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Thermal Analysis of the Compounds Obtained by Copolymerization between Glycomonomers and 2-Hydroxy-Propyl Methacrylate

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Abstract: Most polymeric materials are based on non-renewable fossil resources, respectively petrochemicals. As regenerable resources carbohydrates have attracted great attention in the last decade for production of polymeric materials. The biodegradable polymers are indispensable in the modern society and their importance is continuously growing. In this paper we report the thermal properties of a new class of biodegradable copolymers derived from monosaccharides. The glycomonomers 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, and 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, were co-polymerized with 2-hydroxypropyl methacrylate, using benzoyl and lauroyl peroxide as initiators. The copolymerization process between glycomonomers and 2-hydroxypropyl methacrylate was studied using differential scanning calorimetry analysis (DSC). The storage and loss modulus were evaluated using DMA technigue (dynamic mechanical analysis), while the thermal stability of the obtained products was studied via thermogravimetry (TG).

Keywords: carbohydrate, biodegradable polymer, thermal analysis, DSC, DMA, TG.

1. Introduction

In the context of the oil price crisis and the orientation towards renewable resources, it would desirable to obtain a production of polymers based on agricultural products. Carbohydrates are the most common organic materials on the planet. Due to this reason we have tried to replace the conventional synthetic non-degradable polymers, with polymers obtained using natural materials such as carbohydrates. The limited resources of petroleum and the expensive possibilities of coal conversion have determined the interest [1, 2].

Biodegradable polymers have the potential of being the solution to a range of environmental concerns related to conventional non-biodegradable polymers. Renewable raw materials from biodegradable polymers are to be preferred instead of the petrochemical resources, because the last ones are increasing the amount of carbon dioxide in the atmosphere and causing global warming.

The degradation of synthetic polymers has been studied since their introduction on the market because almost all plastics are affected by exposure to natural factors such as bad weather, sunlight, oxygen, water and heat [3, 4].

We present here the thermal characteristics of a new class of biodegradable copolymers derived from monosaccharides. Two glycomonomers: 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (ADAG) and 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (ADAM) were co-polymerized with 2-hydroxypropyl methacrylate, and were characterized by thermal analysis.

2. Experimental

2.1. Materials

Glucose (Merck), mannose (Merck), sulfuric acid (Carlo Erba), acetone (Carlo Erba), sodium bicarbonate (Chemapol), chloroform (Merck), cyclohexane (Merck), acryloyl chloride (Aldrich), sodium hydroxide (Acros Organics), sodium sulfate (Acros Organics), ethyl acetate (Merck), hexane (Merck), 2-hydroxypropyl methacrylate (HPMA) (Merck), benzoyl peroxide (POB) (Merck) and lauroyl peroxide (POL) (Merck) were used without further purification.

2.2. Glycomonomers synthesis and their copolymerization

Glycomonomers were obtained by the procedure describe previously [5]. For their copolymerization we have used the following procedure: the glycomonomer was dissolved in hydroxypropyl methacrylate (molar ratio 1:2) and then the initiator - POB or POL - is added (1% wt. from the mixture) and the mixture was stirred until the peroxide was dissolved. This mixture was then placed into glass tubes. The temperature was increased gradually with 10 degrees per hour until 110ºC. The glycopolymers obtained by copolymerization of glycomonomers with HPMA, will be further noted as G_HPMAy for the copolymerization of ADAG, and M_HPMAy for the copolymerization of ADAM, where y = B (POB) or L (POL), representing the used initiator.

2.3. Differential scanning calorimetry analysis (DSC)

To determine the activation energy, DSC analysis were performed using Netzsch DSC 204, in nitrogen atmosphere and dynamic conditions, at temperatures ranging between 20 and 200°C, using different heating rates: 2.5, 5, 7.5, 10 and 20 K/min.

2.4. Dynamic mechanical analysis (DMA)

DMA analysis were performed using Netzsch DMA 242 C, in air, at temperature ranging between 20°C ÷ 200°C, heating rate 1 K/min, strain frequencies 0.5; 1; 5; 10; and 20 Hz.

