Synthesis and Characterization of New Glycopolymers Based on Monosaccharides and Maleic Anhydride

II. Mannose derivatives

ANA-MARIA PANA[1]*, LUCIAN-MIRCEA RUSNAC[1], GEZA BANDUR[1], CALIN DELEANU[2], MIHAELA BALAN[2], MIHAELA SILION[2]

[1] "Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 P-ţa Victoriei, 300006, Timisoara, Romania

[2] "Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Gr. Ghica Voda, 700487, Iasi, Romania

This paper presents the synthesis and characterization of a new class of biodegradable copolymers based on carbohydrates. A new oligomer was synthesized by the polycondensation of 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose with propane-1,3-diol in the presence of p-toluenesulfonic acid and then it was copolymerized with 2-hydroxypropyl (meth)acrylate, using benzoyl peroxide as initiator. The mannose based oligomer was characterized by FTIR and NMR spectroscopy and HPLC-MS, and the copolymers were analyzed using FTIR and thermogravimetry.

Keywords: D-mannose, glycopolymers, maleic anhydride

As our fossil raw materials are irrevocably decreasing and the pressure on our environment is building up, the progressive changeover of the chemical industry to renewable feedstocks for their raw materials emerges as an inevitable necessity [1].

In the current world, conventional plastics are derived from petroleum, which is a non-easy renewable resource. However, the usage of these plastics is continuously increasing. On the other hand, the economical and environmental concerns imply to take the problem of post consumer recycling of these materials into consideration. Today, it appears that it is not practical to use synthetic polymers for certain applications such as bags, agricultural mulch films and food packaging, since these artifacts contain many organic residues and have a less life time. This is why many recent investigations are focused to have the biodegradable polymers produced from renewable resources such as plants, animals and microbes through chemical reactions [2].

One group of monomers intended for use in polymeric biomaterial applications are those containing carbohydrate functionality. Copolymerization allows for the creation of hydrophilic materials containing common monomers (e.g., methyl methacrylate) resulting in polymers with high strength, good coating characteristics and the ability to form hydrogels. Copolymerization of carbohydrate monomers not only increases hydrophilicity, there are potential advantages toward biomaterials applications as well. Moreover, polymers with pendant carbohydrate moieties have been useful in clinical diagnostic applications, and for targeted gene therapies. Other applications for polymeric materials containing carbohydrate moieties include cell surface mimics, cell adhesion scaffolds, materials for reduced platelet and protein adsorption, thin film coatings and anticoagulants [3-5].

Until now, polymers containing the carbohydrate into the side chain were synthesized [6]; these are the derivatives of monosaccharide (glucose, galactose, mannose, xylose) acrylates and methacrylates [7] as well as disaccharides (lactose) and polysaccharides (i.e. inulin) [8], with protected or unprotected OH groups. The syntheses of these polymers were carried out by radical polymerization.

This paper presents the synthesis of a new D-mannose based oligomer, the saccharide skeleton being included into the polymeric chain. D-mannose was chemically modified in order to obtain a dicarboxylic acid, 1-benzyl-5,6-(*bis*(maleyloxy))-2,3-isopropylidene-D-mannofuranose which was polycondensed with propane-1,3-diol, using p-toluenesulfonic acid as catalyst. This D-mannose oligomer was then copolymerized with 2-hydroxypropyl acrylate (HPA) and 2-hydroxypropyl methacrylate (HPMA). The structure of the new D-mannose based oligomer was confirmed using FTIR and NMR spectroscopy, the molar weight was determined by HPLC-ESI-MS, while the copolymers were analyzed by thermogravimetry.

Experimental part

Materials and methods

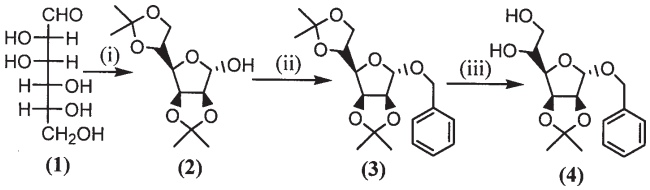
D-(+)-mannose (98%) (Man), benzyl bromide (98%) (BnBr), maleic anhydride (99%) (MAh), triethylamine (99%) (TEA), glacial acetic acid (99%) (AcOH), propane-1,3-diol (98%) (PD), p-toluenesulfonic acid monohydrate (99%) (APTS), 2-hydroxypropyl acrylate (HPA) and 2-hydroxypropyl methacrylate (HPMA) were purchased from Merck and were used without further purification. Acetone (ChimoPar Bucureşti), N,N-dimethylformamide (DMF) (Merck), methanol (MeOH) (Chimopar Bucureşti), n-hexane (Merck), ethyl acetate (AcOEt) (Merck), toluene (Chimopar Bucureşti) and methylene chloride (Chimopar Bucureşti) were purified according to literature [9].

