Modification of poly maleic anhydride by addition of different aldo mono saccharides

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Abstract

This research includes new series of polymers were synthesized starting from polymerization of poly maleic anhydride (3), which were mono esterfication with absolute methanol to give polymer (4), then the acid side chlorination with thionyl chloride to give polymer (5) , which was subjected to esterfication with two different protected sugar moiety (1 and 2) to afford modified polymers (6 and 7). Furthermore the hydrazide polymers (8 and 9) were prepared through addition of hydrazine hydrate to polymers (6 and 7), which upon condensation with different free mono saccharides to give the target polymers(10-13) respectively. The prepared polymers identified by physical properties and spectral methods (FT-IR ,^{1}H-NMR,^{13}C-NMR) .

Keyword :. poly maleic anhydride, galactose , glucose

تحوير بولي انهدريد الماليك باضافة سكريات الدهايديه احاديه مختلفه

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الخلاصة:

يتضمن البحث تحضير سلسله جديده من المركبات البوليمريه تبدا من بلمرة بولي انهدريد الماليك (3) ومن ثم مفاعلته مع الميثانول المطلق للحصول على البولي استر (4) والذي بعد مفاعلته مع كلوريد الثايونيل اعطى البوليمر (5) ، وعند مفاعلته مع نوعين من السكريات المحميه المختلفه (1و2) تم الحصول على نوعين من البوليمرات المحوره (6و7) بالاضافه الى ذلك ومن خلال اضافة الهيدرازين المائي 90% الى (6و7) تم الحصول على البوليمرات (8و9) التي تم تكثيفها مع سكريات احاديه مختلف ه للحصول على البوليمرات النهائيه(10−13) على التوالي . تم تشخيص بعض ا لبوليمرات المحضرة بواسطة الخواص الفيزياؤيه والطرق الطيفيه (FT−IR, ^{1}H−NMR,^{13}C−NMR) .

Introduction

It has been demonstrated that maleic anhydride (MAH) readily undergoes polymerization in the presence of free radical catalysts as well as under gamma and UV radiations [1-3] .The homo polymerization of maleic anhydride is expected to be an important reactive polymer from the structural standpoint that the main chain may have a regular arrangement of anhydride Rings . A series of functionalized polymers can be prepared from poly (MAH) under mild reaction conditions[4-6] . Maleic anhydride (MA) is a multifunctional chemical intermediates that find

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applications in nearly every field of industrial chemistry [7]. It contains two acid carbonyl groups and a double bond in α , β position[8] . Carbohydrates are poly functional compounds having several hydroxyls often in combination with other functionalities such as amino and carbonyl groups, most of these functionalities must be blocked by the choice of a set of protecting groups[9]. Also the carbohydrate contents carbonyl group so inter Schiff base reaction with amino group ,the Schiff base formation is a very important in biological chemistry[10] . The modification of poly (MAH) with mono saccharides give biodegradable polymer . Application of modified sugar-substituted conjugated polymers have been interest in biological field such as utilizing as cell-specific culture substances, as well as targeting drug delivery systems[11].

Experiment

A –Instrumental

1. Melting points were determined on Gallen Kamp melting points apparatus MFB-600-O loft and Stuart Scientific Co. LTD melting point SMP1, in Baghdad University, College of Science.
2. Softening points were determined using thermal microscope (Kofler-Method). Reichert thermovar. SP. 10/0.25, 160, in Baghdad University, College of Science.
3. FTIR spectra were recorded using KBr disc and thin film on SHIMADZU FTIR-8400Fou- rier Transform Infrared spectrophotometer, in college of science, Baghdad University.
4. $^{-1}$H-NMR and ^{13}C-NMR spectra were recorded on a Fourier transform varian spectromet-ry , company**,** Bruker, model, Ultra shield 300MHz origin: Switzerland , with tetramethyl silane as internal standard in DMSO-d^6 as solvent . In Iran , Tarbit Modares University

B-Materials

All materials from BDH and Fluka company .

Preparation of 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose (1)

Compound (1) was prepared according to literature [12]

Preparation of 1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose (2)

Compound (2) was prepared according to literature [13]

Polymerization of maleic anhydride(MAH) (3) [14]

poly maleic anhydride was synthesized according Literature procedures using free radi- cal homopolymerization of poly maleic anhydride with some modification Pure monomer (5g) was dissolved in (25-30) ml of freshly distilled dry THF in a screw-capped polymeri- zation bottle . An amount equal to (2%) of the monomer weight of benzoyl peroxide (BPO) was added . The bottle was flushed with nitrogen for few minutes and firmly stoppered , the clear solution was maintained at (90-120) ^{0} C in a constant temperature oil bath for(8) hrs The poly (MAH) was precipited , dissolved in acetone and reprecipited with toluene, filter- ed and purificated by washing with toluene several times .

Preparation of poly(mono carboxylic acid mono methyl maleate) (4) [15]

A solution of polymer (3) (4g , 0.04mol) in (10ml) dry acetone and (0.04mol,2.5ml) absolute methanol with few drops conc.H_2SO_4 place in round flask and refluxed with stirring for 6hrs. on water bath at(45^{o}c) . The solution was then poured into about 50ml of ice-water to give white precipitate filtered, washed with ether and dried.

Preparation of poly(mono maleoyl chloride mono methyl maleate) (5) [16]

In round bottom flask dissolved (2g, 0.015mol) of polymer (4) dissolved in (10ml) dry acetone and (0.03mol,2.5g) of $SOCl_2$ was added , the mixture was refluxed with stirring on water bath at (40-50)ºC for 3 hrs .The deep brown precipitate was filtered , washed with ether and dried.

Preparation of poly (mono methyl mono protected sugar maleate) (6,7) [17]

A mixture of polymer (5) (2g ,0.013mol) and compound (1or 2) ((3.5g ,0.013mol) in (25ml) dry acetone place in round bottom flask and was stirring(24) hrs. Then the solution was poured into chloroform and water (2:1), oily lower layer was separated , dried over anhy-drous Na_2SO_4 filtered and evaporated to give a brown syrup .

