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Effect of molecular weight on thermal degradation mechanism of the biodegradable polyester poly(ethylene succinate)

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Abstract

A series of aliphatic polyesters, in particular poly(ethylene succinate), having different molecular weights, were synthesized from succinic acid and ethylene glycol, following the melt polycondensation process. Intrinsic viscosities (IV), GPC, DSC, ^{1}H NMR and carboxylic end group measurements were used for their characterisation. From thermogravimetric analysis, it was concluded that the molecular weight of polyesters achieved during polycondensation are strongly related to thermal stabilities of initial oligomers. In order to synthesise high molecular weight polyesters, the number average molecular weight of oligomers must not be lower than 2300–3000 g/mol, since thermal decomposition begins at temperatures lower than 200 °C. However, even in that case, polycondensation temperatures must not exceed 230–240 °C. From TGA studies, it was found that sample having different molecular weights could be divided into two groups characterized by different thermal stability. In the first group, belong samples with intrinsic viscosity of IV = 0.08 dL/g and in the second one all the other samples (IV > 15 dL/g). From kinetic analysis of thermal degradation, it was found that degradation of all polyesters takes place in three stages, its one corresponding to a different mechanisms. Degradation of samples with low molecular weight is more complex that that of polyesters having high molecular weights. The values of the activation energy and the exponent *n* for the two groups of samples—with different molecular weight—are similar, regarding the first two mechanisms, while there is an alteration in the case of the third mechanism.

Keywords: Poly(ethylene succinate); Aliphatic polyester; Biodegradable polymer; Molecular weight; Thermal degradation; Thermogravimetry

1. Introduction

Carother first studied the synthesis of aliphatic polyesters through polycondensation reactions of diols with different dicarboxylic acids or their esters, back in 1930s. However, the low melting points of most of the produced polyesters in combination with the difficulty to obtain high molecular weight materials capable for the production of fibres, bottles, films etc., have prevented their usage for a long time. In the synthesis of the polyesters, it was found that monomer conversion and molecular weight are mutually depended, in a complex way. Reaction times used for polycondensation, reaction temperatures, the effectiveness and the type of the catalyst, as well as their concentration are the most critical parameters [1,2]. In the case of PESu, polyesters with rather similar molecular weights were prepared using dimethyl succinate or succinic acid as monomers [3,4]. High molecular weight polyesters are an essential prerequisite for the production of materials with appropriate processability and acceptable mechanical properties. Thermal degradation reactions that extensively take place during polycondensation procedures at elevated temperatures result in the decrease of the molecular weight of the produced polyesters. Furthermore, various side products such as vinyl end groups, cyclic oligomers, acetaldehyde etc., can also be formed having a strong influence on the quality of the produced polyester. High molecular weight biodegradable polyesters can only be synthesised through ring-opening polymerizations of cyclic esters such as lactones and lactides [5]. Techniques like solid-state polycondensation that are used in other polyesters like PET [6,7], are not possible to be implemented due to the low melting points of aliphatic polyesters. At such low temperatures, the diffusion rates of the by-products formed during polycondensation are very low and thus it is very difficult to be removed.

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From our previous paper concerning the biodegradation rate of polyesters of succinic acid, it was found that poly(propylene succinate) (PBSu) biodegrades faster than poly(ethylene succinate) or poly(butylene succinate), which has the lowest biodegradability [4]. Since chemical composition plays an important role on the biodegradation rates, it was expected that PBSu would biodegrade faster than the other two polyesters of the same family. Fields et al. that studied polyesters prepared from diacids containing C_2–C_{12} and diols with C_4–C_{12}, have found that the distance between ester groups affected the biodegradation rate [8].

Chemical structure in aliphatic polyesters, except of the biodegradation rates seems to also slightly affect the decomposition temperatures [9]. The tendency for chain scission is higher in the polyesters in which monomers with a higher number of methylene groups are used. Indeed, as was found from the peak of the first derivative, the temperatures at which PBSu and PESu decomposition rates take the highest values are at 399 and 413 °C, respectively, at a heating rate of 10 °C/min [9]. Furthermore, from our previous study, it was verified that the maximum rate of mass loss of the aliphatic polyester poly(propylene succinate) of the same family, appeared at a decomposition temperature 408 °C [10], the value lying between the corresponding decomposition temperatures of PESu and PBSu. These findings are in accordance with that mentioned for aromatic polyesters, like PBT, PPT and PET [11], and PET, containing one or two methylene groups less than the other polyesters, is more stable during decomposition.