Synthesis of 1-benzyl-2,3-isopropylidene-D-mannofuranose (4)

The diacetone derivative of D-mannose (1) was obtained according to a literature protocol [10]. 2,3:5,6-di-O-isopropylidene-D-mannofuranose (2) was benzylated using benzyl bromide and basic catalysis (sodium hydride, NaH) in anhydrous DMF. The catalyst excess was neutralized by an excess of MeOH [11]. Then, the selective deprotection of the isopropylidene group linked to the 5th and 6th positions of the furan ring was performed using 80% acetic acid, at 70-75°C. 1-benzyl-2,3-isopropylidene-D-mannofuranose (4)

* *email: ana.chis@chim.upt.ro; Tel.: 0727 853935*

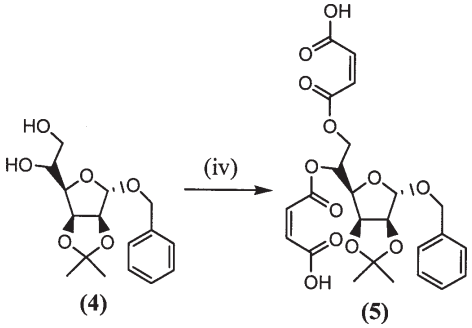
was purified by silicagel column chromatography (hexane: AcOEt = 1:1, v/v) (scheme 1).



Scheme 1. The reactions involved in the synthesis of 1-benzyl-2,3-isopropylidene-D-mannofuranose; i) acetone, H_2SO_4, 0°-r.t., 5h; ii) BnBr, NaH, DMF, MeOH; iii) CH_3COOH, 80%, 45 min, 70-75°C

Synthesis of 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose (5)

A solution of 4.5 g of (4) in 20 mL anhydrous DMF is stirred vigorously and heated to 60-65°C. Then 8.5 g of maleic anhydride are added while stirring and, after complete dissolution, 0.6 mL TEA are poured dropwise (scheme 2). The reaction is monitored using TLC plates (AcOEt : MeOH = 1:1, v/v). After approximately 20 h, the TLC shows only one peak at Rf = 0.33. The reaction is stopped by adding 100 mL of distilled water. The dicarboxylic acid is extracted several times into methylene chloride, then washed with LiCl water solution 10%, distilled water and then dried over sodium sulphate [12-14].



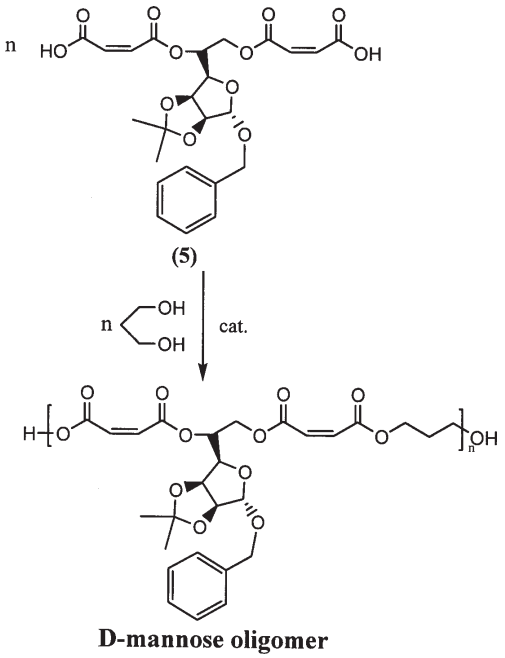
Scheme 2. Synthesis of 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose (5); iv) MAh, TEA, 20 h, 60°C

Synthesis of the oligomer by polycondensation of 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose with propane-1,3-diol

4 g of (5) are vigorously stirred into 20 mL of toluene, whereupon 0.6 mL of propane-1,3-diol were added. The mixture was heated up to 95-100°C and 9.2 mg *p*-toluenesulfonic acid were added (scheme 3). The flask was provided with a Dean-Stark device to collect the water formed during the polycondensation. The reaction was monitored by acidity indices and, as the reaction evolves, the formation of the oligomer at the bottom of the flask can be observed (28 h). The toluene was removed and the product was dissolved in chloroform. The solvent was removed in vacuum (yield aprox. 70%).

Synthesis of the copolymers via free radical bulk polymerization

The D-mannose oligomer was copolymerized with 2-hydroxypropyl acrylate (HPA) and 2-hydroxypropyl methacrylate (HPMA) in weight ratios of 1:1, 1:2, 1:3 and 1:4 (oligomer : acrylate or methacrylate) – benzoyl peroxide was the initiator. The copolymerization was carried out according to the following procedure: the oligomer was dissolved in a certain amount of HPA or HPMA, at 40°C. Then benzoyl peroxide is added (1% wt.) and stirred vigorously. This homogenous mixture was then placed into glass tubes. Gradually the temperature was



Scheme 3. Synthesis of D-mannose oligomer

increased with 10 degrees per hour until 110°C. The copolymers thus obtained are crosslinked.

Characterization of the products

All syntheses were monitored using thin layer chromatography (TLC) performed on silica gel plates, Merk, DC-Autofolien Kiesegel 60 F 254, using different eluants. The FTIR spectra were recorded on a Jasco FT/IR-410 spectrometer. The IR analyses were done using KBr pellets for solid samples and between KBr glasses for the liquid ones; the ATR Diamant device was used for recording the copolymers spectra. The NMR spectra were recorded on Bruker Avance DRX 400 spectrometer in DMSO-d_6 using tetramethylsilane as reference.

Mass spectrometry results were obtained using an Agilent 6500 Series Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) LC/MS. The sample was separated on a Zorbax SB-C18 (4.6 x 150 mm, 5µm) reverse phase column. The mobile phase consisted of water (solvent A) and methanol (solvent B) filtered and degassed under vacuum before use. The gradient program was 95% solvent B followed by ramping up to 100% solvent B at 5 min and then maintaining for 10 min. The total run time was 20 min. The flow rate was 0.5 mL/min; the detector UV-VIS DAD was monitored at 210 nm. The LC System was directly connected to the electrospray ion source. The Q/TOF MS conditions were set as follows: electrospray ionization (positive ion mode), drying gas (N_2) flow rate 5.0 L/min; drying gas temperature 325°C; nebulizer pressure 5 psig, capillary voltage 4000 V; fragmentation voltage 200 V; the full-scan mass spectra of the investigated compounds were acquired in the range *m/z* 50–3000. Data were collected and processed using a MassHunter Workstation software.

