

Synthesis of novel Copolymers from free radical polymerization of D-Fructopyranose derivatives and N-Substituted Maleimides

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Abstract

Several N - substituted maleimides were prepared from the reaction of maleic anhydride with aromatic primary amines to form the corresponding N- substituted maleamicacids. Dehydration of the prepared maleamic acids using acetic anhydride and sodium acetate resulted in the formation of the corresponding maleimides. The prepared maleimides were allowed to polymerize with D-fructopyranose derivatives (compound (II)) free radically using AIBN As the initiator .

The prepared compounds were detected by using C.H.N Analyses , I.R and physical properties.

AIBN

Introduction

Fructopyranosyl derivatives were prepared recently ⁽¹⁻²⁾ because of their biological activity ⁽³⁻⁵⁾, also used in most of carbohydrates synthesis ⁽⁶⁾. Polyamides are well known polymers for their thermal stabilitie ⁽⁷⁻¹⁰⁾ However homopolymerization of N-substituted maleimide have produced low molecular weight polymers in general ⁽¹¹⁻¹³⁾, while copolymerization of N-substituted maleimides have resulted in

higher molecular weight but the products showed lower (Tg) values ^(14,15). This paper reports the results of copolymerization of several N- substituted maleimides with compound (II) free radically using AIBN as the initiator .

Experimental

All solvents used were redistilled, I.R-spectra were recorded on a Shimadzu I.R- 408- spectrophotometer. Elemental analyses was preformed using a perkin -

Elmer 204 B . Instrument .

Preparation of 2, 3- 4,5 - Di - O - isopropylidene - β -D- Fructopyranose (I)

Zinc chloride (24 gm) was added to a solution of (30 gm) of D-fructose in dry acetone (150ml) , then (1-1.5 ml)of phosphoric acid . The temperature was kept at 30C° with continuous stirring for 24-48 hrs. The reaction mixture was neutralized with (18 gm of K_2CO_3 in 100 ml H_2O). The mixture was evaporated under reduced pressure, and The residual syrup was extracted with chloroform (3x50 ml) , washed many times with water , and dried over magnesium sulphate .The solution was filtered off . The syrup residue was cooled to obtain white crystals . The product was recrystallized from n-hexane to give colorless crystals .

Yield (80%) , m.p = 46C°

Anal.calc.for $C_{12}H_{20}O_6$: C% (50.38) , H% (7.69)

Found : C % (51.1) , H % (7.43)

I.R data showed the appearance of aband of (-OH) at 3250 cm^{-1} ,(C-H) at 2980 cm^{-1} and aband assigned for (C-O-C) cyclic ether linkage at ($1235\text{-}1245\text{ cm}^{-1}$) .

preparation of 2,3 4,5- Di-O-Isopropylidene-1-O-acryloate -D-fructopyranosyl (II)

(1gm) of compound (I) was dissolved in (5ml)of dry beryzene and (5ml)dry pyridine . then (3ml) of acryloylchloride was added dropwise with stirring in an Ice bath, the stirring was continous for 24hrs .The reaction mixture was diluted with (20ml) of water then (10 %) HCL and extracted with chloroform (20x3ml), the organic layer was washed several times with water to remove the salt and unreacted materials , and dried over anhydrous sodium sulphate . The drying agent was filtered off and the filterate was evaporated under redused pressure to give crude syrup (75%) yield.

Anal.calc. for $C_{15}H_{22}O_7$: C% (57.32) H % (7.0)

Found : C% (56.77) H% (7.11)

I.R data shows disappearance of (-OH) band and appearance of ester

(C = O) band at 1740 cm^{-1} with vinylic (C = C) at 1440 cm^{-1}

Preparation of N- substituted Amic Acids.

N-aryl substituted Maleamic acids were prepared according to litreature^(15,16). They were purified by either crystallization or by dissolving the amic acid in the least amount of sodium bicarbonate solution followed by precipitation using HCL . Table-1-lists the m.p, percent yields and C.H.N Analyses.

Table-1- Melting points , percent yields and C.H.N Analyses.

