Synthesis and Characterization of Some Carbohydrate Based Monomers

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Carbohydrate based polymers have emerged as exciting topics of the polymer research, due to a worldwide focus on sustainable materials. The biodegradable polymers are indispensable in the modern society and their importance is continuously growing. We report here the synthesis and characterization of a new class of biodegradable copolymers derived from monosaccharides. The synthesis of glycomonomers 3-O-acryloyl-1,2:5,6-di-O-isopropylidene-α-glucofuranose (ADAG), and 1-O-acryloyl-2,3:5,6-di-O-isopropylidene-α-mannofuranose (ADAM) was accomplished by the reaction of the free OH of 1,2:5,6-di-O-isopropylidene-α-glucofuranose (DAG), and 2,3:5,6-di-O-isopropylidene-α-mannofuranose (DAM) with acryloyl chloride. After purification, the resulting unsaturated derivatives of glucose and mannose were characterized by FT IR and NMR spectroscopy and then were copolymerized with some acrylates and methacrylates. The influences of the nature of initiators were investigated using DSC analysis.

Key words: carbohydrate, biomaterials, glycopolymers

The polymers are indispensable materials for the modern society, but their utilization is entailed by the short period of use comparing to the long term pollution they are producing after exploitation [1, 2].

In the last decade, carbohydrates have attracted great attention as renewable resources for the chemical industry [3]. From an economical as well as an ecological point of view, renewable resources have many advantages [4]. There has been a worldwide understanding that mono-, di-, oligo- and polysaccharides can provide the raw material for the production of numerous industrial consumer goods [5], e.g. polymers and co polymers derivatives of carbohydrates offer thrilling opportunities for biomaterials and drug delivery applications [6-8].

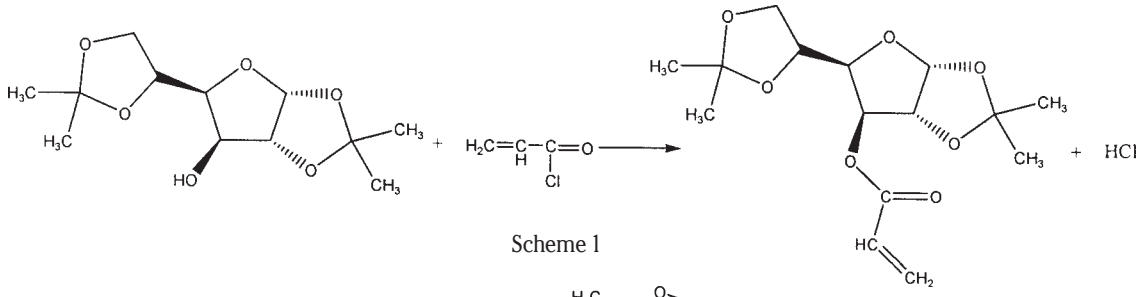
The glycopolymers include both artificial polymers grafted on carbohydrates and polymers derived from modified sugars through chemical syntheses [9].

Copolymerization of modified oligosaccharides with corresponding monomers not only increases their hydrophilicity, but they provide also potential advantages for their use as [10].

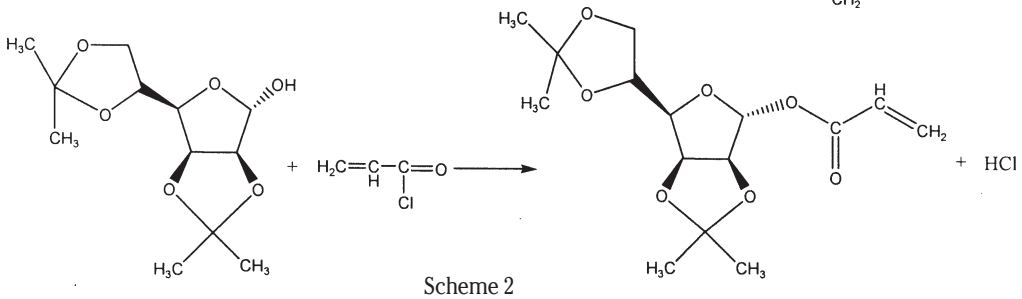
This contribution refers to the syntheses and characterization of glycomonomers derived from glucose and mannose and their copolymerization with some acrylates and methacrylates: butyl acrylate (BA), 2-ethylhexyl methacrylate (2-EHMA), 2-ethylhexyl acrylate (2-EHA) and 2-hexylpropyl methacrylate (2-HPMA).