The thermogravimetric analyses were performed using Netzsch TG 209, in nitrogen atmosphere and dynamic conditions. The data were collected and processed using a Proteus Analysis data system, from Netzsch.

Results and discussions

The products obtained were all characterized using FTIR spectroscopy. Figure 1 comparatively presents the FTIR spectra of diacetonemannose (2), 1-benzyl-2,3:5,6-diisopropylidene-D-mannose (3), 1-benzyl-2,3-iso-

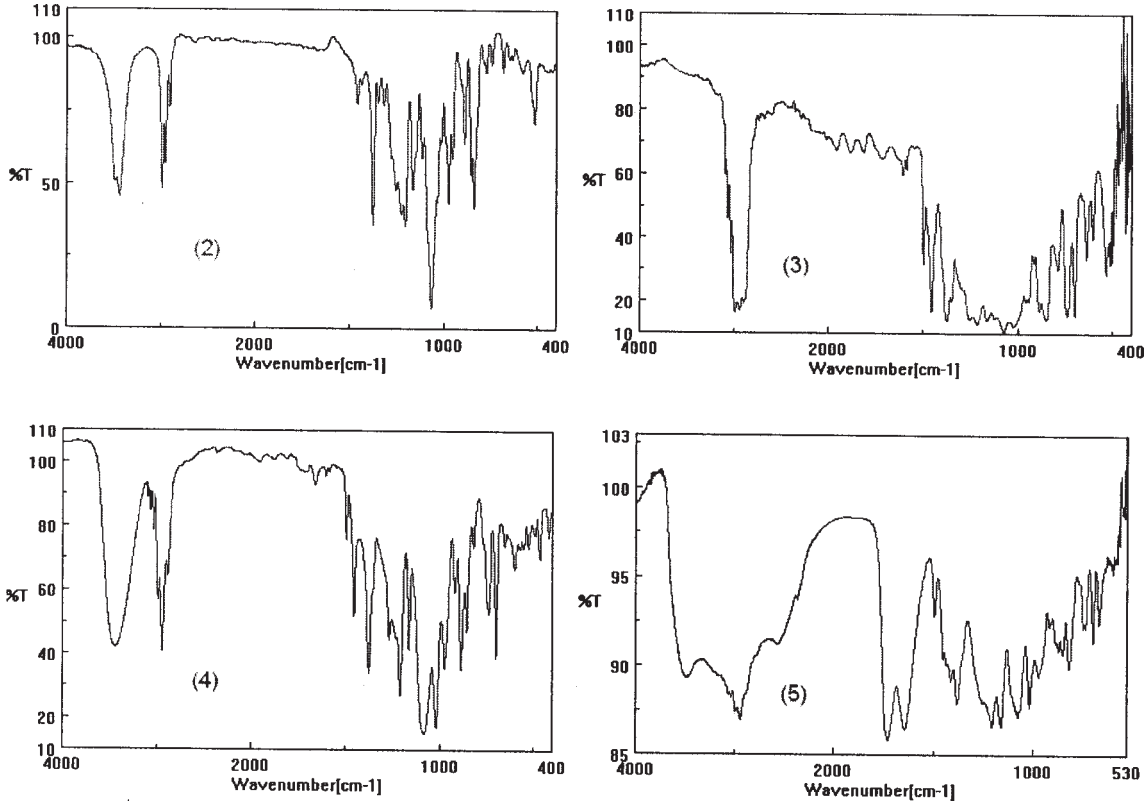


Fig. 1. The FTIR spectra of diacetonemannose (2), 1-benzyl-2,3:5,6-diisopropylidene-D-mannfuranose (3), 1-benzyl-2,3-isopropylidene-D-mannofuranose (4) and 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose (5)

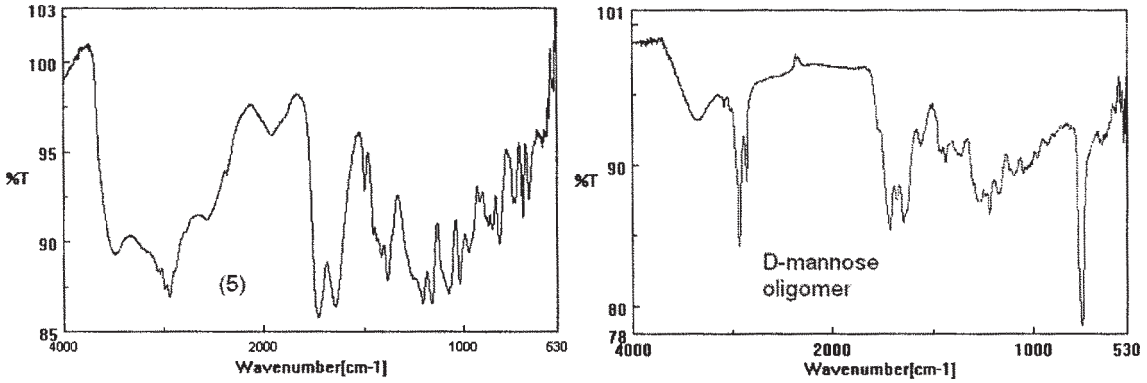


Fig.2. The FTIR spectra of product (5) and D-mannose oligomer

propylidene-D-mannofuranose (4) and 1-benzyl-5,6-(bis(maleyloxy))-2,3-isopropylidene-D-mannofuranose (5).

