International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:6, No:4, 2012

Novel Glycopolymers Containing Carbohydrate Moiety: Copolymerization and Thermal Properties

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***Abstract*—**Polymers are one of the most widely used materials in our every day life. The subject of renewable resources has attracted great attention in the last period of time. New polymeric materials derived from renewable resources, like carbohydrates draw attention to public eye especially because of their biocompatibility and biodegradability. The aim of our paper was to obtain environmentally compatible polymers from monosaccharides. Novel glycopolymers based on D-glucose have been obtained from copolymerization of a new monomer carrying carbohydrate moiety with methyl methacrylate (MMA) via free radical bulk polymerization. Differential scanning calorimetry (DSC) was performed in order to study the copolymerization process of the monomer into the chosen co-monomer; the activation energy of this process was evaluated using Ozawa method. The copolymers obtained were characterized using ATR-FTIR spectroscopy. The thermal stability of the obtained products was studied by thermogravimetry (TG).

***Keywords*—** DSC, glycopolymer, monosaccarides, TG.

I. INTRODUCTION

IN the last period of time considerable attention has been paid in the field of biodegradable polymers. There is a spread worldwide consensus on the necessity for biodegradable plastics [1]. Polymeric biomaterials are of great interest in the medical field, food and cosmetic industries such as molecular recognition processes, drug delivery systems, cell culture and treatment of infectious diseases [2]-[4]. Glycopolymers can be defined as synthetic polymers having a non-carbohydrate moieties as pendant or terminal groups. Glycopolymers have enhanced biodegradability due to the sugar moiety from the polymeric structure [5], [6]. Non-biodegradability of the most commercially available plastics has caused many environmental problems. A feasible option can be provided by bioresources due to their inherent biodegradability and availability [7]. Ecological concerns and limits of petroleum resources have attracted great interest in using carbohydrates as raw materials in polymers synthesis [8], [9].

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Biodegradable polymers are the main type of biomaterials, therefore considerable attention has been given to them. Biopolymers are classified as natural or synthetic polymer. Synthetic biopolymers are very important for the development of biomedical filed [10], [11].

In this paper we describe the preparation of new carbohydrate based polymers. The glycopolymers were obtained from D-glucose which was chemically modified to obtain a new monomer carrying glucose moity. The glycomonomer was then copolymerized with methyl methacrylate (MMA), in bulk, using peroxide benzoyl (BPO) as initiator. These carbohydrate monomer may be useful in obtaining glycopolymers with potential biomedical relevance.

The thermal properties of the glycopolymers obtained were investigated; the glycopolymers are stable to thermal treatment. The structure of the copolymers was confirmed by ATR-FTIR spectra. The copolymerization process was investigated using DSC technique and the activation energy of the polymerization process was calculated using Ozawa method.