Experimental part

The key intermediaries in the synthesis of the glycopolymers, diacetoneglucose (DAG) and diacetonemannose (DAM) were obtained according to the literature [11, 12]. These intermediaries were further reacted with acryloyl chloride (AC) (scheme 1, scheme 2), according to [13]:



Scheme 1



Scheme 2

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Table 1
IR DATA FOR ADAG AND ADAM [ν, cm^{-1}]

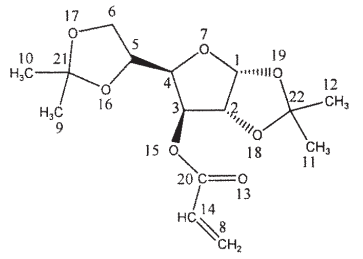
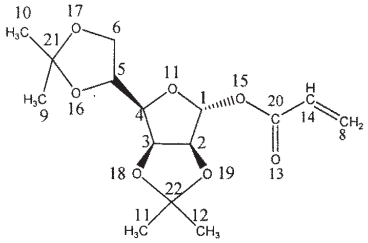
Compound	Peak at (cm^{-1})	Assignment
 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose (ADAG)	2985.4	Aliphatic C-H stretching
	1730.1	Intense vibrations of C=O stretching
	1375.4;1166.2; 1069.8 and 1018.1	C-O frequency of the esters
	846.9	Out of plane γ vibrations for aliphatic C-H stretching
	735.8 and 633.4	Out of plane γ vibrations for aliphatic C-H stretching
 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-mannofuranose (ADAM)	2983.7	Aliphatic C-H stretching
	1733.3	Intense vibrations of C=O stretching
	1374.6;1207.3 and 1061.8	C-O frequency of the esters
	846.0	Out of plane γ vibrations for aliphatic C-H stretching
	753.7 and 663.7	Out of plane γ vibrations for aromatic C-H stretching

Table 2
^{1}H-NMR DATA FOR ADAG AND ADAM [$CDCl_3$, δ (ppm)]

Compound	H_1	H_2	H_3	H_4	H_5	H_6
ADAG	5.893 5.912 d,1H	4.534-4.552 dd,1H	5.307-5.338 dd,1H	4.257-4.272 dd,1H	4.237-4.252 ddd,1H	4.039-4.078 dd,1H
	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{14}
	5.893-5.912 dd,1H 6.422-6.509 dd,1H	1.415 s, 3H	1.535 s, 3H	1.286 s, 3H	1.388 s, 3H	6.071-6.209 dd,1H
Compound	H_1	H_2	H_3	H_4	H_5	H_6
ADAM	6.205 6.255 d,1H	4.740-4.769 dd,1H	4.860-4.908 dd,1H	4.071-4.144 dd,1H	4.369-4.460 ddd,1H	4.006-4.049 dd,1H
	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{14}
	5.931-5.879 dd,1H 6.412-6.499 dd,1H	1.461 s, 3H	1.499 s, 3H	1.256 s, 3H	1.352 s, 3H	6.023-6.185 dd,1H

To a solution containing 5 g of 1,2:5,6-di-O-isopropylidene-α-glucofuranose (DAG), or 2,3:5,6-di-O-isopropylidene-α-mannofuranose (DAM) in acetone, 15 ml 5N NaOH solution was added. The solution was cooled to 0°C and stirred for 2h; then acryloyl chloride (AC) (molar ratio 1:2, DAG (DAM): AC) was added drop wise. The stirring was continued for another 3 h, whereupon 50 mL of water was added. The resulting product was extracted with chloroform, washed with water and dried over Na_2SO_4. The solvent was driven off at low pressure under inert gas. The residue was colorless viscose syrup. The yield was 75%. The product is soluble in acetone, benzene, dichloroethane, chloroform, DMF, DMSO, petroleum ether and alcohols.

After purification using silica gel flash chromatography (hexane: ethyl acetate = 3:1), the glycomonomers were characterized by NMR and FT IR spectroscopy (NMR Bruker Advance 300 spectrometer - at a frequency of 300.133 MHz, for ^{1}H and 75.464 MHz for ^{13}C - and respectively, FTIR BRUKER Vector 22 spectrometer equipped with an ATR DIAMANT cellule).

The copolymerization of these glycomonomers, with BA, 2-EHMA, 2-EHA respectively 2-HPMA (molar ratio 1:2) were carried out using differential scanning calorimetry on a Pyris DSC 200 device. For these studies the following procedure was applied: the glycomonomer was dissolved in the co-monomer and then the initiator - benzoyl peroxide (POB) or lauroyl peroxide (POL) - is added (1% wt. from

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_8
ADAG	105.033	83.249	79.718	77.698	72.404	67.075	131.991
	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{20}	$C_{21, 22}$
	26.169	25.213	26.80	26.684	127,709	164.658	112.942 112,282
Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_8
ADAM	101.071	85.120	82.400	79.318	72.883	66.853	132.192
	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{20}	$C_{21, 22}$
	25.139	24.663	27,010	25,953	127.865	164.426	113,309 109,37

