



Modification of poly maleic anhydride with different mono saccharides

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ABSTRACT

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

Keywords: poly maleic anhydride, fructose, glucose

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^[1-4]. 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^[5-7], maleic anhydride (MA) is a multifunctional chemical intermediates that find applications in nearly every field of industrial chemistry^[8]. It contains two acid carbonyl groups and a double bond in α , β position^[9]. 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^[10]. 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. 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].

EXPERIMENTAL SECTION

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-8400 Fourier Transform Infrared spectrophotometer, in college of science, Baghdad University.
4. ¹H-NMR and ¹³C-NMR spectra were recorded on a Fourier transform varian spectrometry, company Bruker, model, Ultra shield 300MHz, origin: Switzerland, with tetramethyl silane as internal standard in DMSO-d⁶ as solvent In Iran, Tarbit modares University

B - Materials:

All materials from BDH and fluka company

Preparation of 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose^[12](1)

Concentrated sulfuric acid (8.75 ml) was added dropwise with stirring to an ice-cold anhydrous acetone (175 ml) then a finely powdered D-fructose (9g,50 mmol) was added portionwise with stirring until all of the sugar had dissolved. The pale-yellow solution was kept at room temperature (80 min) . Sodium hydroxide (27.5g) in (125 ml) was gradually added , the inorganic salts were removed and the aqueous was extracted with dichloromethane and evaporated to give a pale-yellow solid which recrystallization by dissolving in boiling ether, gave white solid (58%), m.p 94-96°C.

Polymerization of maleic anhydride(MAH)^[13] (2)

poly maleic anhydride was synthesized according Literature procedures were using free radical homo polymerization 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 polymerization 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) ° C in a constant temperature oil bath for(8) hrs The poly (MAH) was precipitated , dissolved in acetone and reprecipitated with toluene, filtered and purification by washing with toluene several times .

Preparation of poly(mono carboxylic acid mono methyl maleate)^[14] (3)

A solution of polymer (3) (0.04mol,4g) in (10ml) dry acetone and (0.04mol,2.5ml) absolute methanol with few drops conc.H₂SO₄ place in round flask and refluxed with stirring for 6hrs. on water bath at(45°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)^[15] (4)

In round bottom flask dissolved (0.015mol,2g) of polymer (4) in (10ml) dry acetone and (0.03mol,2.5g) of SOCl₂ was added , the mixture was refluxed with stirring on water bath at (40-50)°C for 3 hrs .The deep brown precipitate was filtered ,washed with ether and dried.

Preparation of poly(mono methyl mono protection sugar maleate)^[16] (5)

A mixture of polymer (5) (0.013mol,2g) and compound (1) ((0.013mol,3.5g) 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, added anhydrous Na₂SO₄ filtered and evaporated .The product was a brown syrup

Preparation of poly(mono acid hydrazide mono protection sugar maleate) (6)

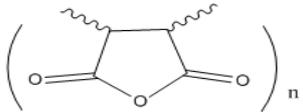
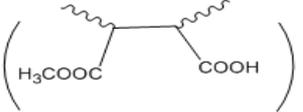
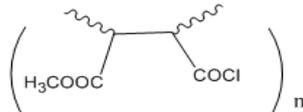
A solution of polymer(5) (0.005mol,2g) and hydrazine hydrate (0.015mol,0.5ml) in absolute ethanol place in round flask and heated on water bath at (50 °C) under stirring for (3) hrs.The oily lower layer was extracted with ether twice time ,dried over anhydrous Na₂SO₄ , filtered and evaporated .The product was a brown syrup.

Preparation of polymer^[17] (7)

A solution (0.002mol,1g) of polymer (6) in (10ml) absolute methanol place in round flask, then (0.002mol) of free glucose in methanol with few drops of glacial acetic acid was added. The mixture was heated on water bath at (40-50) °C under stirring for 6 hrs, then poured into chloroform and water (2:1) ,oily upper layer was separated and evaporated. The product was a brown syrup .