Preparation of poly (mono acid hydrazide mono protection sugar -maleate) (8,9) [18]

A solution of polymer(6 or 7) (2g ,0.005mol) and hydrazine hydrate (0.5ml ,0.015mol) in absolute ethanol place in round flask and heated on water bath at (50 ^{0}C) under stirring for (3) hrs. The oily lower layer was extracted with ether twice time , dried over anhydrous Na_2SO_4 , filtered and evaporated , to afford a brown syrup.

Preparation of polymers (10-13) [18]

(1g,0.002mol) of polymer (8or 9)dissolved in(10ml) absolute methanol and place in round flask, then (0.002mol) of free mono saccharides such as (glucose and arabin- osen) in methanol with few drops of glacial acetic acid was added. The mixture was heated on water bath at (40-50) ^{0}C with stirring for 6 hrs, then poured into chloroform and water (2:1),oily upper layer was separated and evaporated to afford a brown syrup

All physical properties of prepared polymers are listed in Tables(1A,1B,1C)

Table 1A- :physical properties for polymers (3-6

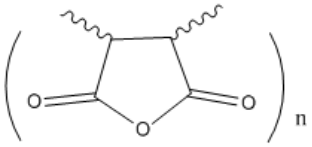
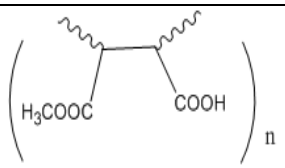
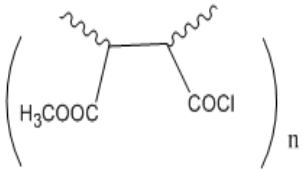
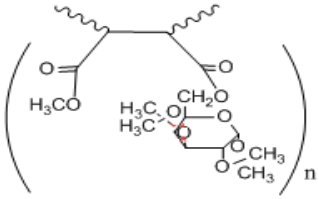
Comp. No	Structure and Nomenclature	Conversion %	Softening point ^{0}C	Color	Solvent of purification
3	 Poly maleic anhydride	86	85-95	Pale yellow	Toluene
4	 Poly (mono carboxylic acid methyl maleate)	68	80-85	White	Water
5	 Poly (mono maleoyl chloride mono methyl maleate)	60.5	60-70	Deep brown	Ether
6	 Poly (mono methyl mono 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose) maleate	78	60-70	Brown	Chloroform

Table-1B- :physical properties for polymers (7-11)

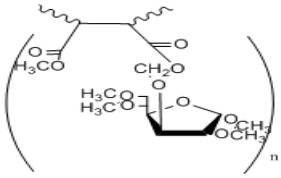
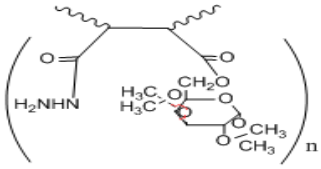
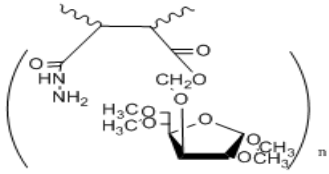
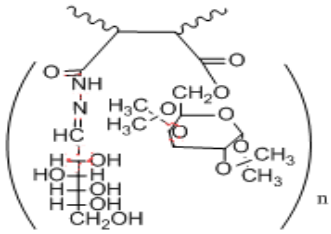
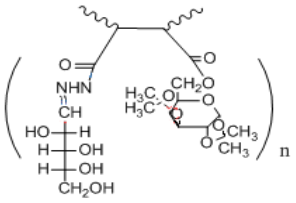
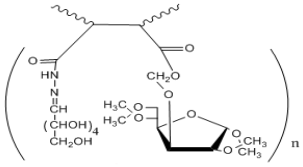
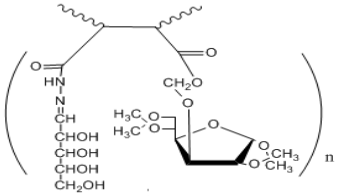
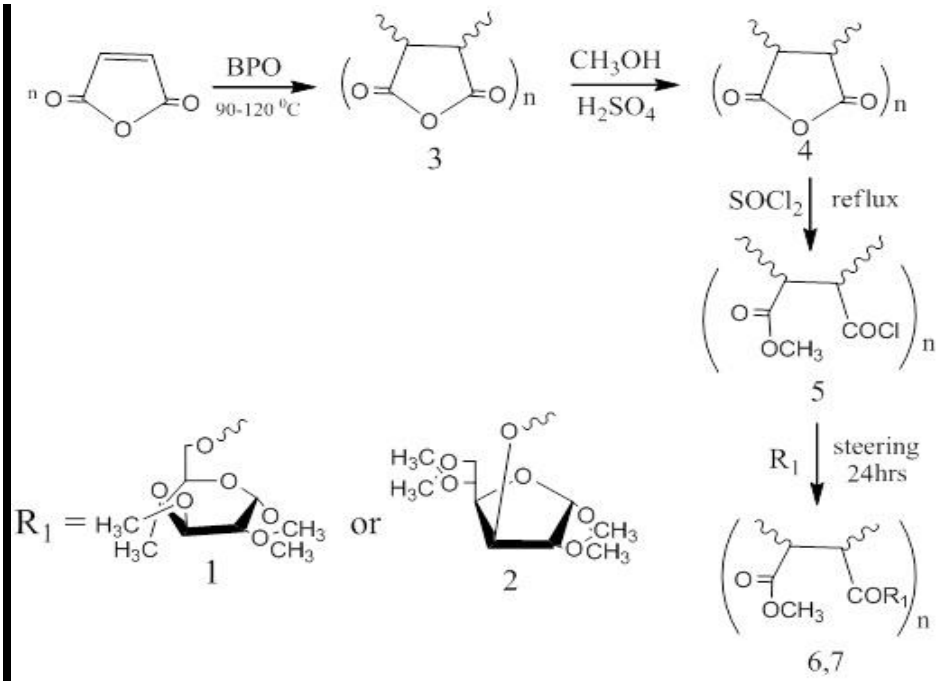
Comp. No	Structure and Nomenclature	Conversion %	Softening point ^{0}C	Color	Solvent of purification
7	 Poly (mono methyl mono 1,2:5,6-Di-O-isopropylidene-α-D-Glucofuranose) maleate	75	75	Brown	Chloroform
8	 Poly (mono acid hydrazide mono 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose) maleate	76	60-70	Brown	Ether
9	 Poly (mono acid hydrazide mono 1,2:5,6-Di-O-isopropylidene-α-D-Glucofuranose) maleate	70	60-70	Brown	Ether
10	 Poly (mono D-glycose imin - N – amide 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose) maleate	80	65-75	Brown	Chloroform
11	 Poly (mono D-arabinose imin - N – amide 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose) maleate	79	65-75	Brown	Chloroform

