

Copolymerisation Kinetic Study for Modified Inulin Esters and 2-Ethylhexyl Acrylate

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Abstract: A kinetic study was conducted on some modified inulin compounds. Several DSC curves were recorded at different heating rates in order to determine the activation energies and the kinetic function together with the pre-exponential factor for the copolymerisation process between some inulin ester and 2-ethylhexyl acrylate. It was found that the activation energies are varying from 68 to 75 J/kmol and the kinetic equation that describes the best the copolymerisation process is the Avrami – Erofeev equation.

Keywords: DSC study, kinetic study, inulin esters

1. Introduction

Synthetic polymers are essential for modern human life, since they are used in industrial and agricultural fields. However, most synthetic polymers that have been developed by using petroleum and coal as raw materials are not compatible with the environment, since they cannot be included in the natural recycling system. Therefore, development of environmentally compatible polymers (green polymers) is the key to sustainable developments that can maintain our rich and convenient life [1].

Naturally occurring plant based polymers are divided in: protein, oil and carbohydrates [2]. In this research we have chosen to promote inulin as polymer with biodegradable potential. Inulin is a polydisperse polysaccharide consisting mainly, if not exclusively, of β (2 \rightarrow 1) fructosyl – fructose links (Figure 1) (F_m) with normally, but not necessarily, one glucopyranose unit at the reducing end (GF_n) [3].

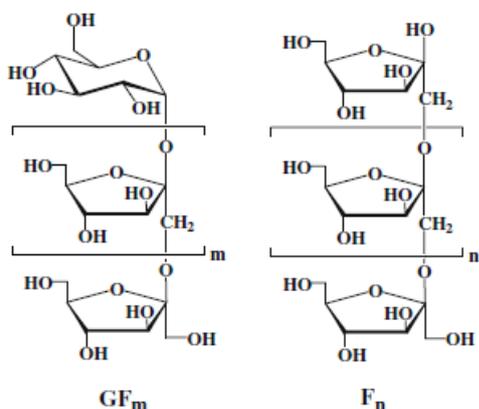


Figure 1. Chemical structure of inulin

The polymerisation degree of inulin varies according to plant origin, weather conditions (during growth) and the physiological age of the plant - in other words the time of its harvest. The main sources of inulin are: Chicory, Dahlia and Jerusalem Artichoke. Native chicory inulin has an average polymerisation degree of 10 to 14. For native Dahlia and native Jerusalem Artichoke an average polymerisation degree of 20 and 6, respectively, has been reported [3,4].

In this study inulin was chemically modified using methacryloyl chloride and palmitoyl chloride. The methacryloyl chloride was used to graft onto the inulin chain a double bond that will be further used in the copolymerisation processes. The palmitoyl chloride is used as internal plasticizer and to transform inulin a hydrophilic compound into a hydrophobic product.

2. Experimental

2.1. Materials

Chicory inulin (Aldrich, average degree of polymerization $n = 10$), N,N -dimethylacetamide (DMAc) (Merck), N,N -dimethyl-4-aminopyridine (DMAP) (Merck), methacryloyl chloride (MCl), (Fluka), palmitoyl chloride (PCI) (Merck), carbon tetrachloride (Merck), 2-ethylhexyl acrylate (EHA) (Merk). All this materials were used as received.

2.2. Esters synthesis

Inulin was dissolved in DMAc in the presence of DMAP as basis catalyst. After complete dissolution MCl was added (1 Eg/fructose unit) and the reaction mixture was stirred for one hour. Further, PCI was added in increasing amount (1 Eg/fructose unit for sample IE1, 1.5

Eg/fructose unit for sample IE1.5 and 2 Eg/fructose unit for sample IE2 respectively). After another hour the inulin esters were isolated from the reaction mixture by separation using distilled water and carbon tetrachloride and were dried first at room temperature and then under vacuum. The inulin esters synthesis and characterisation was previously described [5,6].

2.3. Copolymerisation process

The synthesized inulin esters were dissolved in EHA (1:2 w/w) and benzoyl peroxide was added as initiator. After total dissolution samples were taken and analysed using DSC.

2.4. Differential Scanning Calorimetry (DSC) analysis

Differential Scanning Calorimetric (DSC) analyses were performed on DSC 204 equipment (Netzsch) under nitrogen atmosphere and under dynamic conditions. The DSC curves were recorded from 20 to 150°C using several heating rates (5, 7, 10, 12 and 15 K/min) in order to determine the kinetic behaviour of the copolymerisation process. Samples in liquid form (average mass 5 ± 0.1 mg) were placed in sealed aluminium crucibles (average mass 39 ± 0.2 mg) and analyzed according to the established heating program.