2.5. Thermogravimetric analyses (TG)

In order to determine the thermal stability of the obtained products and the activation energy for the degradation processes we performed TG analysis using a Netzsch TG 209, in nitrogen atmosphere and dynamic conditions, at temperatures range between 20 and 500ºC, using different heating rates: 2.5, 5, 7.5, 10 and 12.5 K/min.

3. Results and Discussion

3.1. The characterization of the copolymerization process using DSC

To assess the kinetics of the copolimerization process between glycomonomers and 2-HPMA in the presence of POB or POL were used several isoconversional methods: Kissinger, Ozawa, KAS. For applying the isoconversional methods of a heterogeneous reaction in the kinetic analysis is necessary to record the DSC thermograms at different heating rates. From the DSC diagrams (fig.1 and fig.2) obtained from the copolymerization of glycomonomers, it can be observed that the peak temperature increases with the rise of the heating rate.

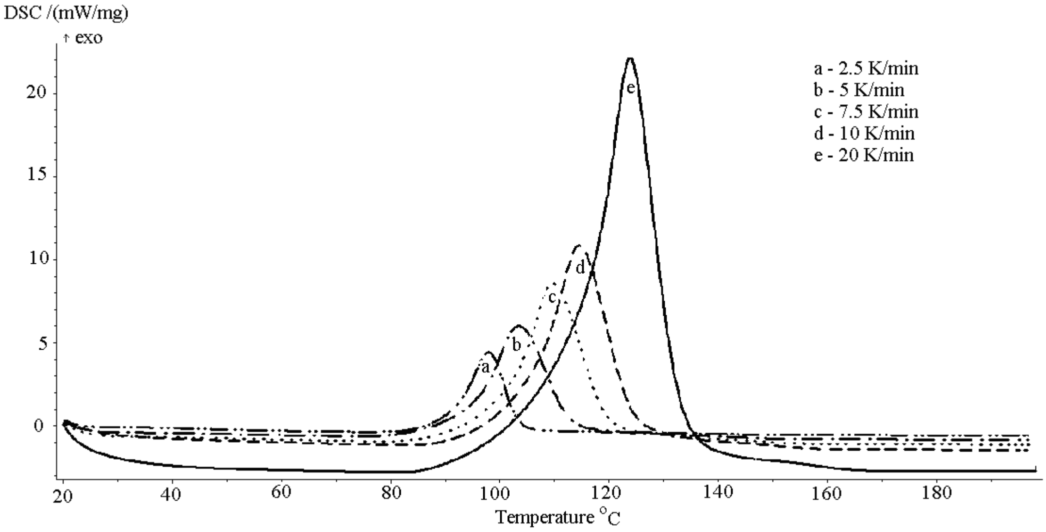

Figure1. DSC diagrams for the copolymerization of D-glucose monomer with 2-HPMA (G_HPMA$_B$)

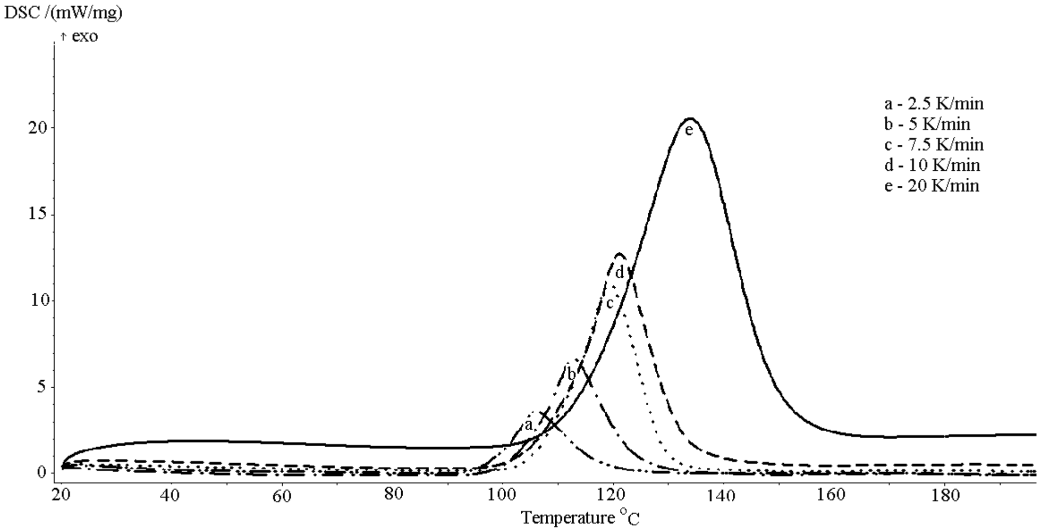

Figure 2. DSC diagrams for the copolymerization of D-mannose monomer with 2-HPMA (M_HPMA$_B$)

The determination of activation energy using Kissinger method is one of the oldest methods for determining the activation energy through thermal analysis and is based on the relationship between temperature peak and the heating rate [6].