By comparing the FTIR spectra of diacetonemannose (2) and benzyldiacetonemannose (3) one can observe that the intense OH band at about 3400 cm^{-1} has disappeared in the case of product (3), while the aromatic C-H bands appeared at about 3000-3100 cm^{-1}. The FTIR spectrum of (4) confirms the selective deprotection of the isopropylidene from the 5th and 6th positions of the mannofuranose ring, by the broad peak at about 3400-3500 cm^{-1} corresponding to the associated O-H bonds, while the C-H aromatic bonds are still present at about 3000-3100 cm^{-1}, which means that the benzyl protective group has not been pushed away from the structure. The FTIR of (5) confirms the formation of the dicarboxylic acid: the C=O ester intense signal at about 1730 cm^{-1}, the broad OH signal at about 3500 cm^{-1} belonging to the carboxylic hydroxyl and the intense peak from about 1650 cm^{-1} characteristic to C=C bond.

The D-mannose oligomer structure was also confirmed via FTIR spectroscopy. Figure 2 comparatively shows the changes occurred during the polycondensation. The C=O intense peak from 1730 cm^{-1} expresses the esteric bond along the C-O stretching from about 1100 cm^{-1}, while the C=C group from the maleic anhydride skeleton is still present in the spectrum at about 1640 cm^{-1}.

The polycondensation was monitored using acidity indices. Figure 3 shows the variation of the acidity index in time for the polycondensation reaction.

The NMR spectrometry confirms also the proposed structure for the D-mannose oligomer. The ^{1}H-NMR spectrum (fig. 4) shows the characteristic signals for the isopropylidene protons between 1.2 and 1.4 ppm, proving that this protective group has not been lost during the polycondensation which took place in rather acid conditions; also, the signals between 7.2 and 7.5 belong to the aromatic ring from the benzyl moiety linked to the sugar ring. The C-H groups from the sugar ring express signals between 4.5 and 5.8 ppm, overlapped with the signals coming from the diol skeleton. The H-C=C=H bonds are

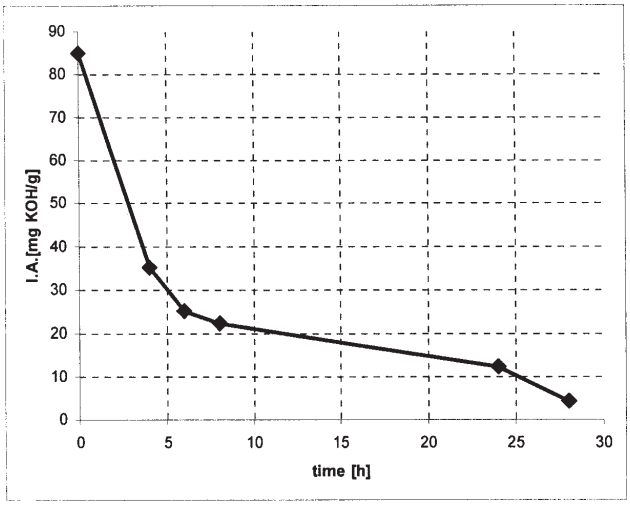


Fig. 3. Variation of acidity indices in time for the polycondensation process

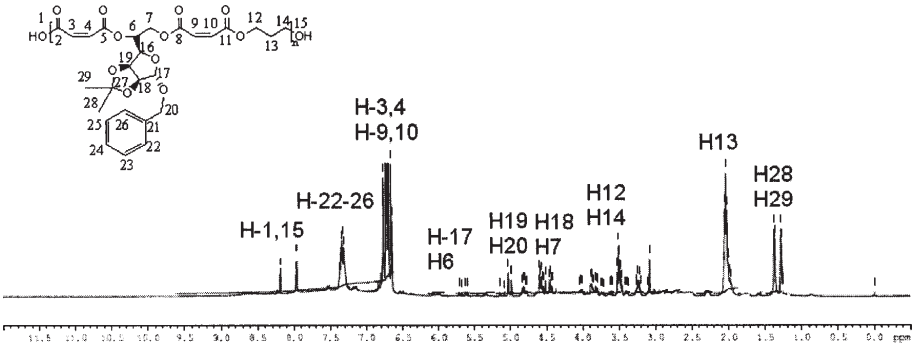


Fig. 4. The ^{1}H-NMR spectra of D-mannose oligomer

placed between 6.26 and 6.85 ppm, while O-H terminal group shows signals at about 8.5 ppm.

The ^{13}C-NMR (fig. 5) confirms the structure as well. The isopropylidene CH_3 can be found at about 26 ppm, while the quaternary carbon is placed at about 112 ppm. The aromatic C-C bonds from the benzyl protective group are expressed by signals between 127 and 136 ppm. The C=C bond can be found between 132 and 135 ppm, while the C=O ester bond is present in the spectrum between 165 and 168 ppm. The anomeric D-mannose center is identified at about 107 ppm. The C-C bond for the sugar ring along with the other aliphatic C-C from the oligomer structure can be identified between 59 and 87 ppm.

