

Copolymerization of 3-*O*-Acryloyl-1,2:5,6-di-*O*-Isopropylidene- α -D-Glucofuranose and Butyl Acrylate at Different Molar Ratios

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Abstract: 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 the copolymerization of sugar-carrying acrylate, 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose, and butyl acrylate at different molar ratios using as initiator benzoyl peroxide. The thermal analysis was carried out with differential scanning calorimetry (DSC). The DSC thermograms show that the activation energies increase with the increase of the molar ratio.

Keywords: carbohydrate, glycopolymers, biodegradable polymers, thermal analysis, DSC

1. Introduction

In the last decade, carbohydrates as renewable resources for the chemical industry have attracted great attention. From an economical as well as an ecological standpoint, renewable resources have many advantages. Furthermore, the rising consumption of petrochemical raw materials has motivated many researchers into finding alternative materials for petrochemical resources. The synthesis of new polymer colloids based on renewable resources, such as sugar derivatives, has attracted our interest [1].

Polymers based on carbohydrate offer exciting opportunities for biomaterials development and drug delivery applications [2].

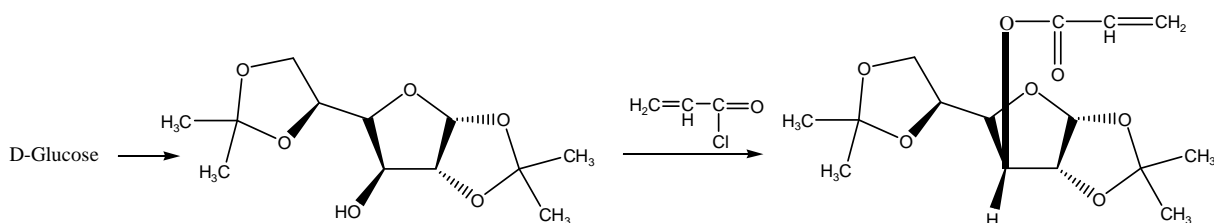
In many biological systems, carbohydrates serve as receptors for protein, often as specific molecular recognition agents, allowing for cell binding and proliferation. Copolymerization of carbohydrate monomers also increases their hydrophilicity [3].

The study of carbohydrates began in the late nineteenth century with the work of Emil Fischer. Carbohydrate ring structure was elucidated in the 1930s by Haworth and colleagues [4].

There has been a worldwide realization that nature derived mono-, di-, oligo- and polysaccharides can provide us the raw materials needed for the production of numerous industrial consumer goods [5].

The definition of glycopolymers has not yet been clearly established. In a very broad sense, glycopolymers may include chemically modified natural polymers. On the other sense, in a narrower sense, glycopolymers refer to synthetic polymers containing sugar moieties which act as specific biological functional groups similar to those of naturally occurring glycoconjugates [6].

The synthesis of sugar monomer 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (ADAG), in a high yield, over 75%, based on glucose is presented in Scheme 1.



Scheme 1.

In this paper we report the copolymerization of sugar-carrying acrylate, 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (ADAG), and butyl acrylate (BA) at different molar ratio using as initiator benzoyl peroxide.

2. Experimental part

The key intermediary in the synthesis of the glycopolymer is diacetoneglucose. Diacetoneglucose was obtained according to the literature [7, 8].

Diacetoneglucose (DAG) was reacted further with acryloyl chloride (AC) in acetone (Scheme 2), according to [9].

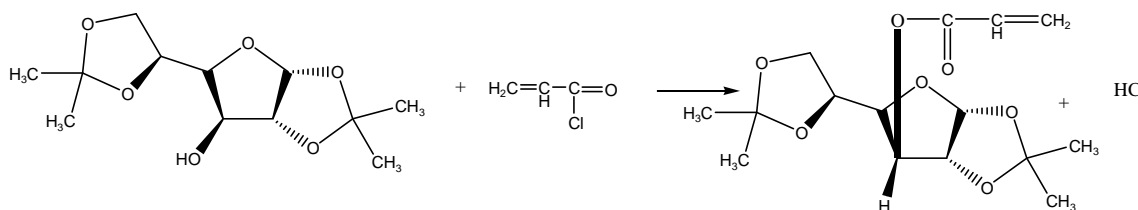
3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (ADAG) was characterized using FTIR and RMN spectroscopy ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) analysis presented in a previous paper [10].