The activation energy was evaluated from the slope of the line obtained by the graphical representation of ln (β/T2) = f (1 / T) (fig.3).

Like Kissinger method, Ozawa is also one of the most used methods in the characterization of the activation energy of different types of processes (fig.4).

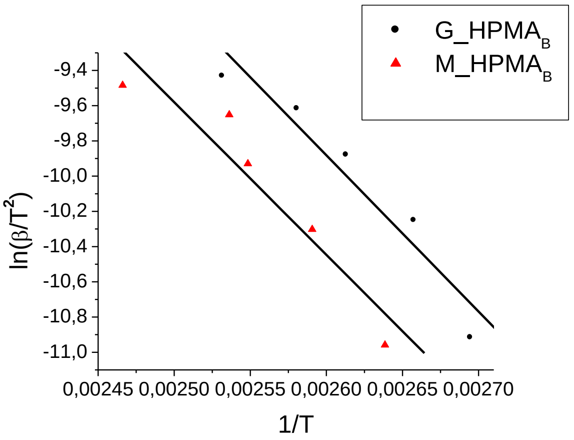

Figure 3. The Kissinger lines for the G_HMPA$_B$ and the M_HPMA$_B$ copolymers

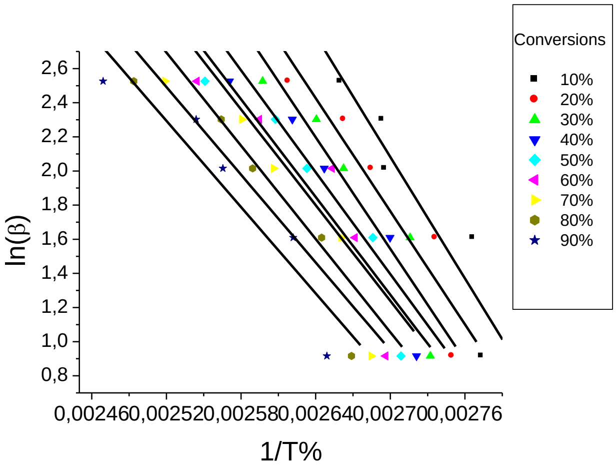

Figure 4. The Ozawa lines for the G_HPMA$_L$ copolymer

The graphical representation of ln (β) = f (1 / T %) at a certain conversion, gives a set of lines with negative slopes, which determined the activation energy of the process.

The Kissinger Akahira Sunrose (KAS) method is similar to the method proposed by Kissinger, except that the temperature values are not considered at the maximum temperature, but at an established conversion [7].

From the slope obtained by the graphical representation of the linear dependence between ln $\beta/T^2{}_{\%}$ and 1/T$_{\%}$, we can determine the activation energy for the same conversion (fig.5).

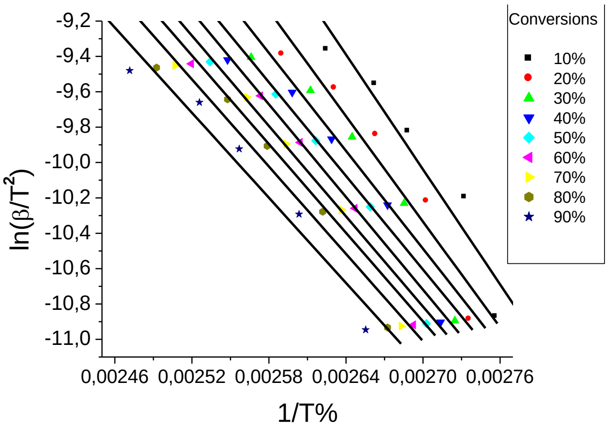

Figure 5. The KAS lines for the G_HPMA$_L$ copolymer

The activation energies for all the copolymers determined using those three isoconversional methods are presented in Table 1.