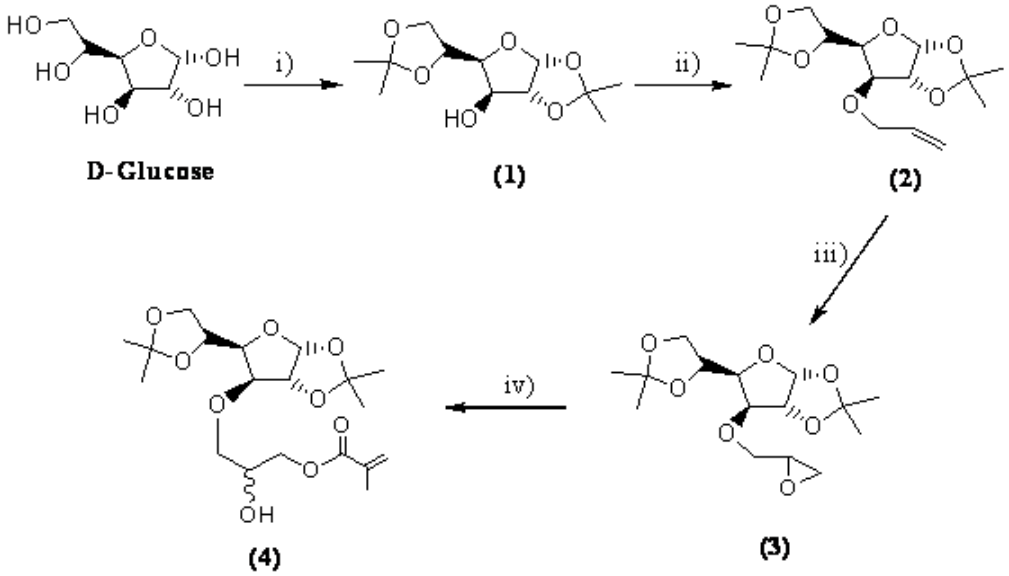

Fig. 1 Preparation of the D-glucose monomer: (i) acetone, H_2SO_4; (ii) AllCl, NaH, DMF; (iii) MCPBA, $CHCl_3$; (iv) methacrylic acid, TEA

II. Experimental

A. Monomer Synthesis and Their Further Copolymerization

The monomer was obtained by the procedure described in our previous paper according to Fig. 1 [12]. To obtain glycopolymers the monomer was dissolved in MMA (mass ratio 1: 1, 1: 2, 1: 3, 1: 4) and then the initiator – benzoyl peroxide (BPO) was added (1% wt. from the mixture); After the perfect omogenity the mixture was then placed into glass tubes and the temperature was increased until 110 ºC with 10 ºC/hour.

B. Preparation of DSC Sample

In table I are presented the samples prepared for the DSC analysis. The monomer was dissolved in MMA until perfect homogenity, then benzoyl peroxide was added (1% from the mixture). The mixture was stirred vigorously until the peroxide was dissolved then the small portions of the mixture were analyzed using DSC.

TABLE I
THE SAMPLES PREPARED FOR THE DSC ANALYSIS

Glycopolymers sample	Mass ratios D-glucose monomer: MMA
G_MMA1	1: 1
G_MMA2	1: 2
G_MMA3	1: 3
G_MMA4	1: 4

III. Materials And Methods

All reagents were used as purchased. The syntheses were monitored using thin-layer chromatography performed on silica gel plates, Merck silica gel 60 F_{254} aluminium sheets, using different eluant mixtures.

ATR-FTIR Analysis. The FTIR-ATR spectra were recorded on a Jasco FT/IR-410 spectrometer.

Differential scanning calorimetry. The copolymerization of D-glucose monomer with MMA was carried out using differential scanning calorimetry. The DSC diagrams were recorded on a Netzsch 204 DSC under nitrogen atmosphere and under dynamic conditions (with 2.5, 5, 7.5, 10, and 20 K/min from 20-200 ºC), operating Proteus Analysis software.

TG Analysis. The glycopolymers were analyzed by thermogravimetry, using a Netzsch TG 209, in nitrogen atmosphere and dynamic conditions with 10 K/min heating rate, at temperatures ranging between 20 and 500 ºC.

IV. Results And Discussion

A. ATR-FTIR Results

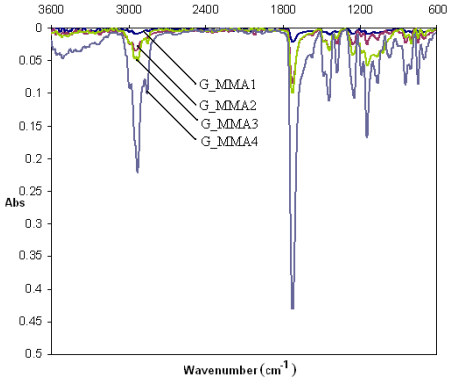

Fig. 2 ATR-FTIR spectra of the copolymers (G_MMAx)

The ATR-FTIR spectra of the G_MMAx glycopolymers are presented in Fig. 2 and confirm that the copolymerization process was complete. The signals at about 3000-3100 cm^{-1} express the C-H aromatic from the sugar skeleton, while the signals from 2800-3100 cm^{-1} are specific to methylene and methyl groups from the glycopolymer skeleton. The C-O and

C=O esteric bond are placed at about 1180 cm^{-1} and respectively at about 1700 cm^{-1}.

