of swelling process were affected by High chain flexibility and the degree of cross linking, i.e., in the graft co-polymer with 1.5 mole of acrylic acid, the values will be low comparing with the values in the graft co-polymer with 2.5 mole of acrylic acids.

Conclusions

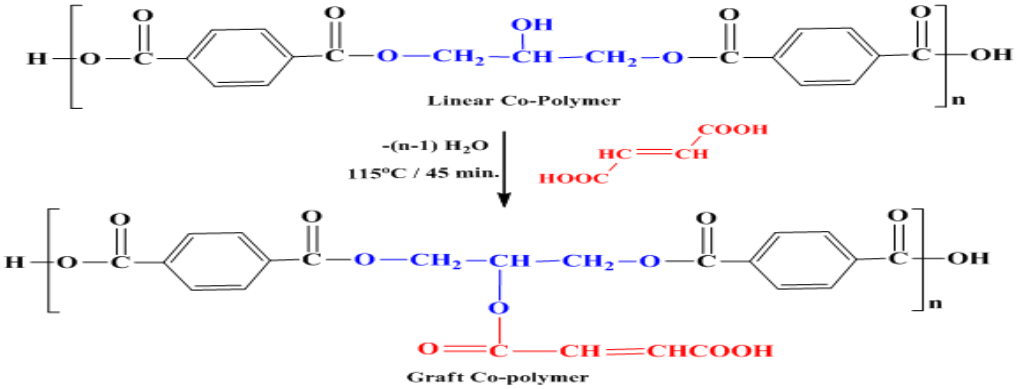
Increasing of the number of moles of the acrylic acid monomer due to, increases the hydroxyl content ratio of the product co-polymer, and thus leads to increases the swelling graft co-polymer, and the results also showed that the effect of the pH of buffer solution on swelling.

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Equation (1): Reaction of step 1



