

Thermal Properties of New D-Mannose Oligomer Copolymerized With 2-Hydroxypropyl Methacrylate

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Abstract: Plastic materials are indispensable to every day but, after their life cycle, they tend to become long-term pollutants. That is the reason why, nowadays, a keen interest is dedicated to research in the field of biodegradable and biocompatible plastic materials. This paper describes the thermal properties of a new class of biodegradable copolymers based on carbohydrates. A new oligomer based on D-mannose was synthesized by polycondensation of 1-benzyl-5,6-(bis(maleoyloxy))-2,3-isopropylidene-D-mannofuranose with propane-1,3-diol in the presence of *p*-toluenesulfonic acid. The copolymerization process between D-mannose based oligomer and 2-hydroxypropyl methacrylate was studied by DSC technique, while the thermal stability of the copolymers was assessed via thermogravimetry. The structure of the copolymers was confirmed by FTIR spectrometry. The activation energies for the copolymerization process and for the thermal decomposition of the new copolymers were calculated using Ozawa method.

Keywords: D-mannose, TG, DSC, activation energy, Ozawa

1. Introduction

The interest in polymers from renewable resources increased considerably in the last few decades. These materials are available in large quantities and they have numerous advantages [1,2]. Among others they are used for the preparation of biocompatible and biodegradable products that makes them even more interesting in quite a few application areas. However, natural polymers, mainly polysaccharides, consist of large, rigid molecules, thus they cannot be processed very easily with the usual processing technologies of thermoplastic polymers [3,4]. As a consequence, they are often modified both to improve processability and to adjust their properties to the intended application. Natural polymers can be modified physically by plasticization, or chemically through the reaction of their active –OH groups [5,6].

Although carbohydrates are abundant, their molecules contain many hydroxyl groups that allow non-selective electrophilic acylation. A possible solution to avoid this problem is the use of specific blocking/deblocking steps. Unfortunately, this conventional chemical process is tedious and expensive. These substances exert tensioactive, insecticidal, antimicrobial and anti-cancer activity [7].

Their excellent biodegradability along with the fact that they are non-toxic, insipid, odorless, biocompatible, nonionic, digestible, water-soluble and can resist adverse temperature, pH and salinity conditions, explain the growing use of these substances in several sectors of the industry [8-10]. This paper presents the thermal properties of new materials obtained by copolymerization of a new D-mannose oligomer with 2-hydroxypropyl methacrylate. D-mannose was chemically modified in order to obtain a diacid, 1-benzyl-5,6-(bis(maleoyloxy))-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 methacrylate (HPMA). The structure of the new D-mannose based copolymers was confirmed using FTIR spectroscopy. The copolymerization process was studied using DSC and the thermal stability of the new copolymers was investigated using thermogravimetry. The activation energies for the copolymerization process and for the thermal decomposition of the new copolymers were calculated using Ozawa method.

2. Experimental

2.1. Materials

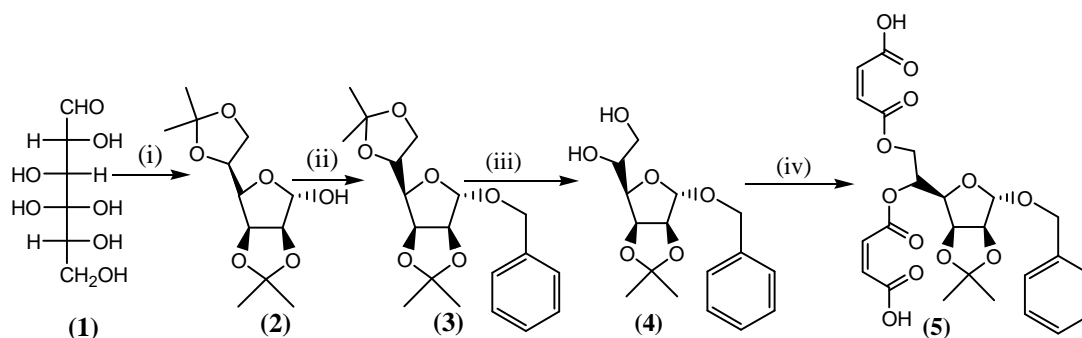
D-(+)-mannose (98%), benzyl bromide (98%) (BnBr), maleic anhydride (99%) (MAh), triethylamine (99%) (TEA), glacial acetic acid (99%) (AcOH), propane-1,3-diol (98%), *p*-toluenesulfonic acid monohydrate (99%), and 2-hydroxypropyl methacrylate (HPMA) were purchased from Merck and were used without further purification. Acetone (ChimoPar București), DMF (Merck), methanol (MeOH) (Chimopar București), n-hexane (Merck), ethyl acetate (AcOEt) (Merck), toluene (Chimopar București) and methylene chloride (Chimopar București) were purified according to literature [11].