B. Differential Scanning Calorimetry (DSC)

We used Ozawa isoconversional method to assess the kinetics of the copolymerization process between glycomonomer and MMA in the presence of BPO. DSC curve were recorded between 20 and 200°C. Fig. 3 shows the DSC diagrams and it can be observed that the copolymerization of the monomer with MMA occurs from about 100°C to about 130°C [13] .

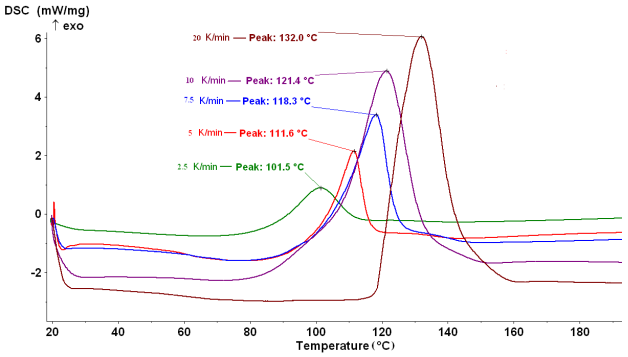

Fig. 3 The G_MMA2 DSC diagram at different heating rates

TABLE II
PEAK TEMPERATURES FOR THE COPOLYMERS AT 2.5 K/MIN

Sample	Peak temperature (ºC)
G_MMA1	97.8
G_MMA2	101.5
G_MMA3	101.8
G_MMA4	102.3

We noticed that the copolymerization process occurs in one step and that the peak temperature increases as the heating rates rises and along the increase of mass ratio (Table II).

C. The Ozawa Method

A widely applied method to study the copolymerization process of the monomer derived from D-glucose into MMA, from the kinetics point of view is Ozawa method [14]. From the slope obtained by the graphical representation of the linear dependence between ln β and $1/T_{\%}$, we can determine the activation energy for the same conversion for a thermal process considered. Nine different conversions were considered and the activation energy of the process was calculated as average of the nine values obtained for each conversion.

In Fig. 4 are presented the Ozawa lines for the copolymerization process of G_MMA2; Since the R-squared value is always above 0.9 for all the cases considered, we can conclude that the Ozawa model is rather accurate for modeling this chemical process.

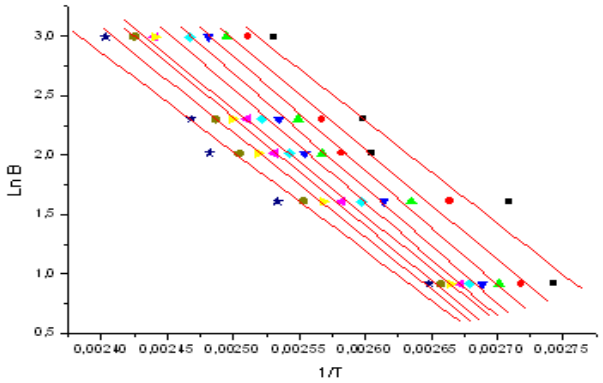

Fig. 4 The Ozawa lines for the copolymerization process of D-glucose monomer with MMA (G_MMA2)

TABLE III
THE ACTIVATION ENERGIES OF THE COPOLYMERIZATION PROCESS BETWEEN THE D-GLUCOSE MONOMER AND MMA BY OZAWA METHOD

Conversion (%)	Ea (kJ/mol)			
	G_MMA1	G_MMA2	G_MMA3	G_MMA4
10	78.021	73.408	70.932	68.215
20	78.191	78.146	77.075	73.347
30	78.194	78.441	78.630	75.760
40	78.010	78.815	78.933	76.236
50	77.822	78.553	78.480	75.259
60	77.810	78.005	77.646	70.762
70	77.723	76.736	76.253	72.012
80	77.268	73.581	74.298	69.527
90	74.996	69.912	70.022	65.650
Ea_{medium} (kJ/mol)	77.559	76.177	75.807	71.863

Activation energies of the copolymerization processes calculated for all the mass ratios considered by using Ozawa method are summarized in table III. We observed that the activation energy decreases along the increase in methacrylate weight ratio.