Table-1C- :physical properties for polymers (12-13)

Comp. No	Structure and Nomenclature	Conversion %	Softening point ^{0}C	Color	Solvent of purification
12	 Poly (mono D-glucose imin - N – amide mono 1,2:5,6-Di-O-isopropylidene-α-D-Glucofuranose) maleate	74.5	65-75	Brown	Chloroform
13	 Poly (mono D-arabinose imin - N - amide mono 1,2:5,6-Di-O-isopropylidene-α-D-Glucofuranose) maleate	74	65-75	Brown	Chloroform

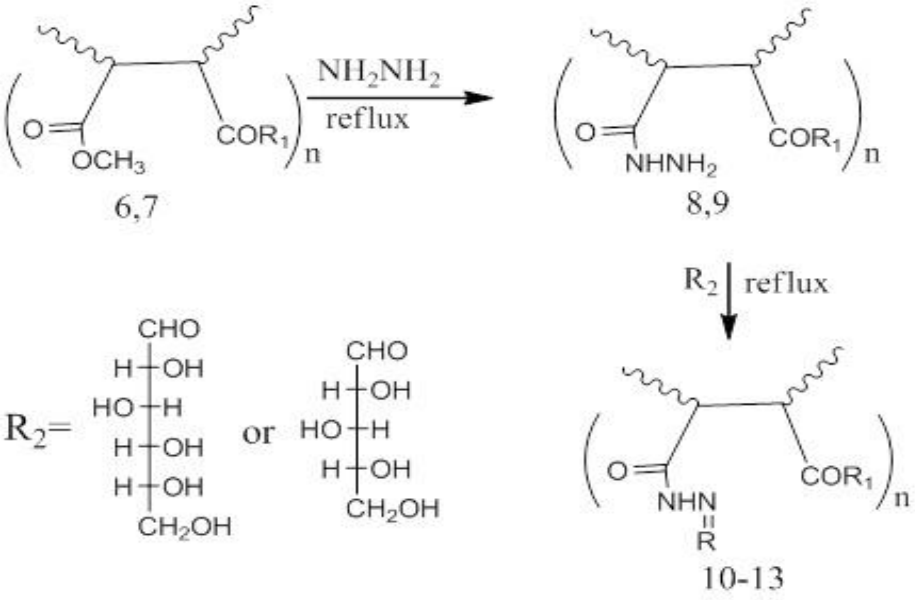
Results and discussion

This research include new polymers which synthesized by modification of polymaleic anhydride with protected and free sugars . There for in D-galactose(1) C_1,C_2,$C_3$and C_4 was pr- otected, leaving the hydroxyl group at C_6 , and in D-glucose(2) the C_1,C_2,C_5 and C_6 was prote- cted , leaving the hydroxyl group at C_3 . The poly maleic anhydride was synthesized due to free radical polymerization (3), then it esterified using absolute methanol in presence of sulfuric acid to give (4) . The polymer (4) was chlorinated with thyionyl chloride to (5) .Nucleophilic substation of (5) was made with protected sugar (1,2) gave the (6 or 7) respectively as in scheme -1 .



Scheme-1. Synthetic route of preparation for polymers (3-7)

Frether nucleophilic substation on polymers (6 or 7) with hydrazine hydrate to give the hydrazide (8 or 9) **.** The free sugar (glucose or arabinose) where reacted with hydrazide to give the target polymers (10- 13) as in scheme -2-



Scheme -2. Synthetic route of preparation for polymers (8-13)

The FT-IR of polymer (3) showed stretching bands at 1855 cm^{-1} due to (C=O) cyclic anhydride , 2940cm^{-1} due to (CH) aliphatic and 1200-1280 cm^{-1} due to cyclic (C-O-C)[18] , the esterfication of (3) gave (4) , the FTIR spectrum of (4) showed stretching band at 1730 cm^{-1} due to (C=O) ester and 2400-3020 cm^{-1} due to (OH) acid group which indicated that the anhydride was esterified . The chlorination of polymer (4) gave (5) . The FTIR of (5) showed stretching band at 1780 cm^{-1} due to (C=O) acid chloride and at 730 cm^{-1} due to (C-Cl) . The reaction between protected sugars (1 and 2) with polymer (5) gave (6 and 7) the FTIR spectrum of these polymers showed stretching bands at 1730 , 1731 cm^{-1} for (C=O) ester and 1110-1275cm^{-1} for (C-O-C) due to polymers (6 and 7) respectively . The reaction between polymers (6 and 7) with hydrazine hydrate gave polymers (8 and 9) respectively, the FTIR spectrum of these polymers showed stretching bands at 1737,1733cm^{-1} for (C=O) ester ,1650,1645 $cm^{-1}$for (C=O) amide , 3278, 3320 cm^{-1} and 3355,3420 cm^{-1} due to (NH_2) for (8 and 9) respectively . Schiff base reaction between polymers (8 and 9) with D-galac- tose and D-arabinose gave target polymers (10- 13) respectively . The FTIR of these poly- ymers showed stretching band at (1730-1735) cm^{-1} for (C=O) ester, 1460 cm^{-1} for (C=N) imine and 3300-3490 cm^{-1} for (OH) . These bands for all polymers are listed in Tables(2,3). The FT-IR spectra of polymers (10 -12) are shown in Figures (1,2, 3)