The copolymerization of 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (ADAG) with butyl acrylate (BA) (molar ratios 1:2, 1:3, 1:4, 1:5) was 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 comonomer at different molar ratio; then the initiator - benzoyl peroxide (POB) - is added (1% wt. from the mixture) and the mixture was stirred at room temperature

until the peroxide was dissolved (depends on the molar ratio of the copolymers).

3. Results and discussion

Copolymerization of 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (ADAG) with butyl acrylate (BA) gives a transparent polymer. To establish the activation energy for the polymerization process, the DSC measurements were performed under nitrogen atmosphere and under dynamic conditions (20 to 200°C with 2.5, 5, 7.5 and 10 K/min). From the DSC thermograms (Figures 1-4) obtained for the copolymerization of ADAG with BA at different molar ratios, it can be observed that the peak temperature increases along the rise of the heating rate.



Scheme 2.

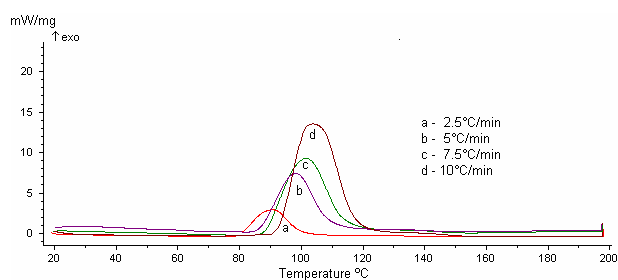


Figure 1. DSC curves for the copolymerization process of ADAG with BA - 1:2 molar ratio

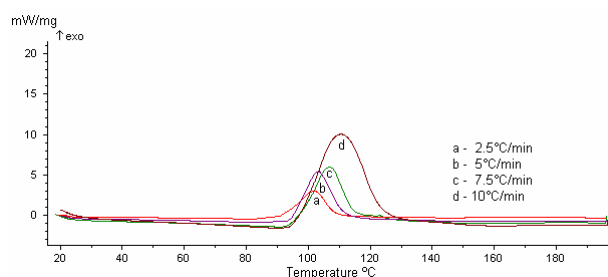


Figure 4. DSC curves for the copolymerization process of ADAG with BA - 1:5 molar ratio

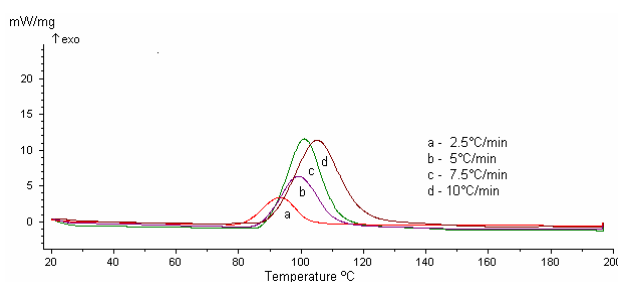


Figure 2. DSC curves for the copolymerization process of ADAG with BA - 1:3 molar ratio

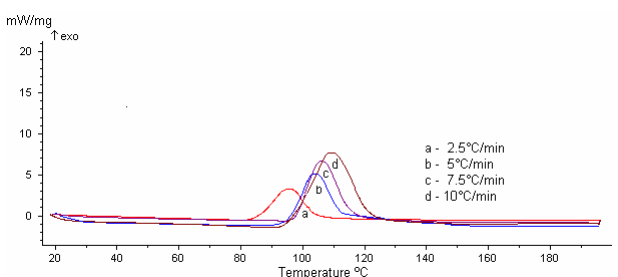


Figure 3. DSC curves for the copolymerization process of ADAG with BA - 1:4 molar ratio

A widely applied method for the determination of the activation energies is the Kissinger method. Kissinger method uses the peak temperature of each DSC curve [11] recorded at different heat rates. Its characteristic equation is:

$$\ln \frac{\beta}{T_p^2} = \ln(AF(\alpha)) - \frac{E}{RT_p} \quad (1)Ea$$

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).

This equation is linear, and its generic form is:

$$y = a + bx \quad (2)$$

Where:

$$y = \ln \frac{\beta}{T_p^2}$$

$$a = \ln(AF(\alpha))$$

$$b = -\frac{E}{R}$$

$$x = \frac{1}{T_p}$$

The graph showing the linear dependence between $\ln\beta/T^2$ and $1/T_p$ allows us to calculate the slope of the line, b. using a simple calculus we obtain the activation energy for each of the polymerization process:

$$E = -b \cdot R \quad (3)Ea$$

Figures 5-8 show the Kissinger line for the copolymerization process for ADAG with BA at different molar ratios (1:2, 1:3, 1:4, and 1:5).