Equation (2): Reaction of step 2

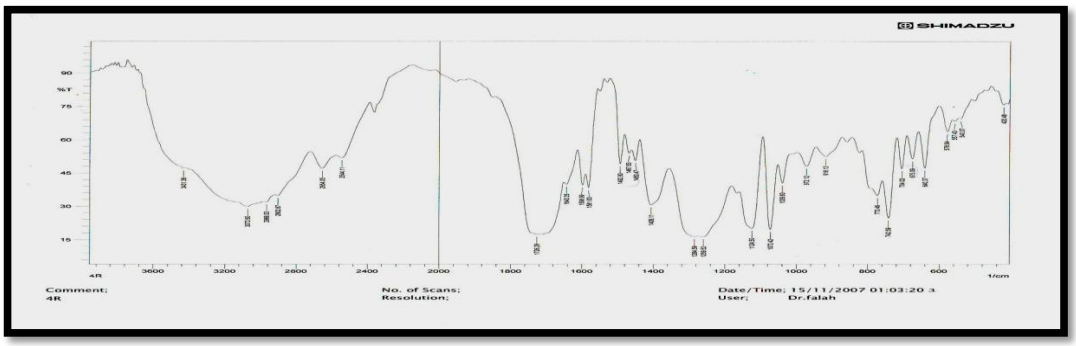


Figure (1): The FT-IR spectrum of linear co-polymer

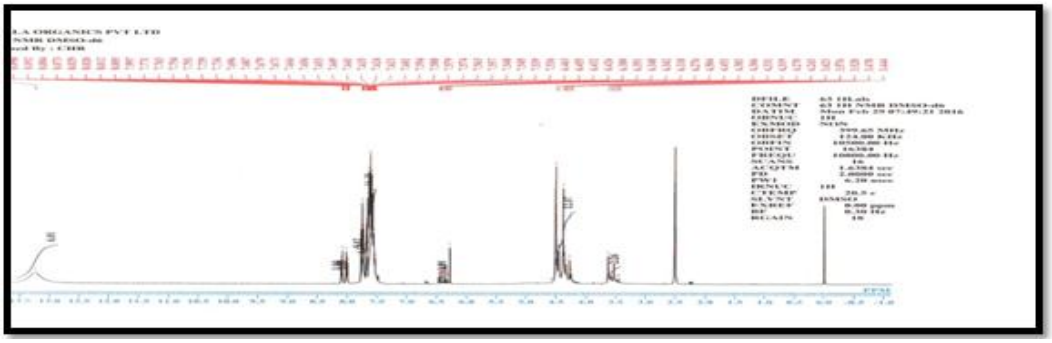


Figure (2): The ^{1}HNMR spectrum of linear co-polymer

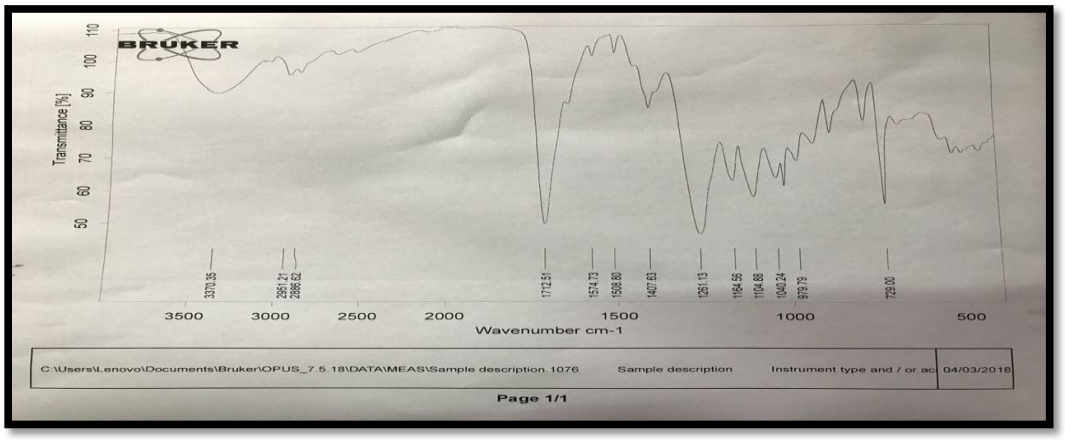


Figure (3): The FT-IR spectrum of graft co-polymer

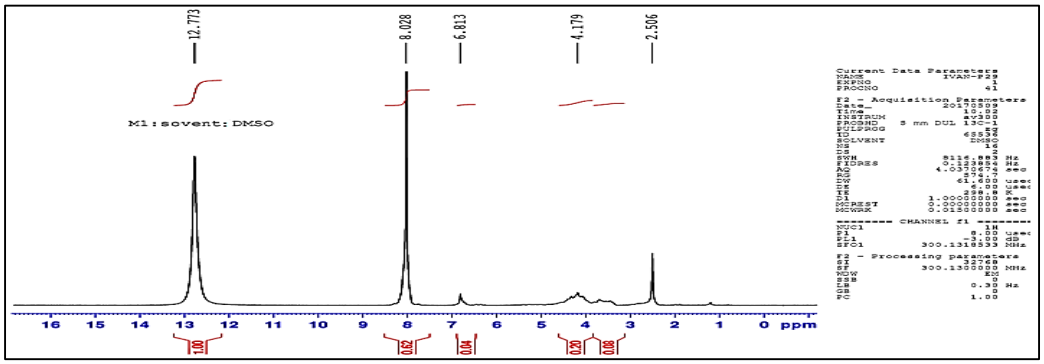


Figure (4): The ^{1}HNMR spectrum of graft co-polymer

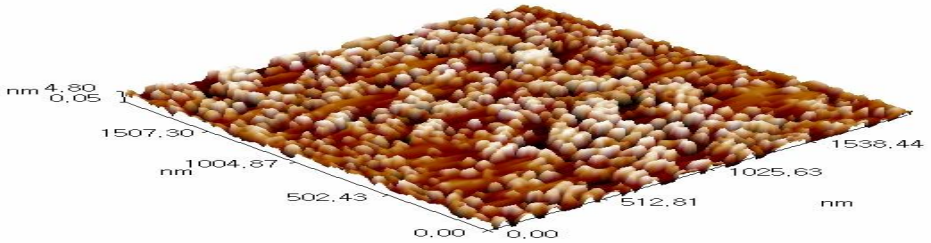


Figure (5 a): Image of Atomic Force Microscope for linear co-polymer shows 3D Image.