Table 2 - FT-IR spectra of polymers and protected sugars (1-7)

Comp. No	V(C=O) Ester	V(OH)	V(CH)	V(C-0-C)	Other Bands
3			2940	1200-1289	1850 (C=0) Cyclicanhydried
4	1730	3020 2400	2910		
5	1731		2875		1780 COCl
6	1730		2950	1110-1270	
7	1731		2920	1165-1275	

Table 3 - FT-IR spectra of polymers and protected sugars (8-13)

Comp. No	V(C=O) Easter	V(C-N) Imine	V(OH)	V(CH)	V(C-O-C)	V(C-N) amide	V(NH_2)
8	1737			2930-2960	1100-1250	1650	3280-3320
9	1733			2870-2950	1160-1250	1645	3355-3420
10	1735	1650	3300-3380	2850-2940	1140-1250		
11	1735	1645	3270-3330	2930-2970	1165-1255		
12	1730	1640	3490	2930-2980	1100-1250		
13	1731	1645	3420	2930-2980	1160-1250		

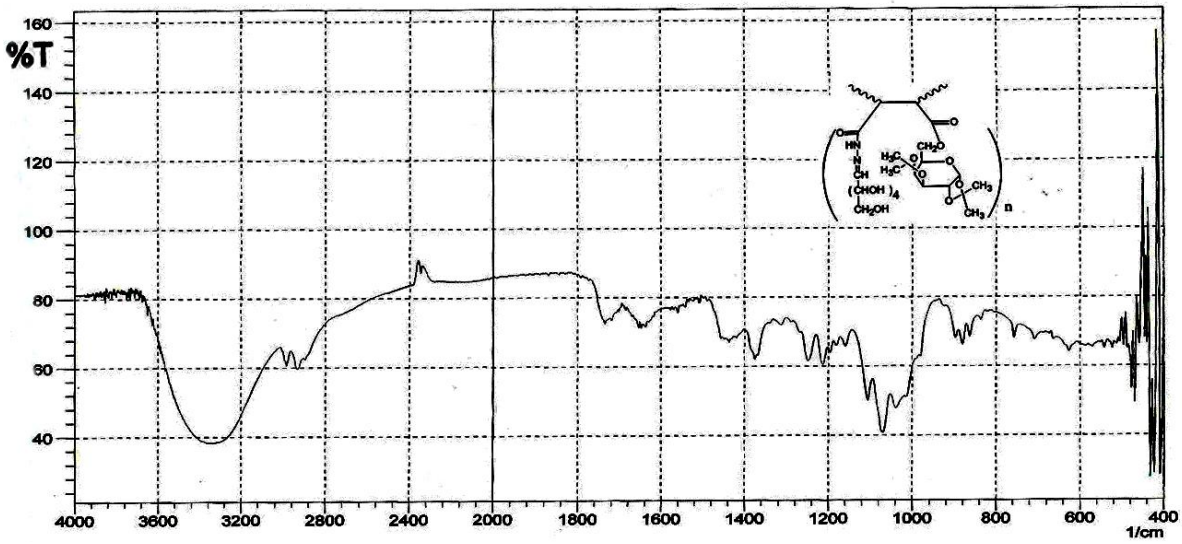


Figure 1- FTIR spectrum of polymer (10)

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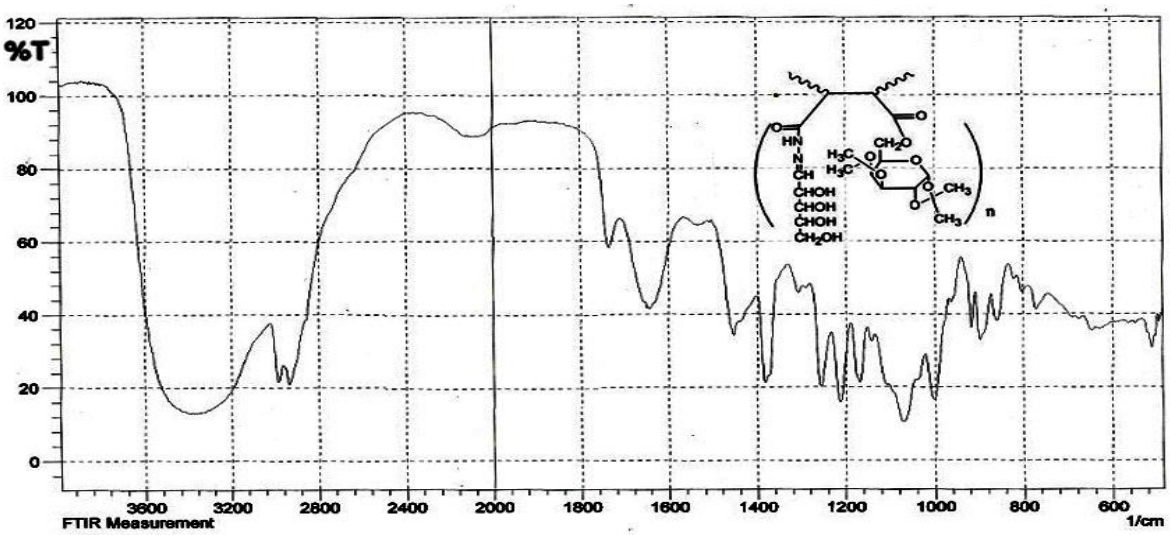


Figure 2- FTIR spectrum of polymer .