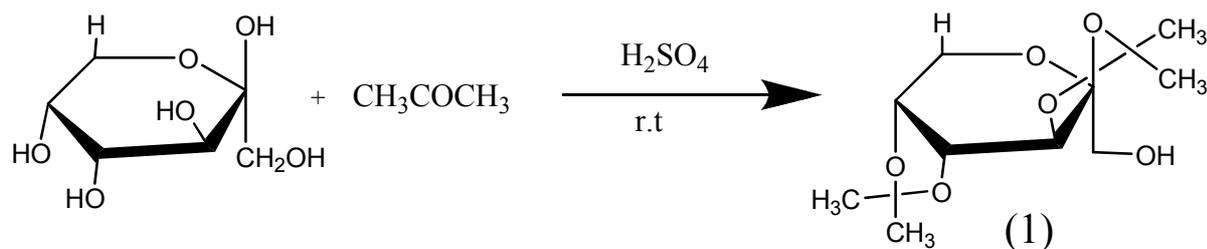
All physical properties of prepared polymers are shown in tables-1.

Table-1 : physical properties for polymers (2-7)

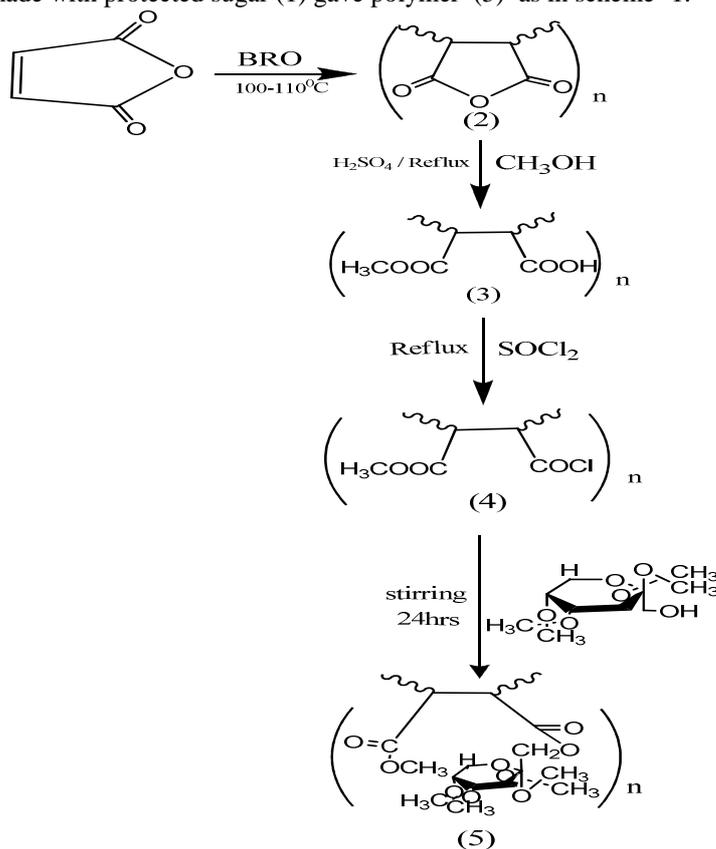
Comp. No	Structure and Nomenclature	Conversion %	Softening point °C	Color	Solvent of purification
1	 Poly maleic anhydride	86	85-95	Pale yellow	Toluene
2	 Poly (mono carboxylic acid methyl maleate)	68	80-85	White	Water
3	 Poly (mono maleoyl chloride mono methyl maleate)	60.5	65-70	Deep brown	ther
4	 Poly (mono methyl mono 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose) maleate	78	60-70	Brown	Chloroform
5	 Poly (mono acid hydrazide mono 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose) maleate	76	65-70	Brown	Ether
6	 Poly (mono D-glycose imin - N – amide 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose) maleate	80	65-75	Brown	Chloroform

RESULTS AND DISCUSSION

This research include new polymers which synthesized by modification of poly maleic anhydride with protected and free sugars . There for in D-fructose(1) ,C₂,C₃, C₄ and C₅ was protected, leaving the hydroxyl group at C₁.