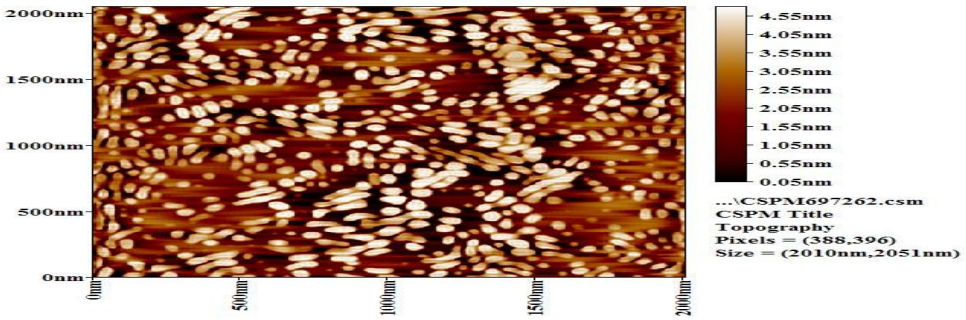


Figure (5 b): Image of Atomic Force Microscope for linear co-polymer shows 2D Image.

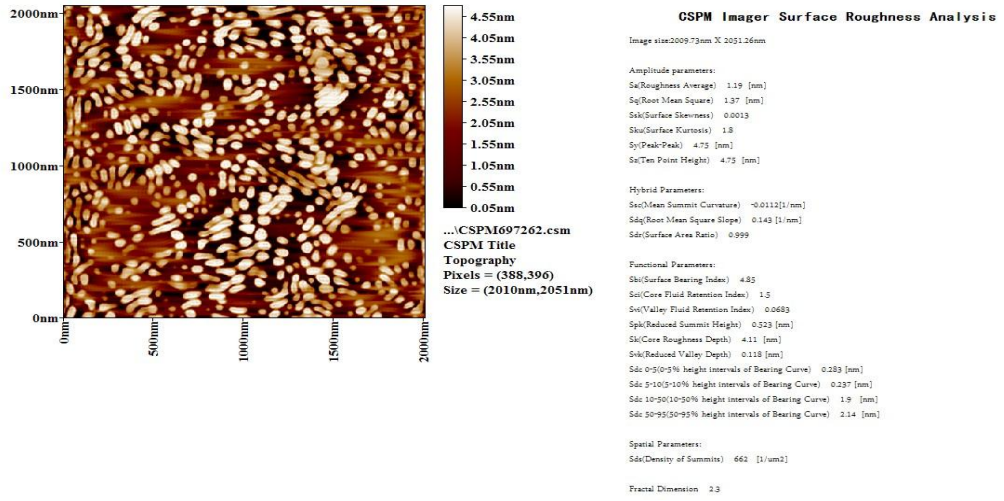


Figure (5 c): Image of Atomic Force Microscope for linear co-polymer shows 2D Image and showing all details of particles

Table (1): The total rate 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			

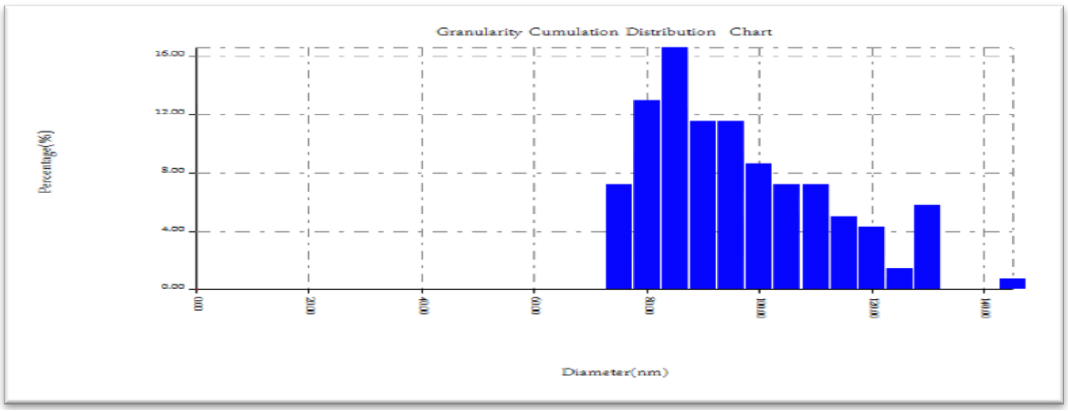


Figure (6) Distribution of the different proportions of particle sizes of the linear co-polymer nanoparticle.