Amic Acid	M.P (C°)	Yield %	C% H% N %		
			Calc	Found	Found
N-phenyl Maleamic acid	198.5	98	62.8	4.71	7.31
			61.9	4.66	7.29
N-(4-chloro phenyl) maleamic acid	195	97	53.2	3.54	6.2
			54.0	3.44	6.7
N-(1-naphthyl) Malemic acid	140	98	69.7	4.56	5.8
			69.4	4.11	5.99
N-(3-nitro phenyl) maleamic acid	203	98	50.84	3.38	11.86
			51.2	3.42	10.73
N-(4-methyl phenyl) maleamic acid	192	96	64.39	5.36	6.83
			63.97	6.11	6.77

Dehydration of the prepared N-aryl maleamic acid

The prepared N-substituted maleamic acids were cyclized by

dehydration using acetic anhydride - sodium acetate according to literature^(16,17). Table -2- lists the melting points, percent yields, and C.H.N Analyses.

Table -2- Melting points, percent yields and C.H.N Analyses.

Maleimide	M.P(C°)	Yield %	C% H% N%		
			Calc found		
N-phenyl Maleimide	78.3	86	<u>69.36</u> 68.91	<u>4.04</u> 4.11	<u>8.09</u> 7.91
N-(4-chloro phenyl) Maleimide	76	115	<u>57.83</u> 56.91	<u>2.89</u> 3.01	<u>6.74</u> 6.82
N-(1-naphthyl) Maleimide	80	109	<u>75.33</u> 74.98	<u>4.03</u> 4.1	<u>6.27</u> 6.32
N-(3-nitro phenyl) Maleimide	77	127	<u>59.40</u> 58.89	<u>2.97</u> 2.97	<u>6.93</u> 6.87
N-(4-methyl phenyl) Maleimide	80	149	<u>70.58</u> 70.44	<u>4.81</u> 4.72	<u>7.48</u> 7.77

CO - polymerization of several - N -aryl maleimides with compound (II) free radically.

Equimolar quantities of N-substituted maleimides and comp. (II) were placed in a polymerization bottle. few milligrams of (AIBN) were added to the mixture. the mixture dissolved in DMF solvent, and the bottle was purged with dry pure nitrogen gas before stoppering the container quickly. The bottle was placed in a water bath provided with a thermometer.

The polymerization mixture was heated to 70C° in case of using (AIBN)

as the Initiator and to 85 C° when benzoyl peroxide was used.

The mixture after heating for an hour was poured into a beaker containing methanol. precipitate was formed, then filtered and washed with water and purified by dissolving in benzene and precipitated with carbon tetra chloride. This process was repeated until pure material was obtained. Table (3) lists names of the prepared copolymers along their softening points, percent conversions, purification solvents and viscosities.

Table-3-Softening points , percent conversions , purification solvents and Viscosities .

CO- polymer	% conversion	S.P C°	Purification solvent	[η] ^a
Poly [N-phenyl maleimide - CO- 2,3-4,5- Di - O- Isopropylidene - 1-O- acryloate - D-fructopyranosyl]	80	180-200	Benzene – CCl ₄	0 . 49
Poly [N-4- chloro phenyl maleimide- CO- 2,3 -4,5- Di-O- Isopropylidene 1-O-acryloate - D-fructopyranosyl]	65	180-195	Hot ethanol water	0. 61
Poly [N-1-naphthyl maleimide -CO- 2,3-4,5-Di-o-Isopropylidene-1-O-acryloate- D-fructopyranosyl]	50	170-190	Benzene Chloroform	0 . 40
Poly [N-3-nitro phenyl maleimide-CO-2,3-4,5 Di-O- Isopropylidene-1-O-acryloate- D-fructopyranosyl]	76	175-197	Benzene ether	0 . 51
Poly [N-4-methyl phenyl maleimide -CO-2,3-4,5-Di-O- Isopropylidene- 1-O- acryloate - D-fructopyranosyl]	46	160-185	Benzene – CCl ₄	0 . 43