Table 1 summarizes the activation energies, calculated using the Kissinger method, for all the copolymerization systems investigated. It can be observed that the activation energy increases along the increase of the acrylate quantity.

TABLE 1. The activation energies for the copolymerization of ADAG with BA at different molar ratios

| Compound | Molar ratio | E [kJ/mol] |
|----------|-------------|------------|
| ADAG_BA | 1:2 | 115.723 |
| ADAG_BA | 1:3 | 119.589 |
| ADAG_BA | 1:4 | 123.455 |
| ADAG_BA | 1:5 | 168.816 |

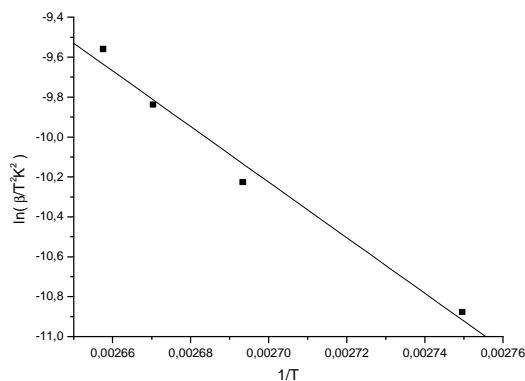


Figure 5. Kissinger lines for the copolymerization of ADAG with BA – 1:2 molar ratio

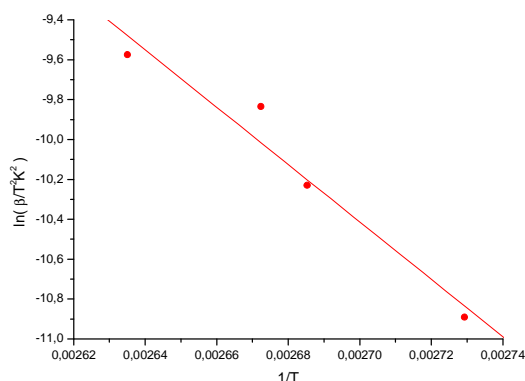


Figure 6. Kissinger lines for the copolymerization of ADAG with BA – 1:3 molar ratio

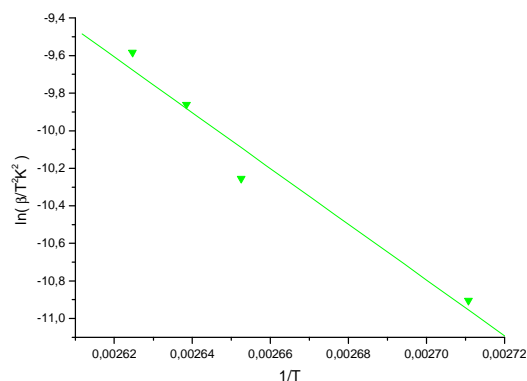


Figure 7. Kissinger lines for the copolymerization of ADAG with BA – 1:4 molar ratio

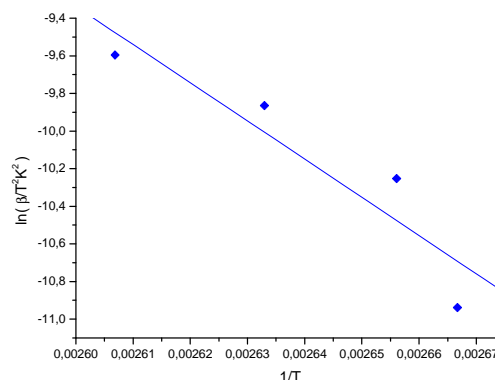


Figure 8. Kissinger lines for the copolymerization of ADAG with BA – 1:5 molar ratio

4. Conclusions

The copolymerization of 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucopyranose (ADAG) with butyl acrylate (BA) at different molar ratios (1:2, 1:3, 1:4, 1:5) was investigated by DSC. In terms of polymerization technique, we can observe a better degree of glycomonomer solubilization when 1:5 molar ratio of ADAG_BA is being polymerized than respectively 1:2. The activation energies for these copolymerization processes were calculated using Kissinger method. The results indicate that the activation energies increase with the increase of the molar ratios. Thus, the greater the molar ratio of the BA the harder the polymerization process occurs.

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