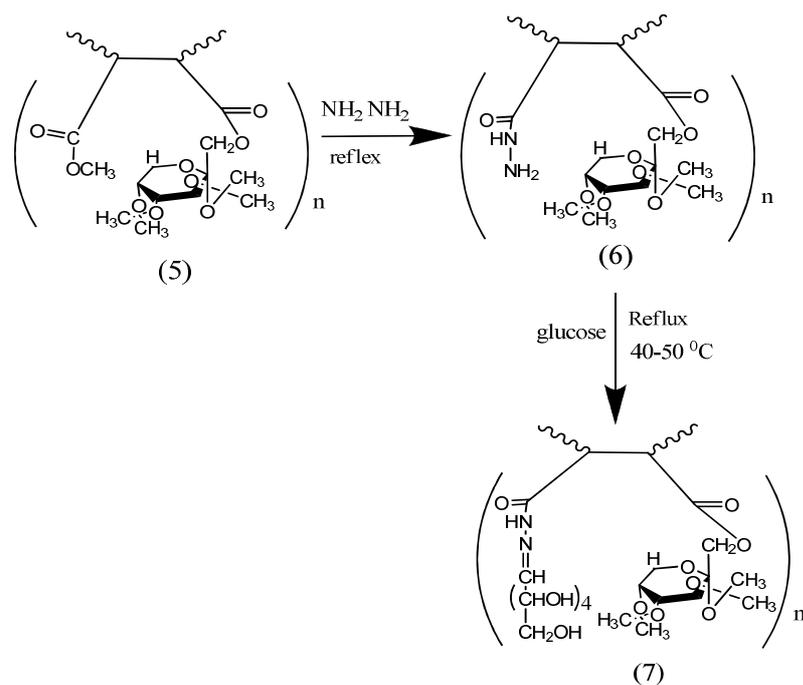
The poly maleic anhydride was synthesized due to free radical polymerization(2),then it esterified using absolute methanol in presence of sulfuric acid (3) . The ester was chlorinated with thionyl chloride(4) .Nucleophilic substitution of ester was made with protected sugar (1) gave polymer (5) as in scheme -1.



Schem-1-

Further nucleophilic substitution on polymer (5) with hydrazine hydrate to give the hydrazide (6). The free glucose where reacted with hydrazide(6) to give the target polymer (7) as in scheme -2.

FTIR spectrum of compound (1) showed stretching bands at 3320 cm^{-1} for (OH) group, $2940, 2880, 2860\text{ cm}^{-1}$ due to $(-\text{CH}_3, -\text{CH}_2, -\text{CH})$ respectively, and $1050-1220\text{ cm}^{-1}$ due to $(\text{C}-\text{O}-\text{C})$ of the five-member cyclic acetal^[18]. The FTIR of polymer (2) showed stretching bands at 1855 cm^{-1} due to $(\text{C}=\text{O})$ cyclic anhydride, 2940 cm^{-1} due to (CH) and $1200-1280\text{ cm}^{-1}$ due to cyclic $(\text{C}-\text{O}-\text{C})$. The esterification of (2) gave (3), the FTIR spectrum of (3) showed stretching band at 1730 cm^{-1} due to $(\text{C}=\text{O})$ ester, 2910 cm^{-1} due to (CH) and $2400-3020\text{ cm}^{-1}$ due to (OH) acid group which indicated that the anhydride was esterified. The chlorination of polymer (3) gave (4), the FTIR of (4) showed stretching band at 1731 cm^{-1} due to $(\text{C}=\text{O})$ ester, 2875 cm^{-1} due to (CH) , 1780 cm^{-1} due to $(\text{C}=\text{O})$ acid chloride and at 730 cm^{-1} due to $(\text{C}-\text{Cl})$. The reaction between protected sugars (1) with polymer (4) gave (5), the FTIR spectrum of this polymer showed stretching bands at 1731 cm^{-1} for $(\text{C}=\text{O})$ ester, $2935 - 2980\text{ cm}^{-1}$ for (CH) , and $1110-1275\text{ cm}^{-1}$ for $(\text{C}-\text{O}-\text{C})$. The reaction between polymer (5) with hydrazine hydrate gave polymer (6), the FTIR spectrum of this polymer showed stretching bands at 1737 cm^{-1} for $(\text{C}=\text{O})$ ester, $2930-2980\text{ cm}^{-1}$ for (CH) , 1650 cm^{-1} for $(\text{C}=\text{O})$ amide, $3280, 3320\text{ cm}^{-1}$ due to (NH_2) . Schiff base reaction between polymers (6) with D-glucose gave target polymer (7), the FTIR of this polymer showed stretching band at 1730 cm^{-1} for $(\text{C}=\text{O})$ ester and 1645 cm^{-1} for $(\text{C}=\text{N})$ imine and $3480-3500\text{ cm}^{-1}$ for (OH) and $2840-2980\text{ cm}^{-1}$ for (CH) aliphatic and $1165-1255\text{ cm}^{-1}$ due to $(\text{C}-\text{O}-\text{C})$. The FTIR spectrum of polymer (7) as shown in Fig.1