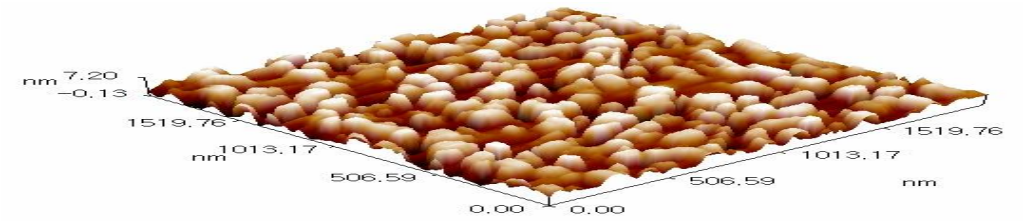


Figure (7 a): Image of Atomic Force Microscope for graft co-polymer shows 3D Image.

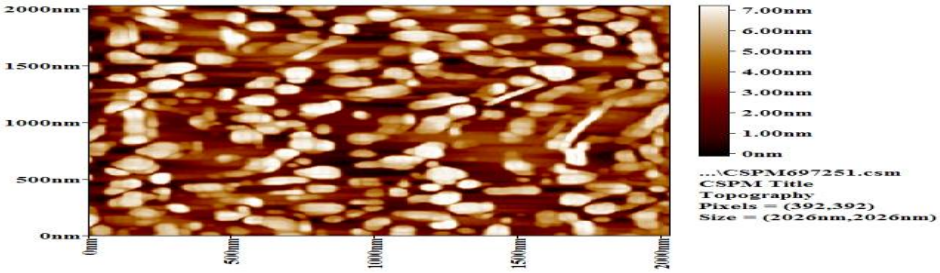


Figure (7 b): Image of Atomic Force Microscope for graft co-polymer shows 2D Image.

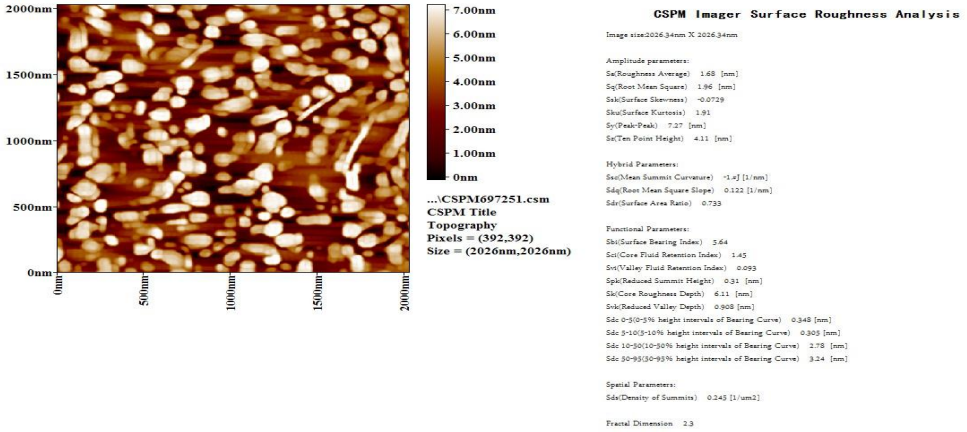


Figure (7 c): Image of Atomic Force Microscope for graft co-polymer shows 2D Image and showing all details of particles

Table (2): The total rate of the particle sizes of the graft co-polymer nanoparticle and the different proportions of these volumes