2.2. Oligomer synthesis

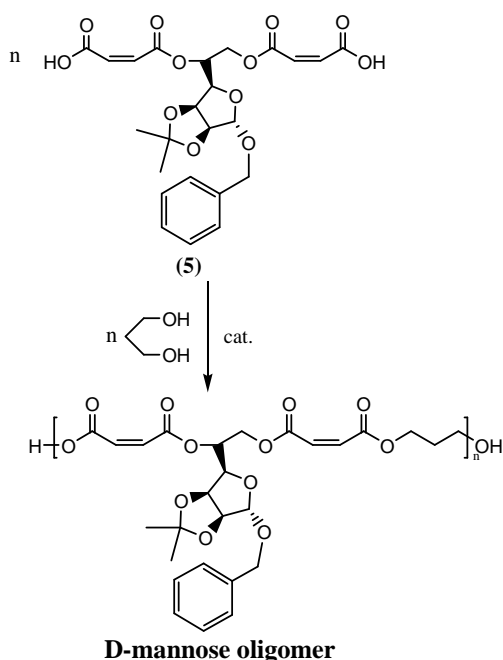
The reactions presented in scheme 1 were carried out using literature protocols [12-15]. The synthesis of the oligomer (scheme 2) was done as follows: 4 g of (5) are vigorously stirred into 20 mL of toluene, whereupon 0.6 mL of propane-1,3-diol were added. The mixture was heated up to 95-100°C and 9.2 mg *p*-toluenesulfonic acid were added. 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 approx. 70%).



Scheme 1. The reactions involved in obtaining 1-benzyl-5,6-bis(maleyloxy)-2,3-isopropylidene-D-mannofuranose (5); i) acetone, H_2SO_4 , 0°-r.t., 5h; ii) BnBr , NaH , DMF , MeOH ; iii) CH_3COOH , 80%, 45 min, 70-75°C; iv) MAh , TEA , 20 h, 60°



Scheme 2. The synthesis of D-mannose oligomer

2.3. The synthesis of the copolymers

The oligomer was dissolved in a certain amount of 2-hydroxypropyl methacrylate (HPMA), at 40°C (see table 1). Then benzoyl peroxide was added (1% wt.) and stirred vigorously. This mixture was then placed into preheated glass tubes.

TABLE 1. The copolymers synthesized

Copolymer	Mass ratio Oligomer: reactive solvent
M_HPMA1	1:1
M_HPMA2	1:2
M_HPMA3	1:3
M_HPMA4	1:4

Gradually the temperature was increased with 10 degrees per hour until 110°C. The copolymers obtained have crosslinked architectures.

2.4. IR spectroscopy

The FTIR spectra were recorded on a Jasco FT/IR-410 spectrometer. The ATR device was used for recording the copolymers spectra.

2.5. DSC analyses

The DSC diagrams were recorded on a Netzsch 204 DSC device in inert atmosphere, operating Proteus Analysis software. For the kinetic study of the copolymerization process several heating rates were used: 2.5; 5; 7.5; 10 and 20 K/min.

2.5. Thermogravimetric analyses

The thermogravimetric analyses were performed using Netzsch TG 209, in nitrogen atmosphere and dynamic conditions, at temperatures ranging between 20 and 500°C, using different heating rates: 2.5; 5; 7.5; 10 and 12.5 K/min.

3. Results and Discussion

The FTIR spectra of the copolymers confirm the structure of the reticulated polymers formed (fig.1). The O-H from the HPMA structure has a broad peak at about 3400 cm^{-1} . The signals between 3000 and 3100 cm^{-1} express the C-H aromatic bond, from the benzyl protective group, while the signals from 2800-3000 cm^{-1} are specific to methylene and methyl groups from the copolymer skeleton. The C=O esteric bond is expressed by signals at 1730 cm^{-1} , while the C-O esteric bond is placed at 1180 cm^{-1} .