Scheme-2-

The $^1\text{H-NMR}$ spectrum of polymer (7) in (δ ppm) showed multi signals at 1.27-1.44 due to protons $-\text{CH}-\text{CH}-$, polymalic anhydride the signals at 2.30 as singlet due to methyl groups of isopropylidene, while the signals 2.54 was due to hydroxyl groups. The free sugar protons ($\text{H}_2', \text{H}_3', \text{H}_5'$ and $2\text{H}_6'$) showed at 2.77-3.00 respectively. The singlet signal at (3.15-3.65) due to ($\text{H}_3, \text{H}_4, \text{H}_5$ and H_6) respectively. The proton H_2 appeared at 5.96 as a singlet signal, while the (SP_2) proton imines appeared at low field 7.17. The amide proton appeared at low field 7.37 as a singlet signals.

The $^{13}\text{C-NMR}$ spectrum of polymer (7) in (δ ppm) polymer showed two signals at 24.293 and 26.912 for carbons $-\text{CH}-\text{CH}-$ poly maleic anhydride, while the signals at 38.755-40.767 assigned to (4CH_3) isopropylidene carbons. The signals at (42.411, 60.495, 62.912, 69.255 and 69.655) for $\text{C}_6', \text{C}_5', \text{C}_4', \text{C}_3'$, and C_2' respectively. other bands at (70.64- 103.482) due to $\text{C}_6, \text{C}_5, \text{C}_4, \text{C}_3$ and C_2 respectively. While C_1 absorbed signal at 107.794 due to its linked with ester group. The imines Carbon appeared signal at (108.245) due to its sp^2 hybridization. Two signals at 166.403, 174.143 due to amide and ester carbonyl respectively. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum of polymer (7) as shown in (Fig.1,2)