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

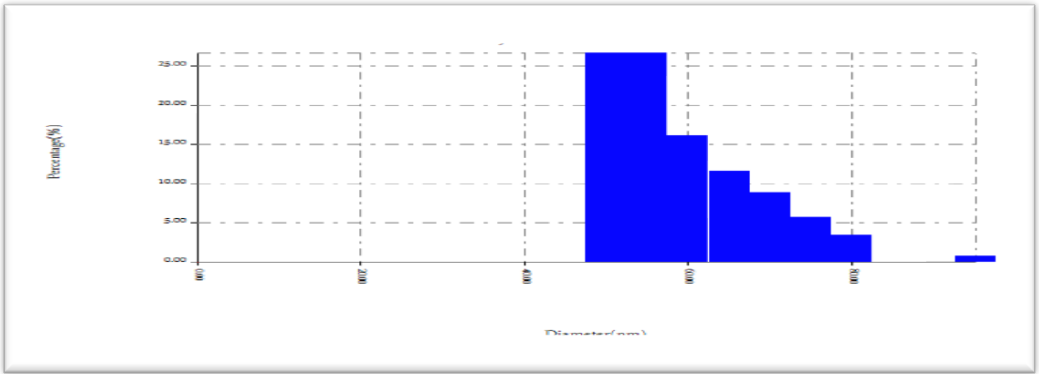


Figure (8): Distribution of the different proportions of particle sizes of the graft co-polymer nanoparticle.

Table (3): Swelling ratio (%) in different time, 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	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	15.9663	22.0779	25.4717
2	17.5824	23.8120	26.5967
3	19.6787	24.9467	26.6888

Table (4): Swelling ratio (%) in different time, 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	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 (5): Swelling ratio (%) in different time, of 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	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