The HPLC-ESI-MS analysis was performed in order to assess the molar weight of D-mannose oligomer synthesized by polycondensation. The oligomer was

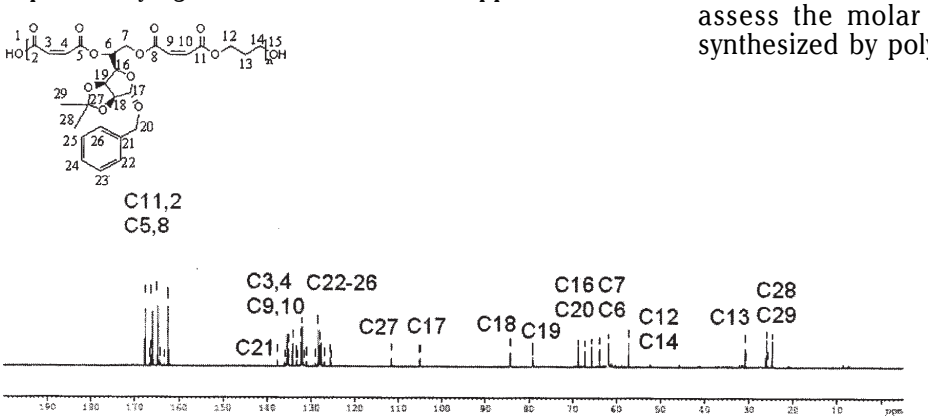


Fig. 5. The ^{13}C-NMR spectrum of D-mannose oligomer

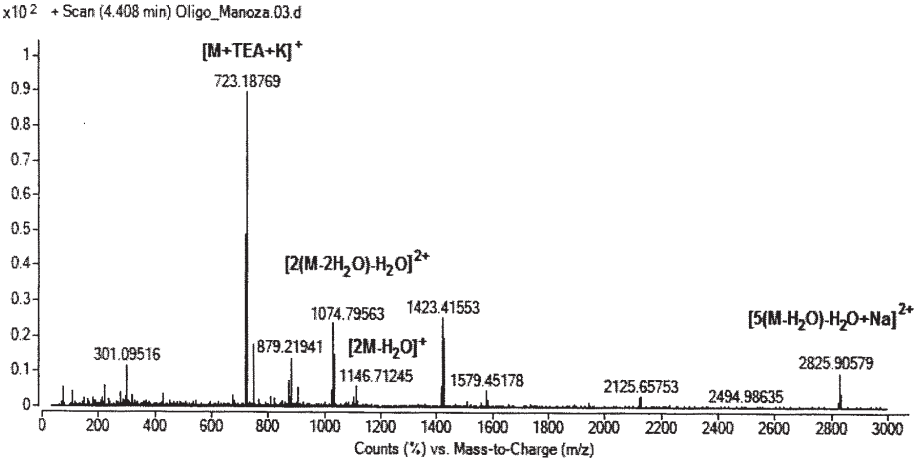


Fig. 6. The HPLC-ESI-MS spectrum of D-mannose oligomer (methanol solution)

Table 1
SOLUBILITY OF D-MANNOSE OLIGOMER INTO DIFFERENT COMONOMERS

Reactive solvent	Butyl acrylate	Methyl Methacrylate	Styrene	2-hydroxypropyl Acrylate	2-hydroxypropyl Methacrylate
Solubility	None	slightly	None	Good	Very good

Table 2
COPOLYMERS SYNTHESIZED

copolymer	copolymer	Mass ratio Oligomer: reactive solvent
M_HPA1	M_HPMA1	1 : 1
M_HPA2	M_HPMA2	1 : 2
M_HPA3	M_HPMA3	1 : 3
M_HPA4	M_HPMA4	1 : 4

dissolved into methanol and 5µL of the 100 µg/mL solution was injected into the HPLC device. The blank chromatogram (not shown) presented no peaks beside the solvent front. The retention time for D-mannose oligomer was 4.408 min.

The collected mass spectrum for the D-mannose oligomer is presented in figure 6. The base peak is observed at m/z = 723.187 and it is associated with the presence of the single charge adduct $[M+TEA+K]^+$ of the oligomer for n = 1, associated with potassium and traces of triethylamine (traces coming from the HPLC column or from the diacid synthesis). The peaks accompanying the base peak are $[2(M-2H_2O)-H_2O]^{2+}$ at m/z = 1074.795 and $[2M-H_2O]^+$ at m/z = 1146.712 representing two mer units which have lost one or two water molecules by successive dehydrations. Finally, the peak at m/z 2825 corresponding to the double charged Na adduct of the dehydrated oligomer ($[5(M-H_2O)-H_2O+Na]^{2+}$), which directly confirmed the D-mannose oligomer n = 10 formation. These results indicate that the actual molar weight of the D-mannose oligomer is 5820 Da and corresponds to 10 mer units connected to one another.

The solubility of the D-mannose oligomer into different reactive solvents was tested in order to further obtain copolymers derived from carbohydrates. The solubility results are presented in table 1.

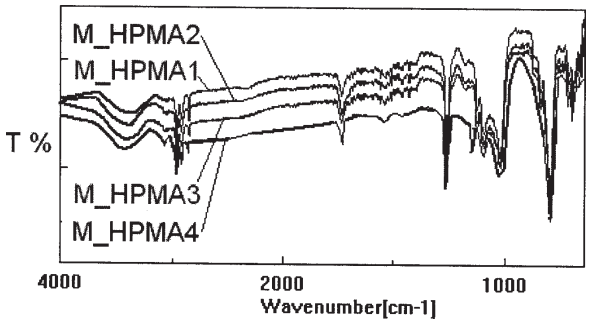


Fig. 7. The FTIR spectra of the copolymers derived from D-mannose oligomer and HPMA

Based on the solubility characteristics, different copolymers of D-mannose oligomer with 2-hydroxypropyl acrylate (HPA) and 2-hydroxypropyl methacrylate (HPMA) were synthesized. The syntheses were carried out considering different mass ratios (table 2) in order to determine the dependence of thermal stability on the oligomer content. The polymerization initiator chosen was benzoyl peroxide.