3. Results and Discussions

In order to perform a kinetic characterisation of the copolymerisation process several methods were employed described by: Ozawa, Kissinger Akahire Sunose (KAS) and Friedman. Using the methods described by Ozawa (eq. 1) and KAS (eq. 2) the activation energy is evaluated. Using the method described by Friedman (eq. 5) the kinetic triplet is determined (activation energy, pre-exponential factor and the kinetic function).

Ozawa method

Ozawa method is an isoconversional method based on equation (1) [7]:

$$\ln \beta = \ln \frac{A \cdot E}{R \cdot g(\alpha)} - 5.331 - 1.052 \frac{E}{R \cdot T} \quad (1)$$

where: β is the heating rate (K/min); A is the pre-exponential factor; R the general gas constant; E the activation energy and $T_{\%}$ (K) is the temperature at a certain conversion.

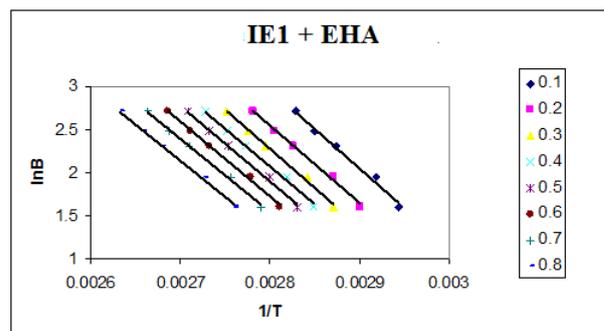


Figure 2. Ozawa plots for the copolymerisation process between IE1 and EHA

By graphical representation of $\ln \beta$ vs. $(1/T)$ (figure 2) several lines are obtained. From their slopes the activation energy at certain conversion is determined. The obtained results and the average value are presented in table 1.

TABLE 1. Activation energies determined using Ozawa method for copolymerisation process between inulin esters and EHA

Conversion	E [kJ/mol]		
	E1 + EHA	E1.5 + EHA	E2 + EHA
0.1	72.20	70.11	69.97
0.2	71.50	70.70	69.75
0.3	70.37	69.96	68.80
0.4	69.98	68.83	67.50
0.5	68.98	68.22	66.87
0.6	68.38	67.02	65.68
0.7	67.30	66.55	64.20
0.8	66.30	65.74	64.40
Average E [kJ/mol]	69.37	68.40	67.14

KAS method

KAS method is an isoconversional based on equation (2) [8]:

$$\ln \frac{\beta}{T^2} = \ln \frac{A \cdot R}{E \cdot g(\alpha)} - \frac{E}{R \cdot T} \quad (2)$$

where: β is the heating rate (K/min); A is the pre-exponential factor; R the general gas constant; E the activation energy and $T_{\%}$ (K) is the temperature at a certain conversion.

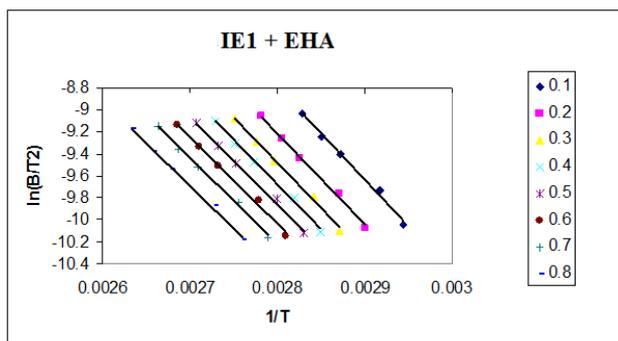


Figure 3. KAS plots for the copolymerisation process between IE1 and EHA

By graphical representation of $\ln \beta/T^2$ vs. $(1/T)$ (figure 3) several lines are obtained. From their slopes the activation energy at a certain conversion is determined. The obtained results and the average value are presented in table 2.

TABLE 2. Activation energy determined using KAS method for the copolymerisation process between inulin esters and EHA

Conversion	E [kJ/mol]		
	E1 + EHA	E1.5 + EHA	E2 + EHA
0.1	70.20	68.04	67.84
0.2	69.35	68.55	67.52
0.3	68.12	67.73	66.45
0.4	67.66	66.50	65.04
0.5	66.57	65.80	64.35
0.6	65.88	64.50	63.05
0.7	64.70	63.95	61.45
0.8	63.56	63.02	61.57
Average E [kJ/mol]	67.00	66.01	64.67

Friedman method

This method [9] uses the logarithmic form of the reaction rate (3) combined with the Arrhenius equation (4).

$$\frac{d\alpha}{dt} = K(t) \cdot f(\alpha) \quad (3)$$

$$K(t) = A \cdot e^{-\frac{E}{RT}} \quad (4)$$

By combing eq. (3) and (4) the Friedman equation (eq. (5)) is obtained:

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + \ln f(\alpha) \quad (5)$$

Using this method the kinetic triplet can be determined: activation energy (E), pre-exponential factor (A) and the kinetic function ($f(\alpha)$).