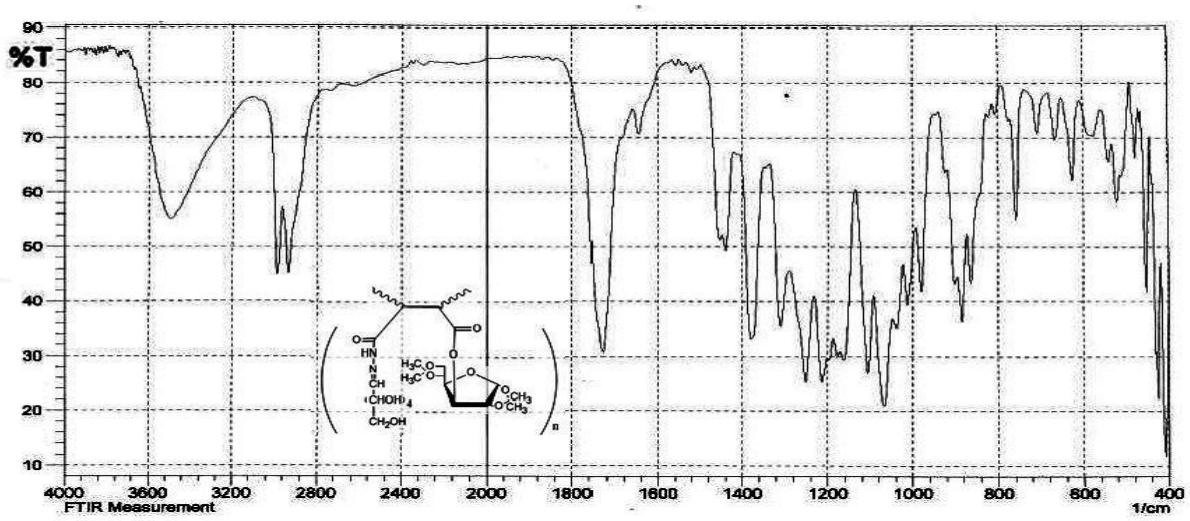


Figure 3- FTIR spectrum of polymer (12)

The ^{1}H-NMR spectrum of polymer (10) in (δ ppm) showed two signals at 1.11,1.44 due to ┼CH-CH┼$_n$ polymer protons ,The singlet signal at 1.91 due to methyl groups of iso- propylidene , while the signal 2.50 was due to hydroxyl groups . The free sugar protons ($H_2^/$,$H_3^/$, $H_4^/$, $H_5^/$ and $2H_6^/$) showed signals at 3.17-3.47 . The maltiplate signals at 3.99 and 5.58 due to (H_1,H_2, H_3 ,H_4 , and H_5). The signal at 5.78 for H_6 , the (SP^2) proton of imine appeared as asinglet at 7.43 . The amide proton appeared at 8.31 as asinglet signal.

The ^{13}C-NMR spectrum of polymer (10) in (δ ppm) showed two signals at 21.470 and 26.168 for carbons ┼CH-CH┼$_n$ poly maleic anhydride , while the signals at 38.797 - 40.796 assigned to ($4CH_3$) isopropyl dine carbons. The signals at 69.524 – 70.430 due to ($C_5^/$,$C_4^/$, $C_3^/$ and $C_2^/$) respectively .The signals between 95.941 – 107.954 for (C_4,C_3,C_5,C_2 and C_1) , the C_6 absorbed at down filed 128.913 due to its linked with ester group. The imines carbon appeared at low filed 130.314 due to (SP^2) hybridization . Two signals at 157.443 , 166.492 due to amide and ester carbonyl respectively .

The^{1} H-NMR spectrum of (11) in (δ ppm)showed two signls at 1.11 and 1.45 (d,d 2H) due to ┼CH- CH┼$_n$ protons of poly maleic anhydride . The signals at 1.609 – 1.912 due to methyl groups of isopropylidene . The hydroxyl group appeared at 2.507 as asinglet signal . The free sugar protons ($H_2^/$,$H_3^/$,$H_4^/$ and $2H_5^/$) showed amultiplate signals at 3.255-3.653. The d,d sign- als at 4.550 and 4.559 due to (H_2 and H_1) respectively , while the maltiplate signals at 5.165- 6.683 due to ($2H_5$,H_4 and H_3) , the H_6 protons appeared at 7.761 . The (SP^2) proton appeared at 8.195 as asinglet . The amide proton showed asinglet signal at 8.565.

The ^{13}C-NMR spectrum of (11) in (δ ppm) showed two signals at 26.166 and 27.413 for carbon ┼CH-CH┼$_n$ polymaliec anhydride. The signal at 38.740- 40.790 assined to ($4CH_3$) isopropylidene carbons. The signal at 60.241due to $C_5^/$, while the signals at 69. 540- 70.437 due to ($C_4^/$,$C_3^/$ and $C_2^/$) respectively . The signal at 95.938 due to (C_5,C_4 and C_3) , while the signal at 107.944 due to (C_2 and C_1) . The carbon C_6 appeared at low field 108.341 due to its linked with ester group . The imines carbon appeared at low field 135.157 due to its (SP^2) hy- pridization . Two signals at 162.526 and 163.377 due to amide and ester carbonyl respectively

The^{1} H-NMR spectrum of (12) in (δ ppm) showed two signls at 1.19 and 1.89 due to ┼CH-CH┼$_n$ protons of poly maleic anhydride .The singlet signal at 2.50 assigned to ($4CH_3$) isopropylidene , while the hydroxyl group signal appeared at 3.36 as asinglet . The maltiplate signals between 3.38-4.83 are due to ($2H_6^/$,$H_5^/$,$H_4^/$,$H_3^/$ and $H_2^/$) , the two dublet signals at 5.41 and 5.62 due to (H_6,H_5) , while the signal at 5.68 – 6.71 due to (H_1,H_2 and H_4) . The H_3 proton appeared signal at 6.19, the (SP^2) proton of an imine appeared signal at 7.39 . The amide pro- ton appeared signal at 8.33