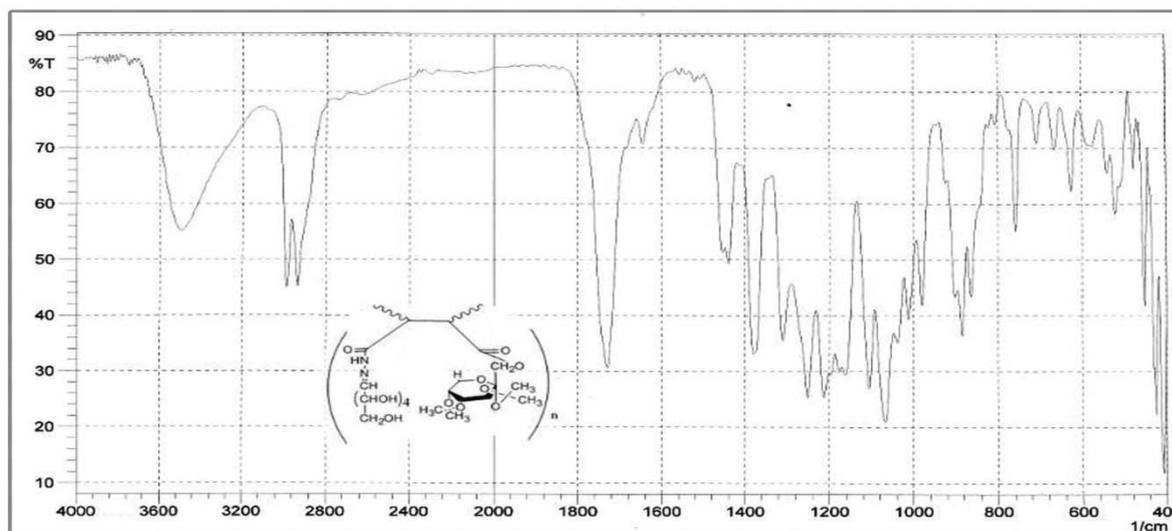
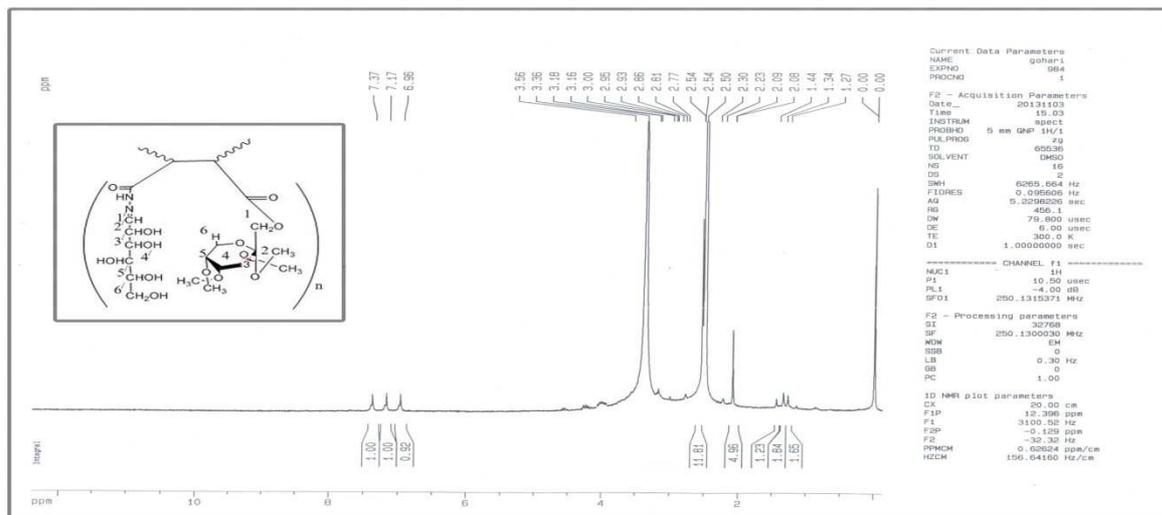
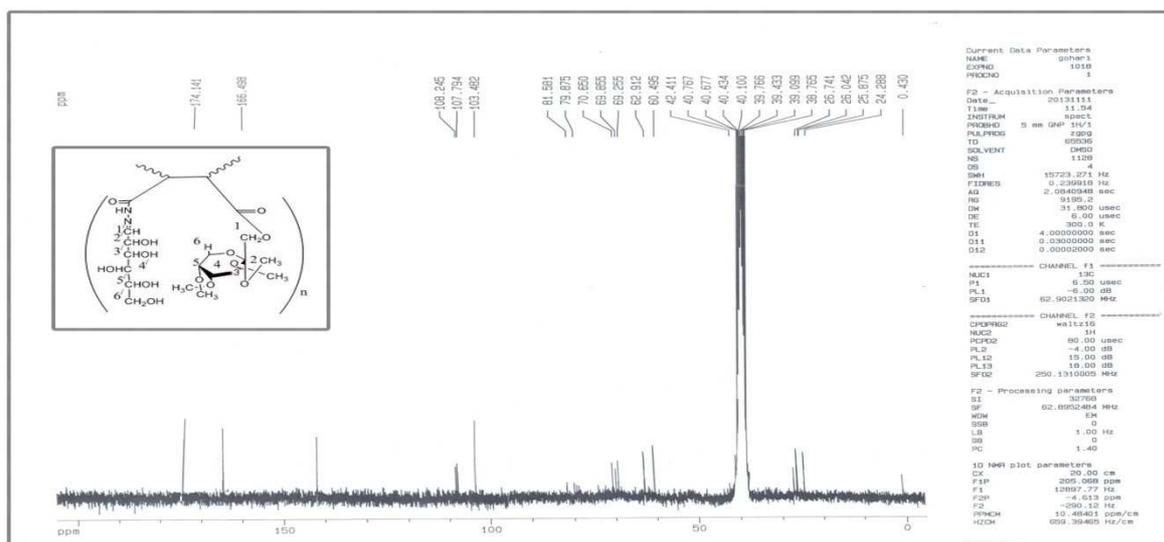


Figure-1: FTIR of polymer (7)

Figure -2: ¹H-NMR of polymer (7)Figure -3: ¹³C-NMR of polymer (7)

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