D. Termogravimetry Analysis

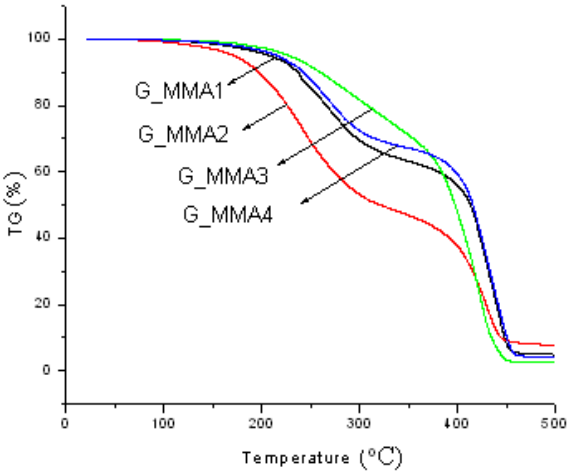

Fig. 5 The TG lines for the D-glucose glycopolymers (G_MMAx)

The TG diagrams for the G_MMAx glycopolymers are presented in Fig. 5; this diagrams shows us that the thermal decomposition of these glycopolymers occurs into two steps. Fig. 6 presents the superimposed TG and DTA diagrams of G_MMA4; we can observe that the TG diagram shows two inflexions, coresponding to two DTA peaks at about 275°C and respectively at about 425°C. The first inflexion can be attributed to the loss of some of the glycomonomer skeleton, while the second may be a result of the MMA residue degradation.

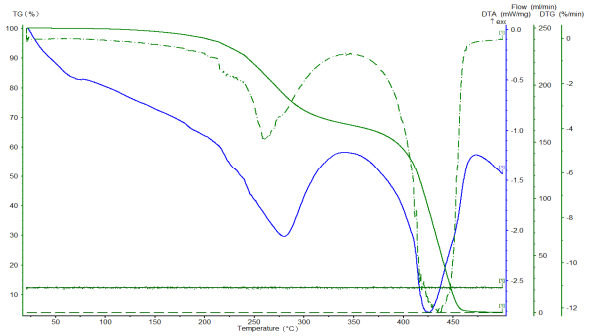

Fig. 6 The thermograms for one D-glucose copolymer (G_MMA4)

TABLE IV
WEIGHT LOSS FOR THE GLYCOPOLYMERS

sample	Weight loss (%)				
	20-100˚C	100-200˚C	200-300˚C	300-400˚C	400-500˚C
G_MMA1	0.24	3.93	26.19	13.69	51.11
G_MMA2	0.72	10.13	36.00	16.51	29.96
G_MMA3	0.09	2.39	15.82	33.72	45.60
G_MMA4	0.23	3.14	24.23	13.16	55.29

Table IV presents the weight losses for the glycopolymers, on different temperature ranges. The glycopolymers loose non-significant weight (less than 4%) up to 200°C, except G_MMA2 (10.13%) and up to 300°C they losse less than 36%; Heating up to 400°C, the glycopolymers looses more on its weight (34%); on the heating range of 400-500˚C glycopolymers losses most of the weight (56%). We can conclude that the higher the percentage in MMA, the more stable the glycopolymers become.

V. CONCLUSION

New D-glucose based polymers have been obtained by polymerization of a new sugar based monomer with methyl methacrylate. The polymerization properties were investigated using differential scanning calorimetry (DSC). The activation energy of this process was evaluated using Ozawa method. The copolymers obtained were characterized via ATR-FTIR, this analysis proving that the copolymerization process was complete. The thermogravimetry (TG) study emphasized that the new plastic materials derived from the glycomonomer have good thermal stabilities.

ACKNOWLEDGMENT

This work was partially supported by the strategic grant POSDRU/88/1.5/S/50783, Project ID50783 (2009) (fellowship of Liliana M. Ştefan), co-financed by the European Social Fund - Investing in People, within the Sectoral Operational Programme Human Resources Development 2007/2013. This paper was supported by the project PERFORM-ERA "Postdoctoral Performance for Integration in the European Research Area" (ID-57649) (fellowship of Ana M. Pană), financed by the European Social Fund and the Romanian Government.

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