From Table 1 we observe that the values of activation energy for the G_HPMA$_y$ copolymers are higher than those for the M_HPMA$_y$ copolymers. The initiator used for the copolymerization process influences the activation energy, and their values are higher when POL was used as initiator.

TABLE 1. The kinetic study of copolymerization process between glycomonomers and HPMA

Determination method	Ea [kJ/mol]			
	G_HPMA$_B$	G_HPMA$_L$	M_HPMA$_B$	M_HPMA$_L$
Kissinger	73,7	73,9	72,1	72,6
Ozawa	77,2	77,9	76,9	77,4
KAS	74,7	75,2	74,5	75,1

3.2. The characterization of the copolymerized products using DMA

The DMA analysis allows us to evaluate the storage modulus (E'), the loss modulus (E''), tan δ and the glass transition temperature (Tg) as function of temperature according to the strain frequencies [8, 9].

The variation of the storage modulus E' and tan δ as function of temperature for different strain frequencies is presented in figure 6 for product G_HPMA$_B$.

Table 2 presents the values obtained for the storage modulus, the loss modulus and tan δ for the copolymers.

It can be noticed that for the same sample, both storage and loss modulus increases along the increase of the strain frequency. For different samples, it can be seen that the storage modulus (E') has a smaller values for the M_HPMAy glycopolymers than for the G_HPMAy glycopolymers. The same behavior is presented for the loss modulus and for the glass transition temperature (considered the maximum of tan δ).

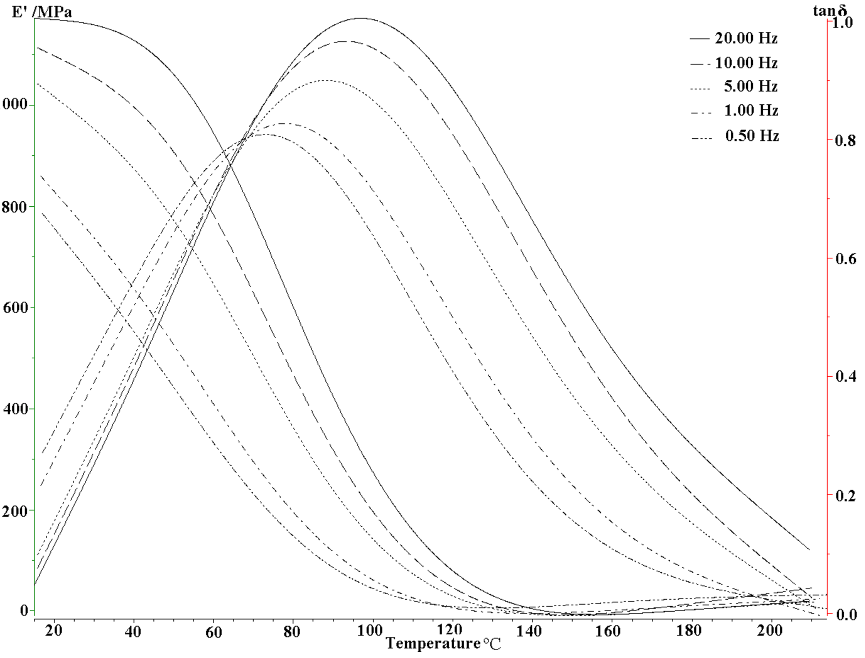

Figure 6. The variation of the storage modulus E' and tan δ as function of temperature for different strain frequencies for the G_HPMA$_B$ copolymer

TABLE 2. The storage modulus, the loss modulus and tan δ for the copolymerized products

Product	Frequency [Hz]		E' [MPa]		E'' [MPa]		max tanδ (Tv)	
Iniţiator	POB	POL	POB	POL	POB	POL	POB	POL
G_HPMA$_y$	0,5	0,5	696	630	263	219	93,0	86,9
	1	1	758	672	292	249	94,8	89,2
	5	5	975	834	385	357	99,7	95,2
	10	10	1100	941	446	434	102,1	98,0
	20	20	1241	1088	507	531	105,0	101,4
M_HPMA$_y$	0,5	0,5	296	253	174	118	73,5	72,6
	1	1	360	286	212	147	75,5	78,8
	5	5	579	411	348	247	79,9	84,5
	10	10	705	494	450	320	81,4	88,1
	20	20	864	604	590	422	83,4	89,6

3.3. The characterization of the copolymers using TG

In order to determine the thermal stability of the copolymerized products, we performed thermogravimetrical analysis in nitrogen atmosphere and dynamic conditions, at temperatures range between 20 and 500ºC, using different heating rates: 2.5, 5, 7.5, 10 and 12.5 K/min [10].