The ^{13}C-NMR spectrum of (12) in (δ ppm) showed two signals at 16.620 and 27.213 for carbon ┼CH-CH┼$_n$ polymaliec anhydride, the signals at 39.003- 41.009 assigned to ($4CH_3$) isopropylidene , while the signals at (50.574,52.719, 66.506, 72.748 and 73.623) due to ($C_6^/$ $C_5^/$,$C_4^/$,$C_3^/$ and $C_2^/$) respectively . The signals at (81.405,85.446,105.022 and 108.350) due to (C_6,C_5,C_4,C_2 and C_1)

respectively . The C_3 absorbed at 111.120 due to its linked with ester group , the imines carbon appeared at low filed 125.500 due to (SP^2) hybridization . Two sig- nals at 142.474 and 162.526 due to amide and ester carbonyl groups respectively .These che-mical shifts are shown in Tables (4A,4-B, 5) and Figures (4,5,6,7)

Table 4-A - The ^{1}H-NMR chemical shifts of the polymers (10-13)

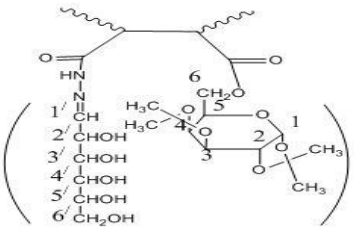
Comp. No.	Structure	Chemical shifts in δ ppm
10		1.11-1.44(m,2H, ┼CH-CH┼ n); 1.90(s,12H,4CH_3); 2.50(s,5H,5OH); 3.17-3.47(6H, $H_2^/$,$H_3^/$,$H_4^/$,$H_5^/$ and $2H_6^/$); 3.99-5.58(m, 5H,H_1,H_2,H_3,H_4 and H_5); 5.78(s,2H,H_6); 7.43(s,1H,H imine); 8.31-8.44(m,1H, NH amide)

Table 4-B - The ^{1}H-NMR chemical shifts of the polymers (10-13)

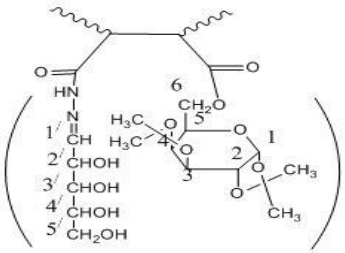
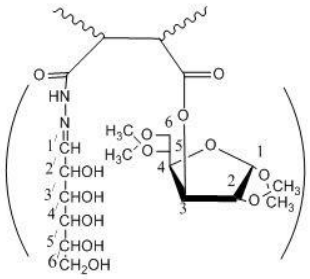
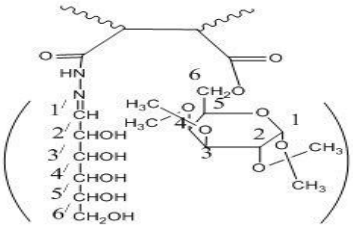
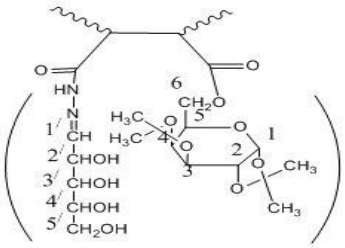
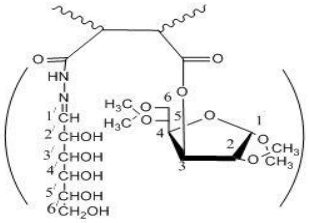
Comp. No.	Structure	Chemical shifts in δ ppm
11		1.11-1.45(d,d,2H, ┼CH-CH┼ n); 1.609-1.912(12H,4CH_3); 2.507(s,5OH); 3.255-3.653(s,5H,$H_2^/$,$H_3^/$,$H_4^/$ and $2H_5^/$); 4.550-4.559(2H,H_1,H_2); 5.163-6.683 (m,3H,H_3,H_4 and H_5); 7.494-7.610(m,1H,H_6); 8.195(s,1H,H imine); 8.565(s,1H,NH amide)
12		1.19-1.89(m,2H, ┼CH-CH┼ n); 2.50(s,12H, 4CH_3); 3.36(s,5H, 5OH); 3.38-4.83 (m,6H,$2H_6^/$,$H_5^/$,$H_4^/$,$H_3^/$ and $H_2^/$) 5.41-5.62(3H, $2H_6$,H_5); 5.68-6.71(H_1,H_2,H_4) ; 6.19(1H,H_3); 7.39 (1H,H imine); 8.33(1H,NH amide)

Table 5 - The ^{13}C-NMR chemical shifts of the polymers (10-13)

Comp. No.	Structure	Chemical shifts in δ ppm
10		21.470, 26.169(┼CH-CH┼ n); 38.797-40.796 ($4CH_3$); 63.239 ($C_6^/$); 69.524-70.430 ($C_5^/$,$C_4^/$,$C_3^/$ and $C_2^/$); 95.941-107.954 (C_1,C_2,C_3,C_4 and C_5); 128.973(C_6); 130.314($C_1^/$); 157.443(C=O) amide, 166.492(C=O) ester.
11		26.166, 27.413(┼CH-CH┼ n); 38.790-40.780($4CH_3$); 60.241($C_5^/$); 69.590-70.437($C_4^/$,$C_3^/$ and $C_2^/$); 95.938(C_5,C_4 and C_3); 107.944(C_2, and C_1); 108.341(C_6); 135.157($C_1^/$); 162.526(C=O) amide; 163.377(C=O) ester.
12		16.620, 27.213(┼CH-CH┼ n); 39.003-41.009($4CH_3$); 50.574-73.623 ($C_6^/$,$C_5^/$,$C_4^/$,$C_3^/$ and $C_2^/$); 81.405-108.350 (C_6,C_5,C_4,C_2 and C_1); 111.120(C_3); 125.500($C_1^/$); 142.474(C=O) amide ; 162.526 (C=O) ester.