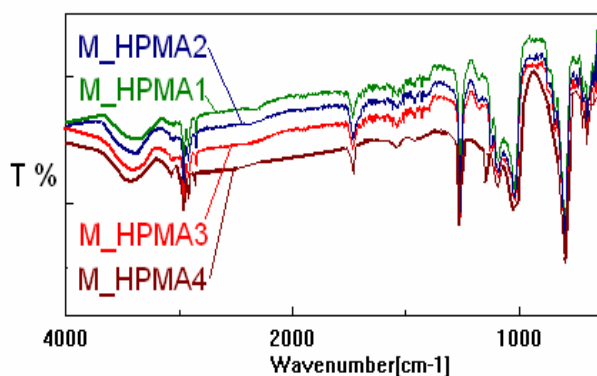


Figure 1. The IR spectra of the copolymers

The copolymerization properties of D-mannose oligomer into 2-hydroxypropyl methacrylate (HPMA) were studied via DSC analysis. 2-hydroxypropyl methacrylate monomer was chosen because of its relative polarity which provides a rather high solubility of the oligomer. The samples were prepared according to the protocol mentioned in the experimental part, using benzoyl peroxide as the free radical initiator. The weight ratios were chosen in order to ensure the homogeneity of the system (table 1). Figure 2

shows the DSC diagrams of the copolymerization process of M_HPMA4 using different heating rates.

The DSC diagram (fig. 2) shows that the copolymerization of D-mannose oligomer with HPMA occurs from about 80°C to 140°C.

The mass ratios have proved to be wisely chosen as the DSC diagrams for the process of copolymerization shows only one peak. The peak temperature increases along the increase of the heating rate.

The activation energy of the copolymerization process was calculated using Ozawa method. Ozawa (1) has expressed the dependence of the activation energy on the temperatures registered at different conversions.

$$\ln \beta = C - 1.052 Ea/RT_{\%} \quad (1)$$

Where:

β – The heating rate (K/min);

$T_{\%}$ – temperature at a certain conversion (K);

E_a – activation energy (J/mol);

C – Constant;

R – Gas constant (J/mol K).

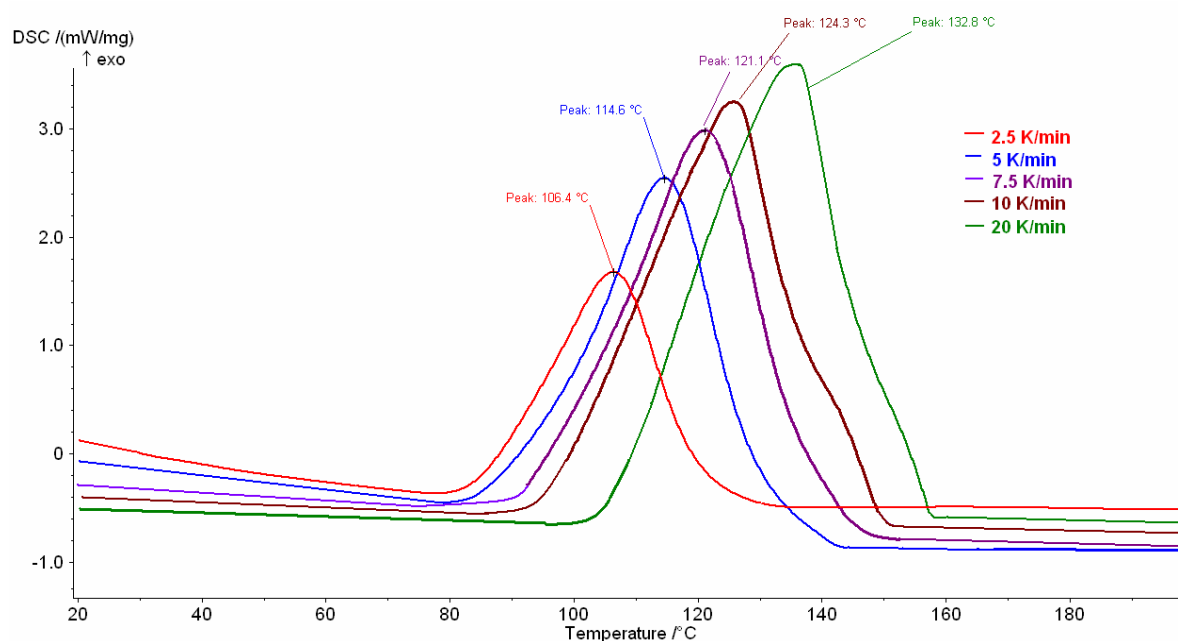


Figure 2. The DSC diagrams for the copolymerization process of M_HPMA4

Figure 3 shows the linear dependence between $\ln \beta$ and $1/T_{\%}$, in the case of conversions ranging between 10 and 90% for the M_HPMA2 copolymerization process. The slope of the lines allows calculating the activation energy.