The thermograms and their first derivative show that the thermal decomposition of the copolymers occurs in two steps (fig.7). The first step corresponds to the decomposition of the glycomonomer, whereas the second step coincide with the methacrylate decomposition [11].

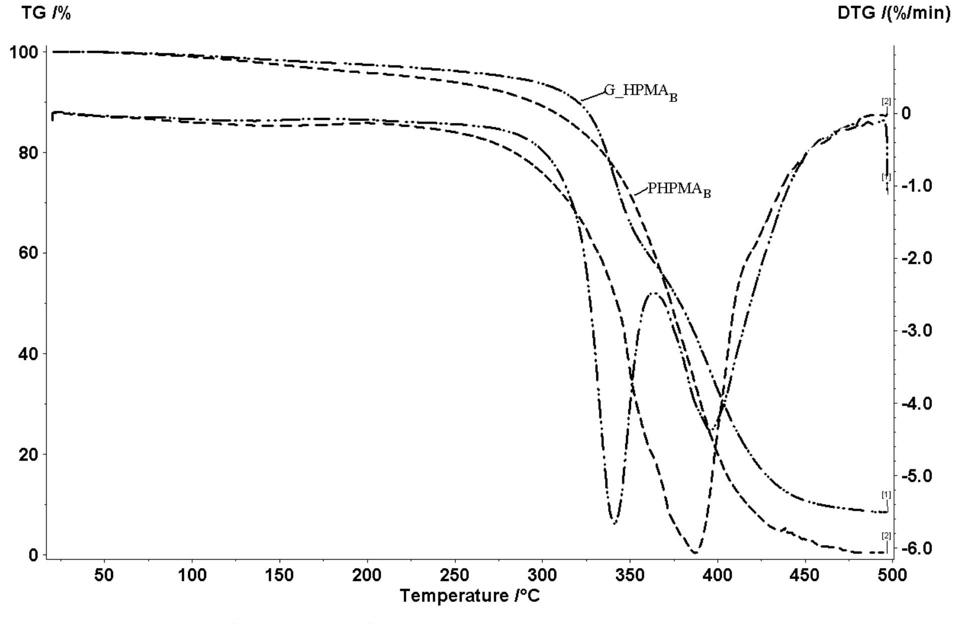

Figure7. The thermograms and their first derivative, for the HPMA homopolymer and one copolymer (G_HPMA$_B$)