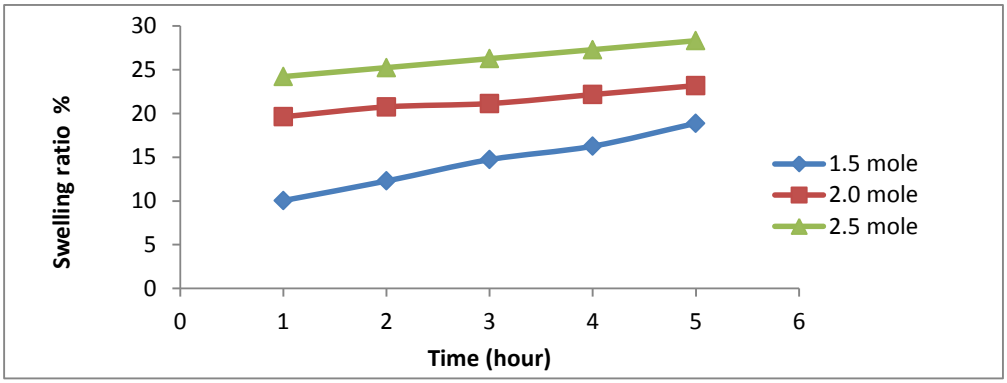


Figure (9): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

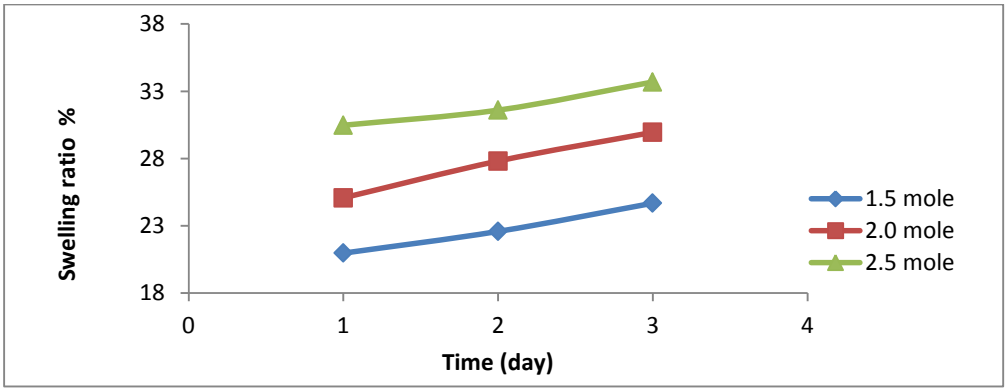


Figure (10): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

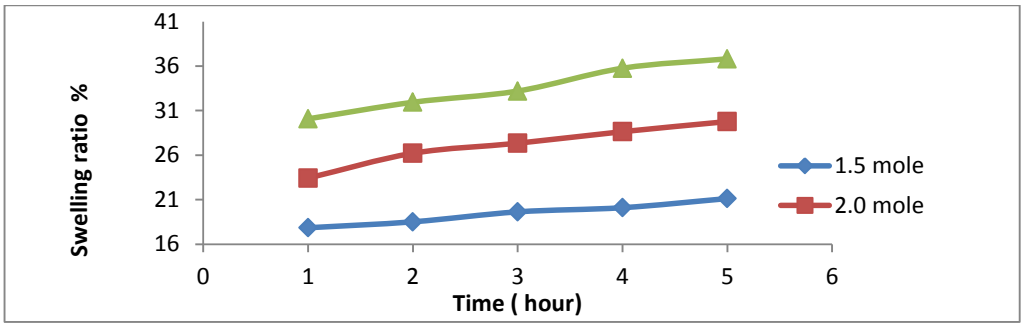


Figure (11): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

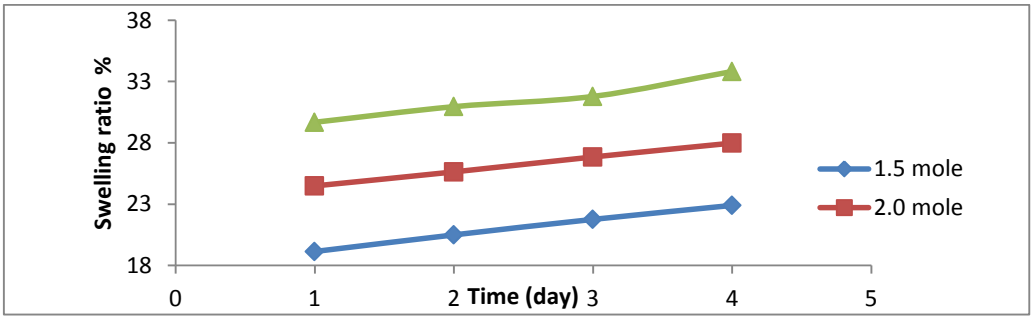


Figure (12): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

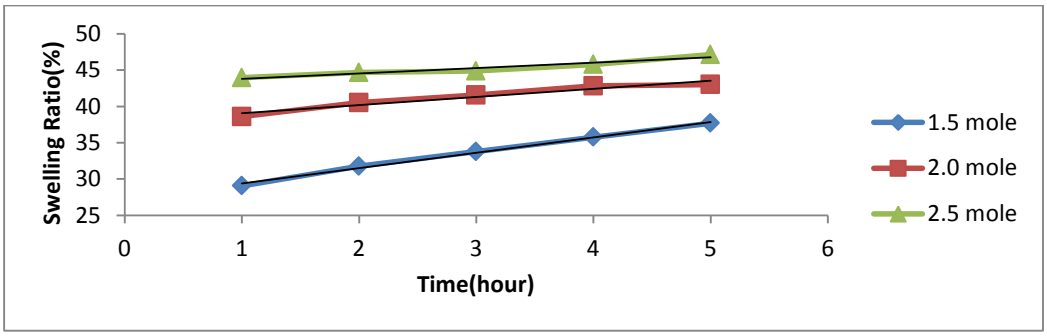


Figure (13): Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

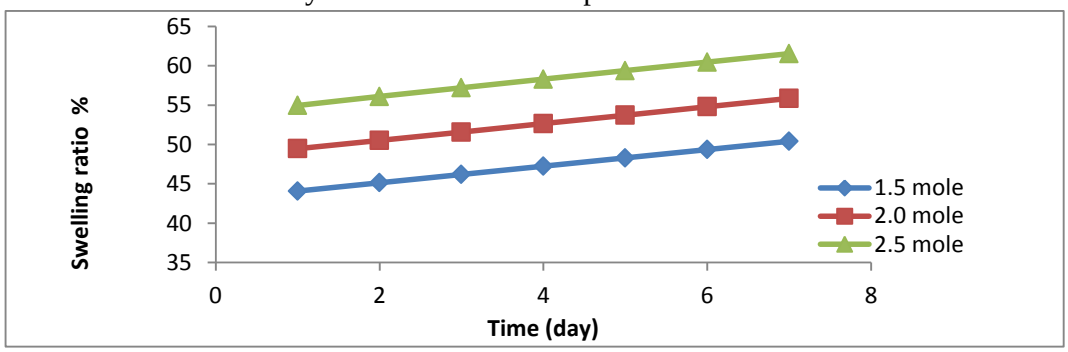


Figure (14): Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K