The activation energies determined via Ozawa method are presented in table 2. The activation energy of the copolymerization process varies between 43.37 and 104.63 kJ/mol and it increases along the HPMA ratio. We can observe that the activation energy usually increases

along the increase in conversion and the activation energy for the copolymerization can be estimated as an average of the activation energy calculated for all nine conversions considered.

Furthermore, the thermal behavior of the copolymers was investigated. The temperature interval chosen for assessing the thermal stability of the copolymers, D-mannose oligomer and 2-hydroxypropyl methacrylate homopolymer (PHPMA) was 20-500°C.

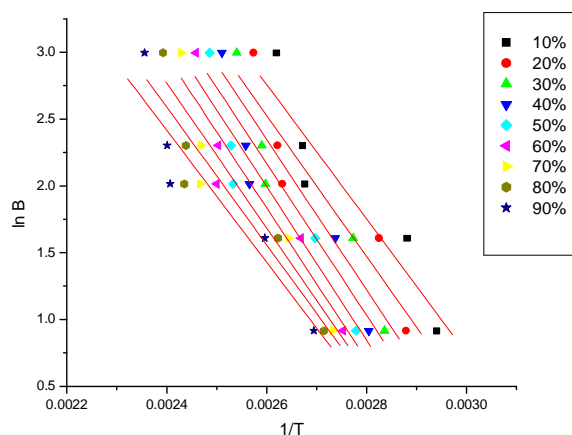


Figure 3. The Ozawa lines for the copolymerization process of M_HPMA2

The thermogram and its first derivative for M_HPMA1 copolymer overlapped with the TG diagram of the PHPMA show that the thermal decomposition of the copolymers occurs in two steps, while the homopolymer decomposes in only one step of thermal degradation (fig.4). The first step of thermal decomposition for the copolymer (inflexion temperature: 234°C) corresponds to the decomposition of the sugar moieties from the oligomer, while the second step (inflexion temperature: 368°) belongs to the methacrylate skeleton. The inflexion temperature for the homopolymer is 387.5°C, very similar to that of the second step of thermal decomposition for the copolymer [16,17].

The copolymers have good thermal stabilities; the decomposition process starts generally at temperatures above 250°C. Fig. 5 shows the thermograms for the copolymers with HPMA.

TABLE 2. The activation energies for copolymerization process of D-mannose oligomer with HPMA

Conversion (%)	Ea (kJ/mol)			
	M_HPMA1	M_HPMA2	M_HPMA3	M_HPMA4
10	39.818	72.365	79.235	77.776
20	41.716	73.242	85.068	86.041
30	42.896	74.97	89.923	88.628
40	44.92	75.379	93.563	100.828
50	45.436	75.612	94.03	103.948
60	45.793	76.398	109.92	111.225
70	46.785	77.907	105.068	115.687
80	40.683	79.559	111.235	120.468
90	42.359	81.733	113.563	137.075
Ea medium (kJ/mol)	43.37	76.35	97.95	104.63