The aim of the present work is to study the effect of molecular weight of the biodegradable polyester poly(ethylene succinate) (PESu) on its thermal degradation stability and decomposition rates. Furthermore, a possible correlation of the molecular weights of the initial oligomers with the polycondensation temperature used for polyester preparation was investigated, in order to find the appropriate temperature for the synthesis of high molecular weight polyesters. For this reason, samples with different molecular weights were synthesized according to the two-stage melt polycondensation method—using different polycondensation temperatures—and characterized. The thermal degradation mechanism was also investigated.

2. Kinetic methods

Kinetic information and activation energy E can be extracted from dynamic experiments by means of various methods. The first method, the isoconversional method of Ozawa, Flynn and Wall (OFW) [12,13] is in fact, a “model free” method in which it is assumed that the kinetic function $f(\alpha)$ does not change with the alteration of the heating rate for all values of α. The measure of the temperatures corresponding to fixed values of α from experiments at different heating rates β is involved. Therefore, plotting $\ln(\beta)$ against $1/T$ according to:

$$\ln(\beta) = \ln \frac{A f(\alpha)}{\frac{d\alpha}{dt}} - \frac{E}{RT} \tag{1}$$

should give straight lines and its slope is directly proportional to the activation energy ($-E/R$). If the determined activation energy is the same for the various values of α, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of E with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [14]. These complications are being significant, in the case that competitive mechanisms are involved in the total reaction.

The second method is also an isoconversional one. Friedman [15] proposed to apply the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature:

$$\ln \frac{d\alpha}{dT} = \ln \frac{A}{\beta} + \ln(f(\alpha)) - \frac{E}{RT} \tag{2}$$

It is obvious from Eq. (2) that if the function $f(\alpha)$ is constant for a particular value of α, then the sum $\ln(f(\alpha)) + \ln(A/\beta)$ is also constant. In this case, by plotting $\ln(d\alpha/dT)$ against $1/T$, the value of the $-E/R$ for a given value of α can be directly obtained. Using this equation, it is possible to obtain values for E over a wide range of conversions.

3. Experimental

3.1. Materials

Succinic acid (purum 99%), ethylene glycol (purum 99%) and tetrabutoxytitanium (TBT) used as catalyst (analytical grade) were purchased from Aldrich Chemical Co. Polyphosphoric acid (PPA) used as heat stabilizer was supplied by Fluka. All other materials and solvents that were used for the analytical methods were of analytical grade.

3.2. Synthesis of poly(ethylene succinate)

Poly(ethylene succinate) (PESu) was prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [1,16]. In briefly, the proper amount of succinic acid and ethylene glycol in a molar ratio 1/1.1 and the catalyst (3×10^{-4} mol TBT/mol SA) were charged into the reaction tube of the polyesterification apparatus. The apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture was heated at 190 °C under argon atmosphere and stirring at a constant speed (500 rpm). This first step (esterification) is considered to be completed after the collection of an H_2O amount close to the theoretically calculated according to the monomer ratios. The amount of H_2O was removed from the reaction mixture by distillation and collected in a scaled cylinder.

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol SA), in order to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period time of about 30 min, to avoid excessive foaming and to minimise oligomer sublimation, which is a potential problem during the melt polycondensation. In order to prepare samples with different molecular weight, polycondensation was performed at different temperatures such as 170, 200, 220, 230 and 250 °C. The polycondensation time was stable, about 60 min, for all prepared polyesters while stirring speed was increased at 720 rpm. After the polycondensation reaction was completed, the polyesters were easily removed, milled and washed with methanol.

3.3. Measurements

3.3.1. Intrinsic viscosity

Intrinsic viscosity [η] measurements were performed, by using an Ubbelohde viscometer at 25 °C in chloroform. All polyesters were dissolved at room temperature in order to prepare solutions 1 wt.% and filtered through a disposable membrane filter 0.2 μm (Teflon). Intrinsic viscosity was calculated after the Solomon-Ciuta equation [17]:

$$[\eta] = \frac{2\left\{\frac{t}{t_o} - \ln\frac{t}{t_o} - 1\right\}^{1/2}}{c}$$

where c is the concentration of the solution; t the flow time of solution and t_o is the flow time of pure solvent.