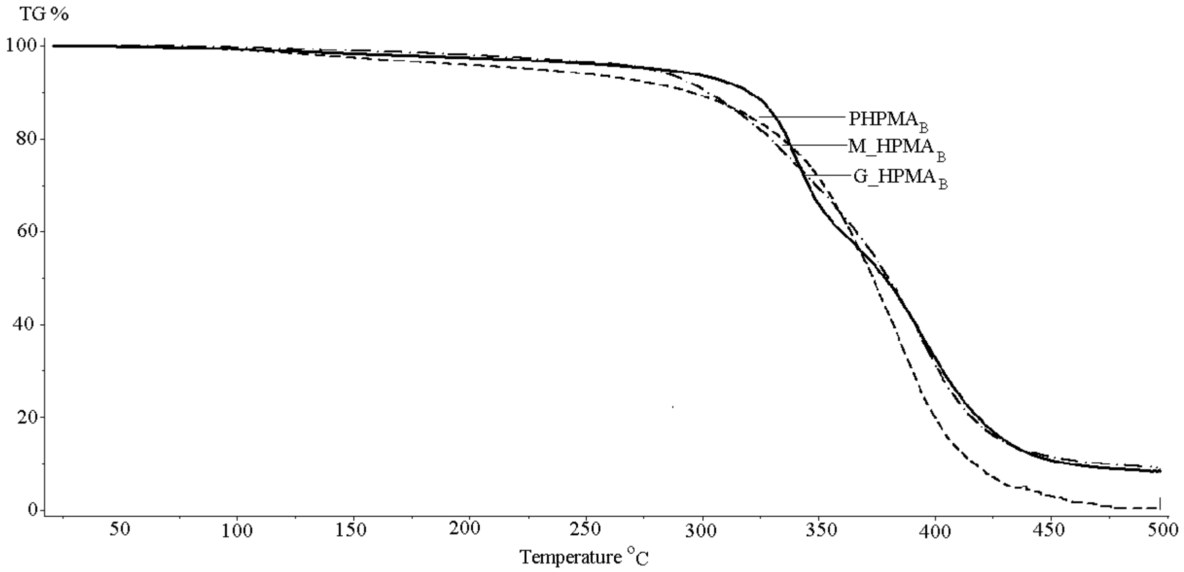

Figure 8. The thermograms of the copolymers with HPMA

Comparing the thermal stability of the copolymerized products with that of the glycomonomers, it can be seen that the copolymers have a better thermal stability [12]. Figure 8 shows the termograms for the copolymers with HPMA.

The kinetics of the thermal decomposition was investigated and the activation energy was determined using three different methods of evaluation. Kissinger was the first method used for determining the activation energy of the thermal degradation (fig.9).

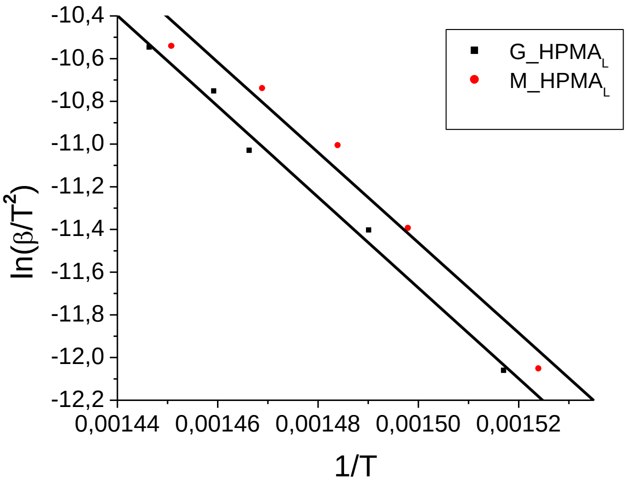

Figure 9. The Kissinger lines for the first step of degradation in the case of HPMA copolymers

The activation energies of the copolymerization processes were also determined through Ozawa method. Thus, by the graphical representation of ln (β) = f (1/T%), where β is the heating rate and T% is the temperature at a certain conversion, we obtain a set of lines with negative slopes, which determine the activation energy of copolymerization process.

Figure 10 present the linear dependence between ln β and 1/T%, for the G_HPMAL copolymer in its second step of thermal decomposition, using conversions from 10, 20, 30, 40, 50, 60, 70, 80 to 90%. The activation energy can be calculated from the slope of the lines, and it can be observed that the activation energy increases along the increase of conversion.

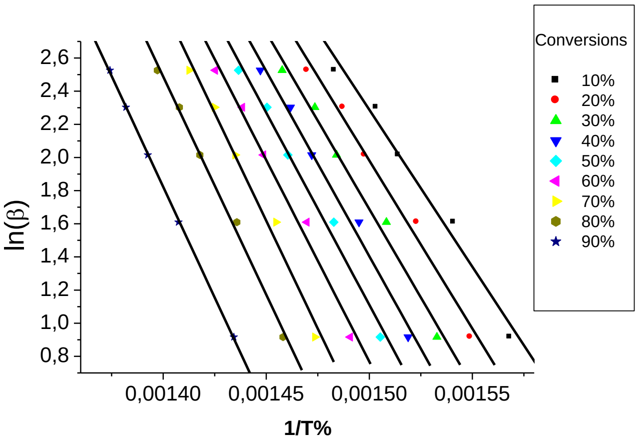

Figure 10. The Ozawa lines for the G_HPMA_L copolymer in its second step of thermal degradation

The method Kissinger-Akahira-Sunrose (KAS) is similar to the method proposed by Kissinger, except that the temperature values are not considered at the temperature peak, but at an established conversion. The activation energy was evaluated for conversions of 10, 20, 30, 40, 50, 60, 70, 80 and 90%. The KAS lines for the G_HPMA_L copolymer at all conversions are presented in figure 11.