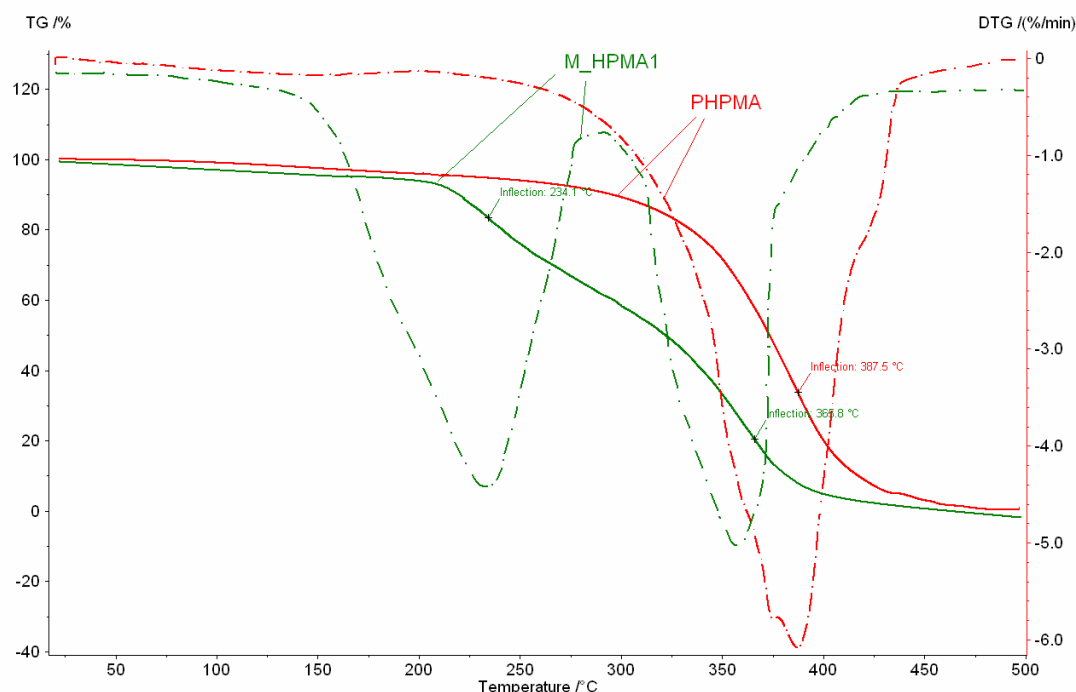


Figure 4. The thermograms and their first derivative for M_HPMA1 and PHPMA

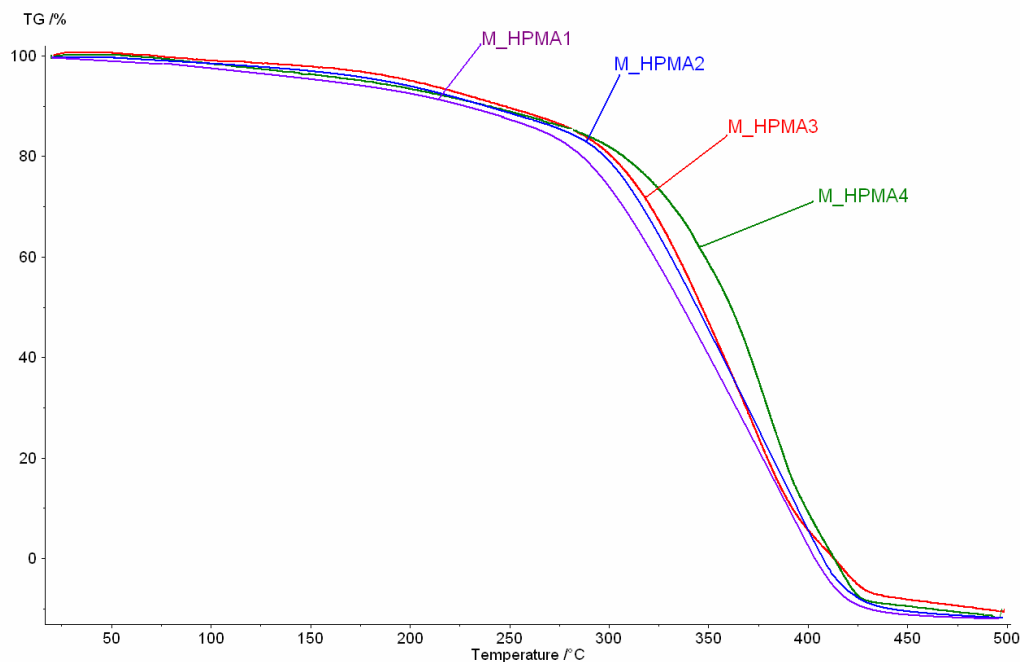


Fig.5. The thermograms for HPMA copolymers of D-mannose oligomer

The weight losses of the copolymers, 2-hydroxypropyl methacrylate homopolymer (PHPMA) and the pure oligomer were determined for different temperature intervals (table 3).

TABLE 3. Weight losses of copolymers, HPMA homopolymer and D-mannose oligomer

sample	Weight loss (%)			
	20 - 100°C	20 - 200°C	20 - 300°C	20 - 400°C
oligomer	1.95	6.25	24.93	85.88
PHPMA	1.02	4.21	10.74	79.79
M_HPMA1	1.52	5.23	14.25	77.83
M_HPMA2	1.33	4.85	13.35	75.65
M_HPMA3	1.07	4.03	12.83	74.37
M_HPMA4	0.98	4.15	10.57	71.53

For temperatures ranging below 100°C, the weight loss is inessential (less than 2%), but for higher temperatures the thermal decomposition process increases. Surely, on the highest temperature interval considered the most stable is the homopolymer succeeded by the copolymer with the highest HPMA ratio. The most temperature susceptible sample is the oligomer which losses almost 89% of its weight on the highest temperature interval discussed. We can conclude that by copolymerization, the thermal stability of the new material has been drastically increased. The thermal analyses of the copolymers were carried out using a dynamic program. Moreover, the kinetics of the thermal decomposition was investigated and the activation energies were determined using Ozawa method.