The FTIR spectra of the copolymers confirm the crosslinked structure of the new glycopolymers obtained (fig. 7). The O-H stretching from the HPMA skeleton expresses signal at about 3400 cm^{-1}, while the C-H aromatic bond is present in the spectrum between 3000 and 3100 cm^{-1}; the C-H aliphatic stretching from the polymer chain or from the oligomer structure are found between 2800 and 3000 cm^{-1}. The C=O esteric bond is

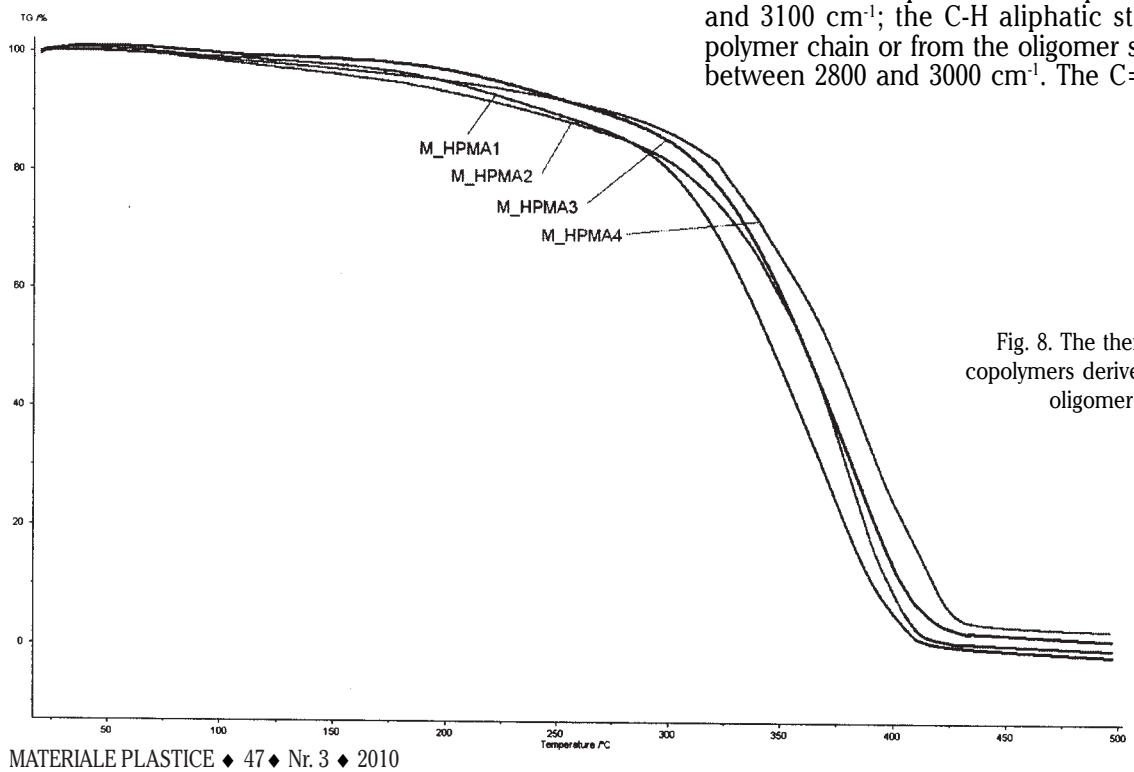


Fig. 8. The thermograms of the copolymers derived from D-mannose oligomer and HPMA