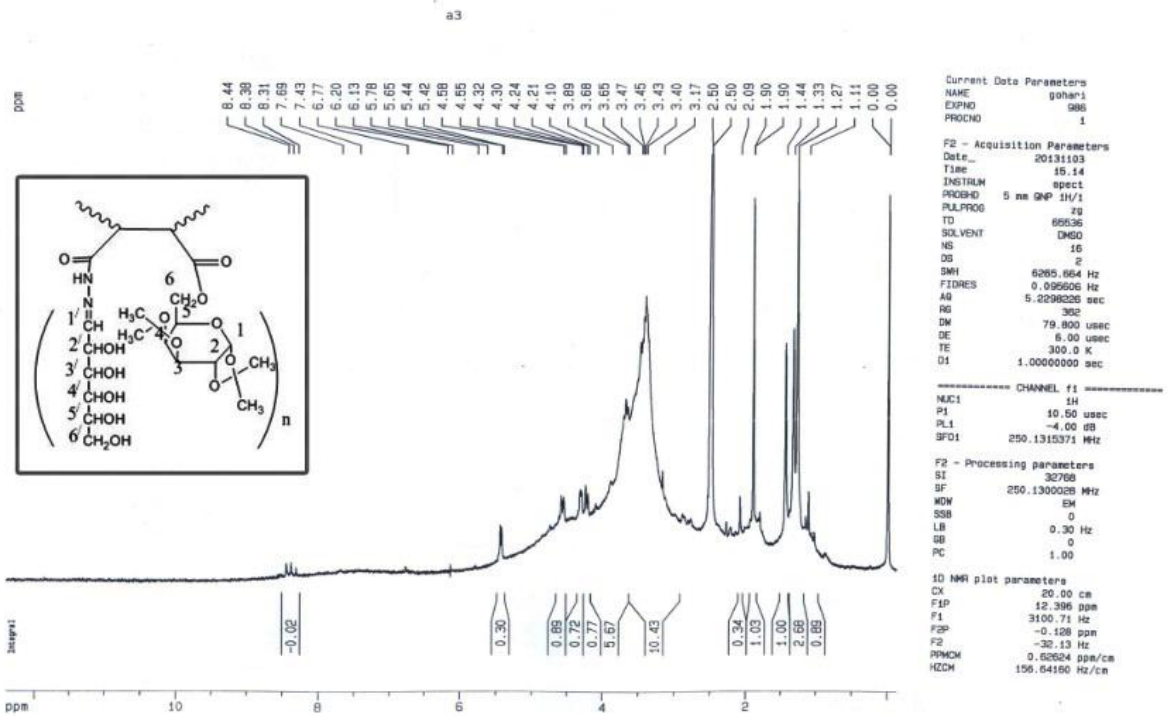


Figure 4- ^{1}H-NMR spectrum of polymer (10)

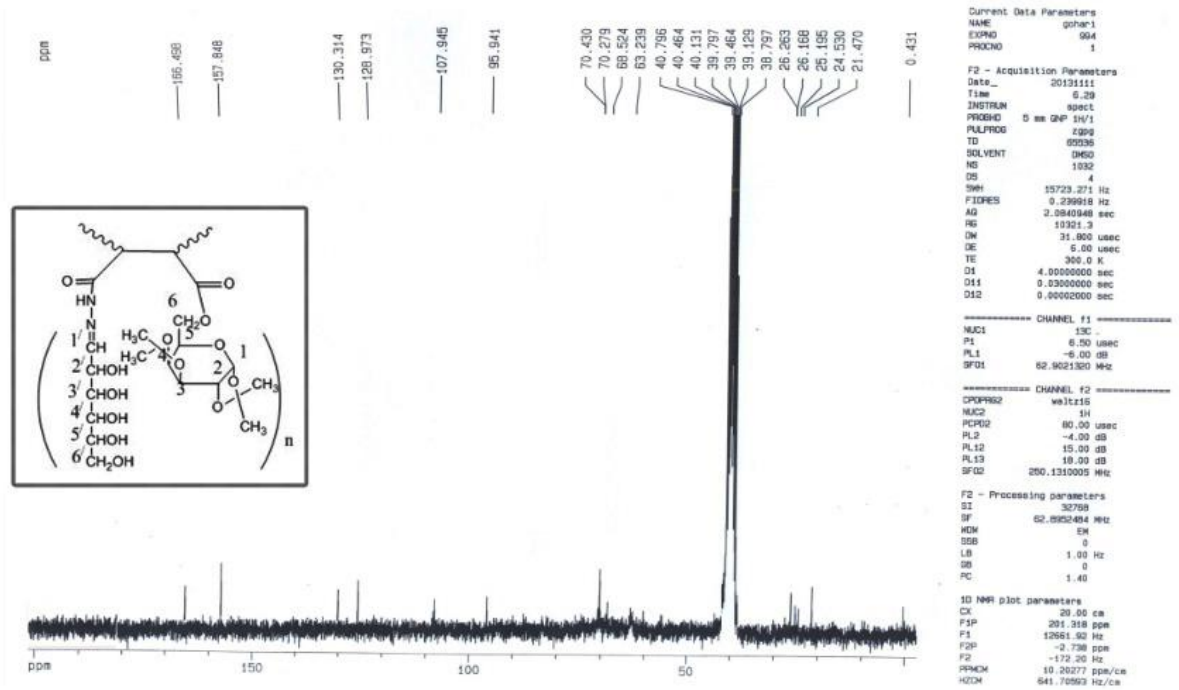


Figure 5- ^{13}C-NMR spectrum of polymer (10)