The activation energies for the both steps of decomposition of the copolymers determined using Ozawa method are presented in table 4. It was seen that the activation energy for the first step of decomposition (81.83 to 112.98 kJ/mol) has smaller values than for the second step of decomposition. The activation energy values

calculated for the second step of thermal decomposition has larger values (146.67 to 160.24 kJ/mol). We can observe that the activation energy usually increases along the increase in conversion. The activation energy for one sample can be estimated as an average of all nine conversions considered. We can conclude that the activation energy increases along the HPMA ratio and along the increase in conversion.

Table 4 presents the activation energies calculated for all copolymers at different conversions using Ozawa method. Thus, the biggest value registered was for the activation energy for the M_HPMA4 copolymer, in the second step of thermal degradation, while the smallest was for the M_HPMA1 copolymer in the first step.

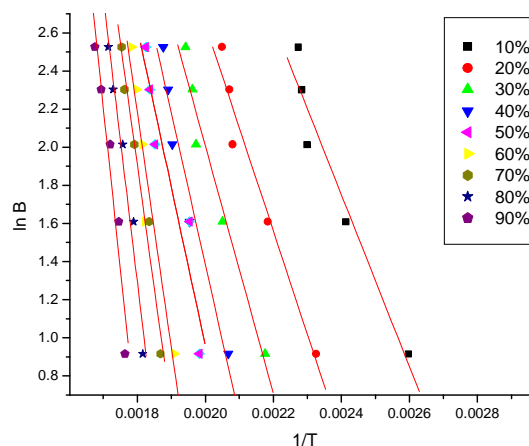


Figure 6. The Ozawa lines for the first step of thermal decomposition of M_HPMA1

Figure 6 shows the linear dependence between $\ln \beta$ and $1/T$, in the case of conversions ranging between 10 and 90% for the M_HPMA1 copolymer in its first step of thermal decomposition.

The slope of the lines allows calculating the activation energy. The linear regression had R squared values that surpassed 0.9 which indicated that the Ozawa

approximation was appropriate for calculating the activation energy of the thermal decomposition.

TABLE 5. The activation energies for thermal decomposition of the HPMA copolymers via Ozawa method

Conversion (%)	Step I				Step II			
	M_HPMA1	M_HPMA2	M_HPMA3	M_HPMA4	M_HPMA1	M_HPMA2	M_HPMA3	M_HPMA4
10	67.95	71.5	91.5	107.55	140.03	138.23	157.45	150.45
20	75.89	86.85	92.45	107.7	150.2	137.02	173.53	144.1
30	83.85	89.72	93.25	108.81	135.82	141.23	143.62	156.65
40	84.83	98.85	95.59	140.97	171.38	150.1	140.61	167.075
50	85.12	103.26	99.6	106.32	173.14	149.85	144.13	185.4
60	86.52	105.23	105.97	106.85	116.79	155.69	133.65	160.3
70	89.46	106.148	109.85	111.25	149.75	156.23	143.95	143.77
80	83.86	105.85	114	117.94	127.84	160.14	165.23	168.73
90	95.35	106.25	117.42	109.48	153.36	165.3	175.35	165.73
Ea medium (kJ/mol)	81.83	97.02	102.18	112.98	146.47	150.42	153.05	160.24

4. Conclusions

We have synthesized new carbohydrate-based copolymers by copolymerization of an oligomer derived from D-mannose with 2-hydroxypropyl methacrylate. The structure of these copolymers was confirmed using FTIR spectroscopy. The DSC technique was used to study the copolymerization process and thermal analysis allowed evaluating the thermal stabilities of the new copolymers compared to D-mannose oligomer and HPMA homopolymer. The best thermal stability was registered for the copolymer having the greatest HPMA ratio, while the least stable was D-mannose oligomer. The activation energy of the copolymerization process and of thermal decomposition was evaluated for all copolymers using Ozawa method. The activation energies for the copolymerization process increased along the increase in HPMA ratio. For the thermal stability, the activation energies were calculated for both steps of thermal degradation and generally they increased along the HPMA ratio.

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