Table 3
^{13}C-NMR DATA FOR ADAG AND ADAM [$CDCl_3$, δ (ppm)]

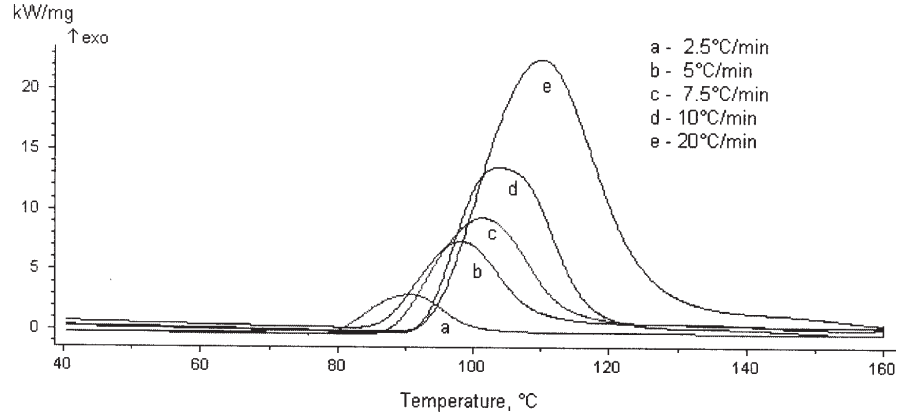


Fig. 1. DSC curves for the copolymerization process of ADAG with BA at different heating rates using POB as initiator

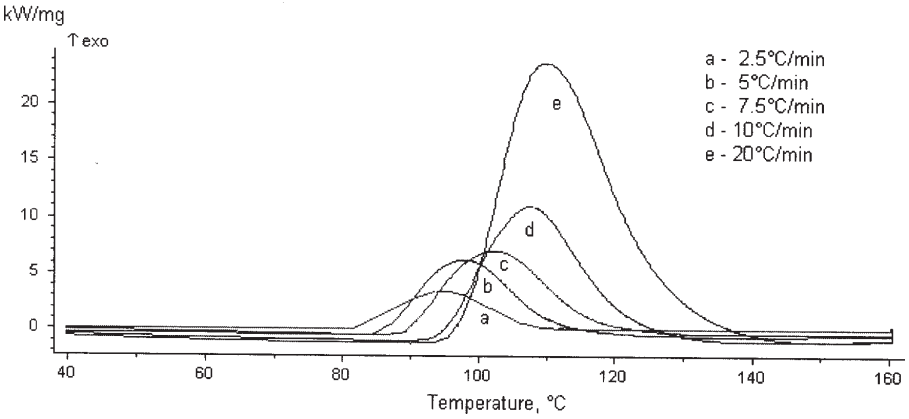


Fig. 2. DSC curves for the copolymerization process of ADAG with BA at different heating rates using as initiator POL

the mixture) and the mixture was stirred until the peroxide was dissolved.

Results and discussions

The structure of the new compound was confirmed by spectral analysis.

Thus, from the FTIR spectra of ADAG and the ADAM (table 1), comparatively to FTIR spectra of DAG and DAM [11, 12], it can be observed that the absorption bands specific to OH groups were no longer present in the spectrum, while the intense absorption bands characteristic to the C=O ester group were found in the region 1730.1 cm^{-1} for ADAG and 1733.3 cm^{-1} for ADAM. The absorption bands characteristic to esters can be also identified.

Both the ^{1}H-NMR spectrum (table 2) and ^{13}C-NMR spectrum (table 3) confirm the presence of the double bond in ADAG and ADAM by specific protons signals specific to C=C-H group and respectively by the carbon signals characteristic to C=C groups (C1, C7). Furthermore, the structures of acrylic ester are indicated by the carbon signals characteristic to O=C-O groups (C6).

The batch copolymerization of ADAG and respectively ADAM with the mentioned acrylates and methacrylates (BA, 2-EHMA, 2-EHA and 2-HPMA) gives transparent polymers with different degrees of elasticity.

To establish the activation energy for the polymerization processes, the DSC measurements were performed under nitrogen atmosphere and under dynamic conditions (40 to 200°C with 2.5; 5; 7.5; 10 and 20 K/min).

Figures 1 and 2 exemplify the DSC thermogram for the copolymerization of ADAG- BA system. As expected, the peak temperatures increase along the rise of the heating rate. Similar behaviors were observed for all the copolymerization systems.

A widely applied method for the determination of the activation energies, the Kissinger method, uses the peak temperature of each DSC curve [14]. Its characteristic equation is:

$$\ln\frac{\beta}{T^2_p} = \ln(ARF(\alpha)) - \frac{E}{RT_p} \quad (1)$$

where:
β – heating rate (K/min);
T_p – peak temperature;
A – pre-exponential factor;
$F(\alpha)$ – kinetic model function;
E – the activation energy (J/mol)
R- gas constant (J/mol K).