Table 3 presents the activation energies determined using the three presented methods for the first step of thermal degradation, and table 4 presents those for the second step.

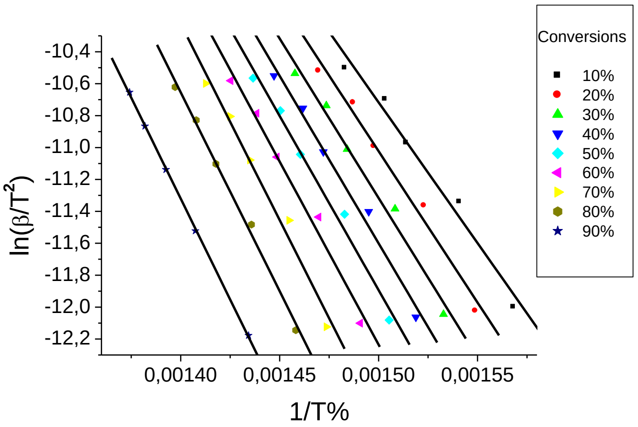

Figure 11. The KAS lines for the G_HPMA$_L$ copolymer in its second step of thermal degradation

TABLE 3. The activation energies of the copolymers for the first step of thermal decomposition

Determination method	Ea [kJ/mol]			
	G_HPMA$_B$	G_HPMA$_L$	M_HPMA$_B$	M_HPMA$_L$
Kissinger	127,1	131,5	101,9	106,9
Ozawa	133,8	137,6	124,8	126,9
KAS	130,7	134,1	121,5	123,5

TABLE 4. The activation energies of the copolymers for the second step of thermal decomposition

Determination method	Ea [kJ/mol]			
	G_HPMA$_B$	G_HPMA$_L$	M_HPMA$_B$	M_HPMA$_L$
Kissinger	175,2	176,7	174,2	175,7
Ozawa	179,9	183,9	174,8	179,7
KAS	178,1	182,2	172,8	177,8

The activation energy of the thermal decomposition process for all methods have similar results. We can observe that the activation energy for the first step of thermal degradation is smaller than that for the second step. For both steps of thermal degradation the activation energy has bigger values for the copolymers derived from glucose than those derived from mannose.

4. Conclusion

The aim of this paper was the thermal characterization of the copolymers obtained using different glycomonomers (ADAG and ADAM) and 2-HPMA.

The copolymerization of the glycomonomers with 2-HPMA was investigated by DSC. The activation energy for these copolymerization processes were calculated using three different methods. The results indicate that the activation energy values are higher for the G_HPMA$_y$ copolymers than for the M_HPMA$_y$, so the copolymers derived from glucose are more reactive than the ones derived from mannose. Also, the initiator used for the copolymerization processes influences the activation energy; POL determined bigger activation energies.

From DMA analysis we observed that the storage modulus, the loss modulus and glass transition temperature (which is the maximum tan δ) for the same copolymer increases as the increase of the strain frequency. Considering different samples, it can be seen that they have smaller values for M_HPMA$_y$ copolymers.

The thermal stability of the copolymerized products is higher than for the glycomonomers. However, the homopolymer has a better thermal stability than the crosslinked products, and the copolymerized products are degraded in two steps, while the correspondent homopolymer is degraded in one step. This behavior is caused by the different chemical structure of the two products: the homopolymers have the esteric bond only as a side group while the copolymers contain it in the main polymer chain, so the thermal stability of the first is lower.

The activation energy of the thermal degradation processes was evaluated for all copolymers using three different methods (Kissinger, Ozawa and Kissinger-Akahira-Sunrose). All methods have shown similar results.

By comparing the activation energy for the first step of thermal degradation we can observe that the activation energy values are quite close one to another; and the copolymers derived from glucose have higher values. We also observed that the activation energy for the first step of thermal degradation has smaller values.

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