(a) - The viscosities were measured in CH₂Cl₂

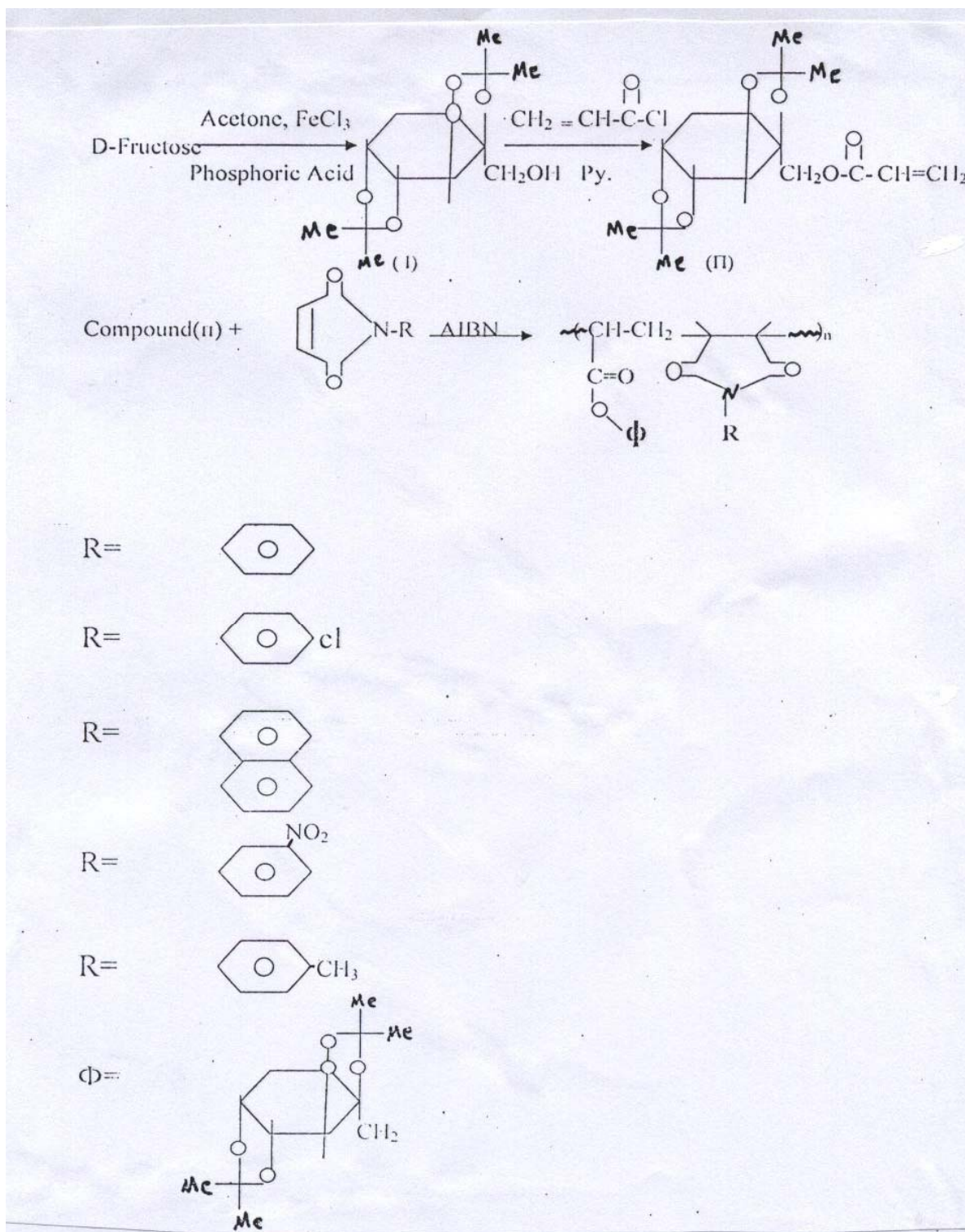
Results and discussion

Compound (II) was allowed to CO-polymerize with several N-aryl substituted maleimides using free radical chain growth polymerization .

N- substituted maleimides were prepared starting with reacting of maleic anhydride and primary aromatic amines to form several N-aryl substituted maleamic acids in high yield.

Table (1) lists the physical properties of prepared amic acids elemental analyses showed good agreement of the calculated and the found percentages and also I.R spectrum shows appearance of (C = O) band at (1700 - 1720 cm⁻¹) and (C = C) aromatic at (1400 - 1480 cm⁻¹). The amic acid allowed to react with acetic anhydride, sodium acetate mixture

according to literature ^(16,17). These compounds were characterized by C.H.N Analyses and I.R spectram which showed (C = O) at 1675 cm⁻¹ and (C-N) band at 1135 cm⁻¹ with aromatic (C = C) at (1470 cm⁻¹) . yields of the corresponding N-aryl maleimides were fair and were used for copolymerization with compound (II) using AIBN or benzyl peroxide as the initiator . Table (3) lists softening points , viscosities and solvents used for purification of the prepared copolymers . I.R spectrams were used to detect copolymers wich showed the major absorption bands like (C = O) at (1700 cm⁻¹) , aromatic (C = C) at (1420 - 1480 cm⁻¹) , (C-O-C) cyclic ether at (1250 cm⁻¹) and disappearance of vinylic (C = C) band.



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