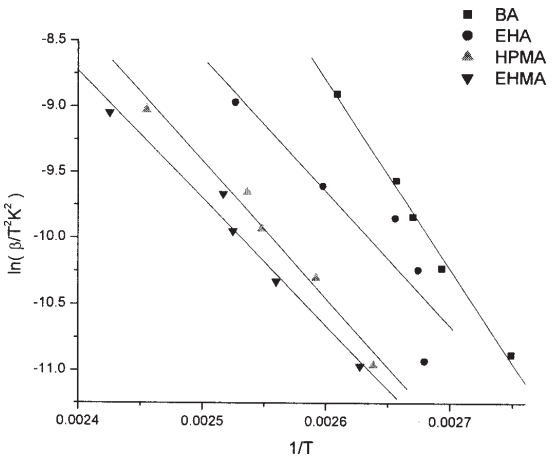


Fig. 3. Kissinger lines for the copolymerization of ADAM with: BA, 2-EHMA, 2-EHA and, respectively, 2-HPMA using POB as initiator

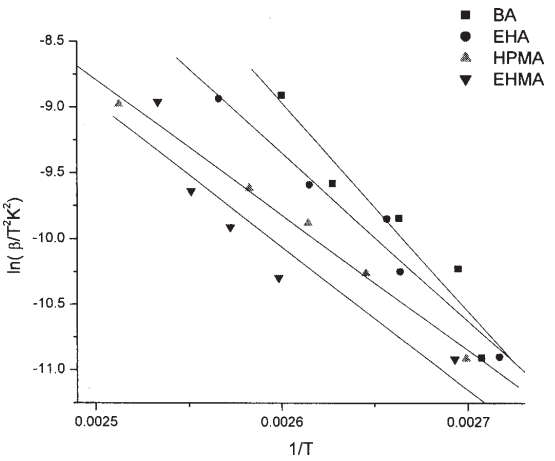


Fig. 4. Kissinger lines for the copolymerization of ADAM with BA, 2-EHMA, 2-EHA and, respectively, 2-HPMA using as initiator POL

Table 4
ACTIVATION ENERGIES VALUES FOR THE COPOLYMERIZATION OF THE GLYCO MONOMERS WITH DIFFERENT ACRYLATES AND METHACRYLATES

Co-monomers	E [kJ/mol]			
	ADAG		ADAM	
	POB	POL	POB	POL
BA	77.114	97.099	67.036	93.540
2-EHMA	80.252	91.370	76.272	89.833
2-HPMA	71.407	70.112	64.365	59.599
2-EHA	88.212	99.842	79.992	90.780

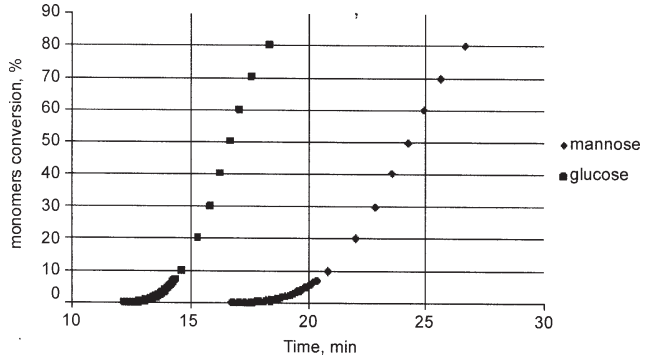


Fig. 5. Monomers conversion vs. time (copolymerization system glycomonomer – BA – POB)

Figures 3 and 4 show the Kissinger line for the copolymerization process for ADAM with BA, 2-EHMA, 2-EHA and 2-HPMA using POB, respectively POL as initiator.

Table 4 summarizes the activation energies, calculated using the Kissinger method, for all the copolymerization systems investigated. The activation energies obtained for the copolymerization using as initiator POL are higher than the activation energies values obtained using as initiator POB.

The monomers conversions vs. time (fig. 5) indicate a better reactivity of the monomer derived from glucose: a shorter induction period and a higher rate of reaction (see slope of the curves).

Conclusions

Two glycomonomers 3-O-acryloyl-1,2:5,6-di-O-isopropylidene-α-glucofuranose (ADAG) and 1-O-acryloyl-2,3:5,6-di-O-isopropylidene-α-mannofuranose (ADAM) were synthesized, purified and characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

The copolymerization of the glycomonomers with different acrylates and methacrylates was investigated by DSC. The activation energies for these copolymerization processes were calculated using Kissinger method. The results indicate that the monomer derived from glucose is more reactive than the one derived from mannose.

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