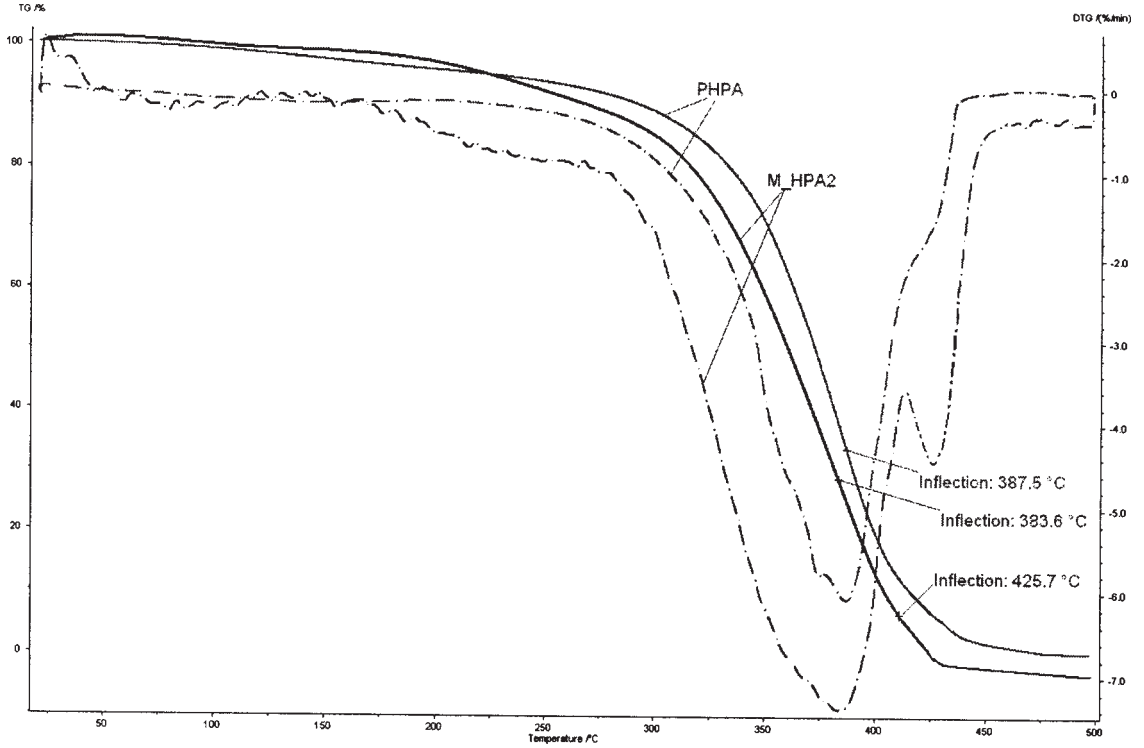


Fig. 9. The thermograms and their first derivative for the HPA homopolymer (PHPA) and one copolymer (M_HPA2)

expressed by signals at about 1730 cm^{-1}, while the C-O esteric bond is placed at 1180 cm^{-1}.

The copolymers were analyzed by thermogravimetry, in nitrogen atmosphere; the temperature was ranging between 20 and 500°C. The thermograms were registered using a heating rate of 5 K/min (fig. 8). The copolymers have good thermal stabilities and show two inflexion points (fig. 9): one corresponding to the decomposition of the oligomer skeleton (310÷360°C), while the other (370÷410°C) to the (meth)acrylic linkages within the complex crosslinked structure. This statement is confirmed by the thermograms (TG) and their first derivative (DTG) for the HPA homopolymer (PHPA) and one copolymer (M_HPA2).

The thermal stabilities of the D-mannose oligomer, HPA and HPMA homopolymers and all the new glycopolymers synthesized by copolymerization are analyzed on different temperature intervals; the corresponding weight losses are presented in tables 3 and 4. On the first temperature interval analyzed (20-100°C) for all copolymers the weight loss is inessential (less than 2%). For higher temperatures the weight loss increases, especially along the increase in oligomer content; the weight loss at temperatures ranging between 20 and 200°C does not exceed 6%. For temperatures between 20 and 300°C, the copolymers register a weight loss of about 14 to 16 percent, while the mannose oligomer is less stable and losses about 25% of its mass. The greatest weight loss is registered for temperatures ranging up to 400°C, and, of course, at 500°C almost all of the copolymers' mass are decomposed. It can be stated that by copolymerization the thermal stability of the crosslinked plastic materials improves significantly. By comparing the thermal stability of the HPA and HPMA copolymers, it can be observed that at lower temperatures (up to 200°C) the most stable materials are the ones based on the mannose oligomer and HPMA [15]. The thermal stability of the copolymers is superior to the thermal stability of the oligomer but significantly inferior to the homopolymers.

The activation energy for the thermal decomposition was evaluated as a result of a kinetic study. The thermal analysis was carried out using different heating rates: 2.5; 5; 7.5; 10 and 12.5 K/min. The activation energy was evaluated using Kissinger method; it can be calculated

sample	Weight loss (%)				
	20 - 100°C	20 - 200°C	20 - 300°C	20 - 400°C	20 - 500°C
oligomer	1.95	6.25	24.93	65.88	98.6
PHPMA	1.02	4.21	10.74	79.79	99.7
M_HPMA1	1.52	5.23	14.25	77.83	99.68
M_HPMA2	1.33	4.85	13.35	75.65	99.39
M_HPMA3	1.07	4.03	12.83	74.37	99.32
M_HPMA4	0.98	4.15	10.57	71.53	99.74

Table 3
WEIGHT LOSSES FOR THE HPMA HOMOPOLYMER (PHPMA), D-MANNOSE OLIGOMER AND THEIR CORRESPONDING COPOLYMERS

sample	Weight loss (%)				
	20 - 100°C	20 - 200°C	20 - 300°C	20 - 400°C	20 - 500°C
oligomer	1.95	6.25	24.93	65.88	98.6
PHPA	1.74	2.88	6.46	57.38	98.97
M_HPA1	1.83	5.63	15.82	78.95	98.93
M_HPA2	1.79	4.95	14.65	76.53	99.21
M_HPA3	1.33	4.72	13.87	75.95	99.45
M_HPA4	0.92	4.02	11.93	71.36	99.18