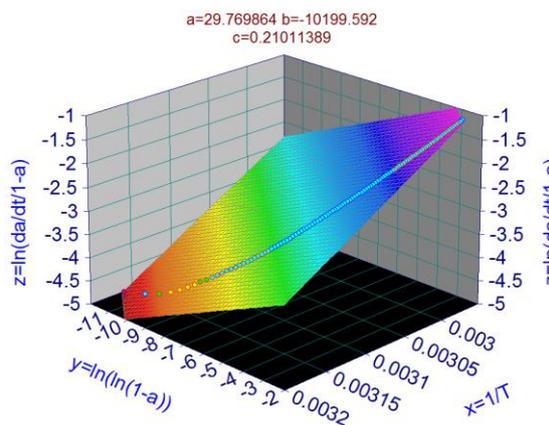


Figure 4. Friedman plot for the copolymerisation process between IE1 and EHA obtained at 5 K/min

Several kinetic functions were used and it was found that for eq. (6) (the Avrami – Erofeev model) r^2 had the best results (0.982) and the activation energy have similar values to the other employed methods.

$$f(\alpha) = n(1-\alpha)[- \ln(1-\alpha)]^{(n-1)/n} \quad (6)$$

By combing eq. 5 with eq. 6, eq. 7 is obtained:

$$\ln \frac{d\alpha/dt}{(1-\alpha)} = \ln(A+n) - \frac{Ea}{RT} + (1-\frac{1}{n}) \ln[- \ln(1-\alpha)] \quad (7)$$

This equation is solved by graphical representation in the form: $z = a \cdot x + b \cdot y + c$. Using the software TableCurve3D the constants a, b and c are determined (figure 4) and thus the activation energy for the copolymerisation processes, the pre-exponential factor and the reaction order are determined. The obtained results and their average are presented in table 3.

TABLE 3. Activation energies determined using Friedman method for the copolymerisation process between inulin esters and EHA

Sample	β [K/min]	$\ln A$ [1/mol s]	E [kJ/mol]	n
E1 + EHA	5	31.43	90.75	1.24
	7	29.04	83.89	1.25
	10	27.36	79.28	1.33
	12	22.22	63.82	1.34
	15	21.26	60.96	1.32
	Average	26.26	75.74	1.29
E1.5 + EHA	5	29.52	84.80	1.28
	7	27.35	78.46	1.27
	10	25.76	73.95	1.38
	12	20.60	58.87	1.56
	15	20.57	58.70	1.42
	Average	24.76	70.96	1.38
E2 + EHA	5	28.91	83.30	1.39
	7	22.96	74.80	1.52
	10	23.43	67.73	1.56
	12	17.92	58.52	1.57
	15	18.33	58.79	1.52
	Average	22.31	68.63	1.51

The used kinetic model is called the Avrami – Erofeev model [10]. The shape of the curve α vs. temperature (figure 5) is also confirmation of the correct selection of the kinetic model.

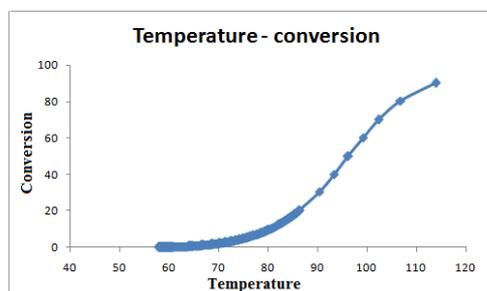


Figure 5. α – temperature dependence for the copolymerisation process of IEI with EHA

4. Conclusions

In this study a new class of polymers with biodegradable potential was obtained. Inulin was chemically modified: first by double bond grafting and then by grafting a long alkyl chain. The double bond is further used into copolymerisation process and the long alkyl chains are used to transform the hydrophilic inulin into a hydrophobic product.

The copolymerization of inulin esters with 2-ethyl hexyl acrylate was studied from the kinetic point of view using DSC technique, by evaluating the activation energies and kinetic model that describes the best the copolymerization process.

Thus, the activation energy values determined using both isoconversional methods (Ozawa, KAS) and differential method proposed by Friedman are in good agreement and have a slight decrease tendency as the acylation degree of the inulin ester increase. The kinetic function that describes the best the copolymerisation process is the Avrami – Erofeev equation. This assumption is supported by the fact that the activation energies have similar values to those evaluated with Ozawa and KAS methods, and furthermore the shape of the conversion – temperature plot has typical Avrami – Erofeev shape.

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