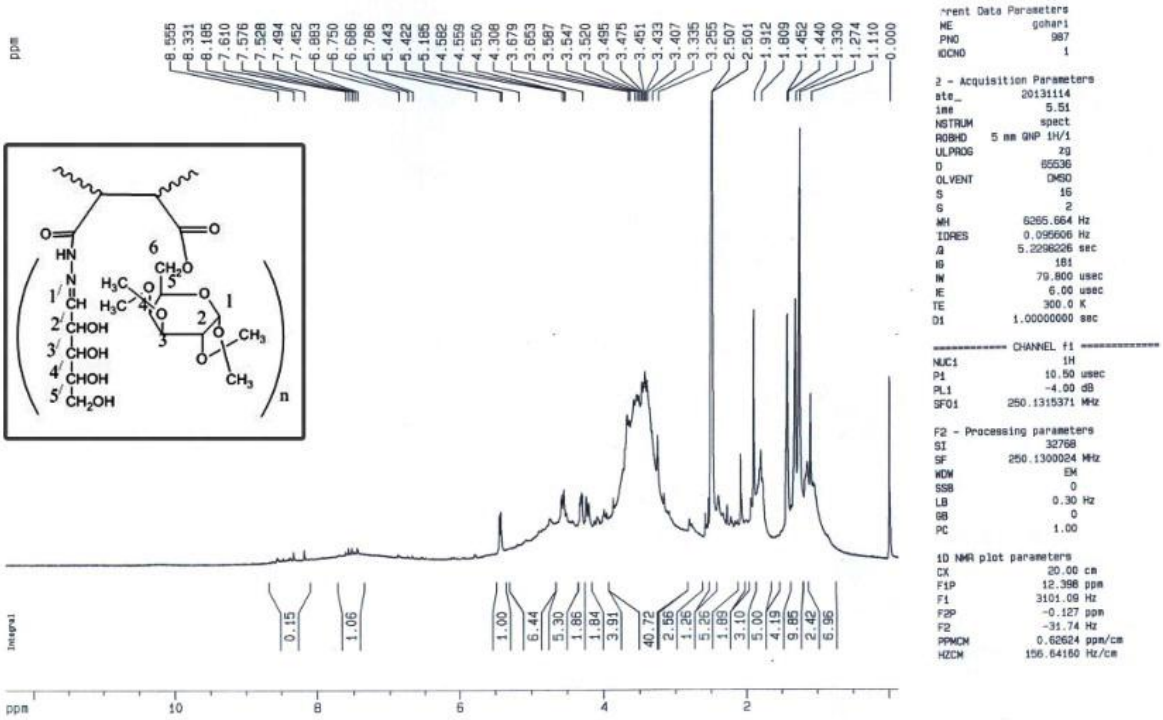


Figure 6- ^{1}H-NMR spectrum of polymer (11)

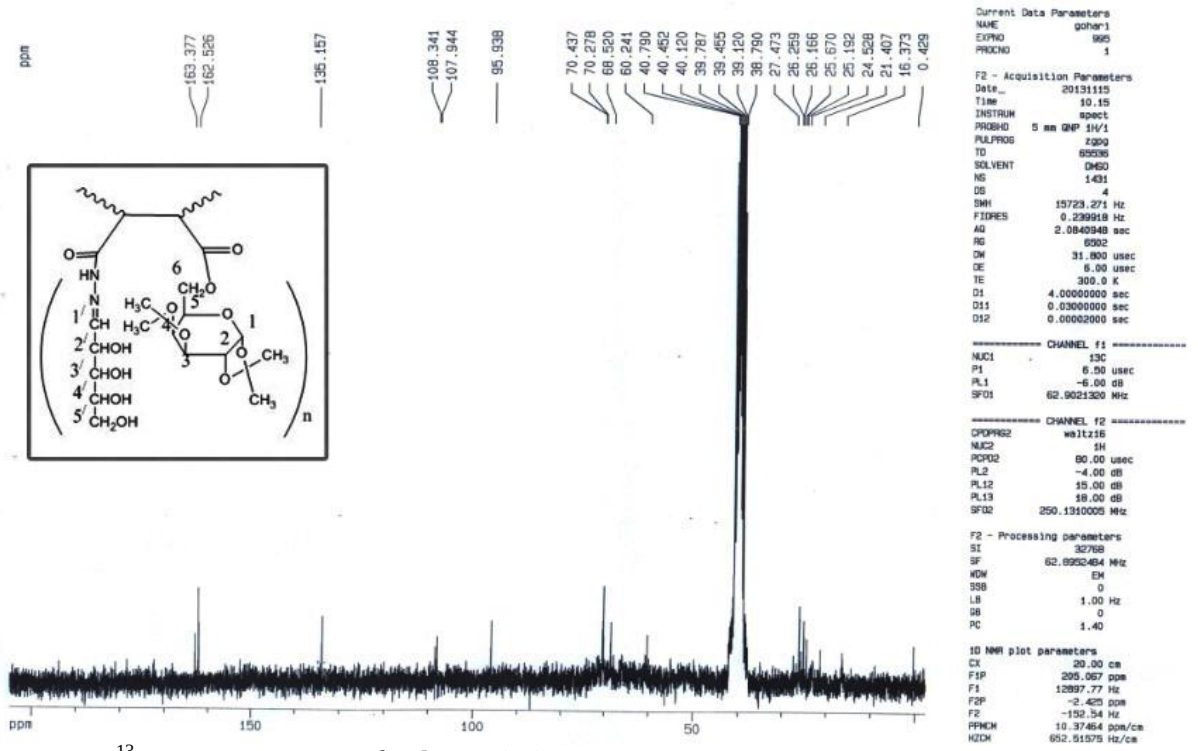


Figure 7- ^{13}C-NMR spectrum of polymer (11)

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