Table 4
WEIGHT LOSSES FOR THE HPA HOMOPOLYMER (PHPA), D-MANNOSE OLIGOMER AND THEIR CORRESPONDING COPOLYMERS

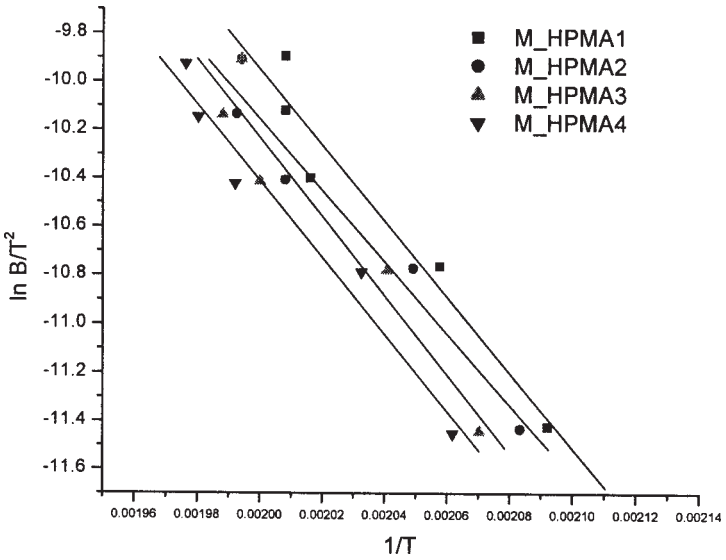


Fig. 10. The Kissinger lines for the first step of thermal decomposition in the case of HPMA copolymers

sample	Activation energy (kJ/mol)	
	First step	Second step
M_HPMA1	79.56	145.23
M_HPMA2	95.89	156.2
M_HPMA3	105.59	154.4
M_HPMA4	115.63	163.5

Table 5
ACTIVATION ENERGY VALUES OF THE THERMAL DECOMPOSITION PROCESS OF THE COPOLYMERS WITH HPMA

sample	Activation energy (kJ/mol)	
	First step	Second step
M_HPA1	84.56	148.23
M_HPA2	98.53	146.25
M_HPA3	116.2	175.23
M_HPA4	121.5	167.24

Table 6
ACTIVATION ENERGY VALUES OF THE THERMAL DECOMPOSITION PROCESS OF THE COPOLYMERS WITH HPA

from the slope of the linear dependence $\ln(\beta/T_i^2) = f(1/T_i)$, where T_i is the inflexion temperature from the thermogram and β is the heating rate. Figure 10 shows the Kissinger linear dependence for the first step of degradation in the case of the HPMA copolymers.

The thermal decomposition activation energy has similar values for the copolymers and it increases along the increase in HPA and HPMA content (table 5 and 6). The smallest value is registered for the HPMA copolymer with a weight ratio of 1:1 and the first step of degradation. It is logical that the first step of decomposition has lower activation energy values than the second step of thermal decomposition. The biggest value for the activation energy is registered for the HPA copolymer which has the biggest acrylate content.

Conclusions

A new D-mannose oligomer was synthesized; the structure contains the sugar moiety inside the main polymeric chain. The structure proposed was confirmed via FTIR and NMR spectroscopy and the molar weight was evaluated using HPLC-ESI-MS. The double bonds of the D-mannose oligomer structure were used in order to copolymerize with a usual comonomer; the HPA and HPMA reactive solvents were chosen because of their mutual solubility in the presence of the oligomer. The crosslinked copolymers obtained were analyzed using thermogravimetry and it was concluded that by copolymerization the thermal stability of the new oligomer was significantly increased. The kinetic study for the thermal decomposition was carried out in order to evaluate the activation energy of the degradation process and the method applied for calculating the energy was Kissinger.

References

1.LICHTENTHALER, F.W., PETERS, S., C.R.Chimie, 7, 2004, p. 65
2.SAIAH, R., SREEKUMAR, P.A., LEBLANC, N., SAITER, J.M., Industrial crops and products, 29, 2009, p. 241
3.STANEK, L.G., HEILMANN, S.M., GLEASON, W.B., Carbohydrate Polymers, 65, 2006, p. 552
4.SANCHEZ-CHAVES, M., RUIZ, C., CERRADA, M.L., FERNANDEZ-GARCIA, M., Polymer, 49, 2008, p. 2801
5.VARMA, A.J., KENNEDY, J.F., GALGALI, P., Carbohydrate Polymers, 56, 2004, p. 429
6.DE MENEZES, A.J., PASQUINI, D., DA SILVA, CURVELO, A.A., GANDINI A., Carbohydrate Polymers, 73, 2009, p. 437
7.SALAGEAN, I.R., BANDUR, G., MARTIN, P., LEQUAR,T V., RUSNAC, L., Rev. Chim. (Bucharest), **60**, no. 9, 2009, p. 905
8.RUSU, G., BANDUR, G., RUSNAC, L., MANOVICU, I., PODE, V., JOLY, N., MARTIN, P., Mat. Plast., **44**, no.2, 2007, p. 112
9.ARMAREGO, W.L.F., PERRIN, D.D., Purification Of Laboratory Chemicals, Fourth Edition, Butterworth-Heinemann Linacre House, Oxford, 1996, p. 176
10.HANESSIAN, S., Preparative Carbohydrate Chemistry, CRC Press, 1997, p. 18
11.OSBORN, H.M.I., An introduction to carbohydrate synthesis, Academic Press, 2002, p. 50
12.PANĂ,, A.M., RUSNAC, L.M, BANDUR, G., ŞIŞU, E., BADEA, V., SILION, M, Mat. Plast., **47**, no. 1, 2010, p. 28
13.PANĂ, A.M., PASCARIU, M.C., BANDUR, G., RUSNAC, L.M., Chemical Bulletin of "Politehnica" University of Timişoara, 54(68), 2009, p. 93
14.PANĂ, A.M., RUSNAC, L.M., BANDUR, G., SILION, M., DELEANU, C., BĂLAN M., e-Polymers, 2010, in press
15.MENSZEL, J., PRIME, B., Thermal Analysis of Polymers, Wiley and Sons, Publications, 2009,p. 50

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