3.3.2. Gel permeation chromatography (GPC)

GPC analysis was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyragel (103, 104, 105 Å) columns in series. $CHCl_3$ was used as the eluent (1 mL/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

3.3.3. Carboxyl end-group content

Carboxyl end-group content (–COOH) of the resins was determined as follows: About 0.1 g of polyesters was dissolved in chloroform at room temperature and the solution was titrated by using a standard NaOH in methanol (N/10) and phenol red as indicator.

3.3.4. Nuclear magnetic resonance (NMR)

^{1}H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated chloroform ($CDCl_3$) was used as solvent in order to prepare solutions of 5% (w/v). The number of scans was 10 and the sweep width was 6 kHz.

3.3.5. Thermal analysis

A Setaram, DSC 141, Differential Scanning Calorimeter (DSC), calibrated with Indium, Tin and Zinc standards, was used. A sample of about 10 mg was used for each test, placed in an aluminium crucible and heated to 35 °C above the melting point of particular polyester at a heating rate 10 °C/min. The sample remained at that temperature for 5 min in order to erase any thermal history. After that it was quenched into liquid nitrogen and scanned again using the same heating rate as before. The glass transition temperature (T_g), the melting temperature (T_m) and the heat of fusion (ΔH_m) were measured.

Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 1750 °C. Samples (11.0 ± 0.5 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 500 °C in a 50 mL/min flow of N_2. Nominal heating rates of 5, 10, 16 and 22 °C/min were used and continuous records of sample temperature, sample weight, its first derivative and heat flow were taken.

4. Results and discussion

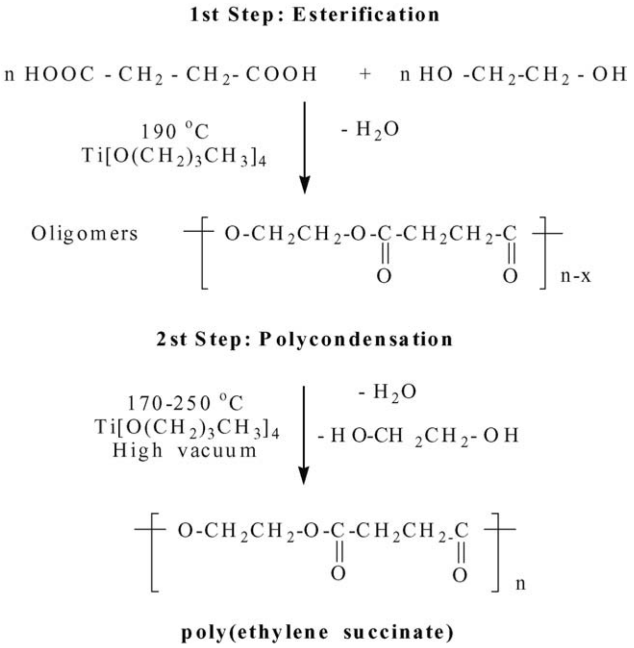
4.1. Characterization of poly(ethylene succinate)

In the first stage of the polymerisation process, succinic acid reacts with ethylene glycol and water eliminates as by-product. The reaction takes place at elevated temperature (190 °C), so the formed water can be easily removed from reactor and oligomers were prepared. Their measured intrinsic viscosity is 0.08 dL/g corresponding to a number for average molecular weight ranging between 1500 and 2000 g/mol, without being possible to be measured exactly, due to the limitations of GPC method. In order to prepare polyesters with different molecular weights, polycondensation of oligomers was performed at different temperatures—range 170–250 °C—keeping stable the reaction time 1 h, with the application of high vacuum. As long as the temperature is increased, the ability of polycondensation by-products (ethylene glycol and water) removal, becomes higher. Thus, samples with higher molecular weights are prepared only at elevated temperatures, as can be seen, also, from Table 1. The highest molecular weight was achieved for polycondensation temperature 250 °C. Due to thermal sensitivity of PESu, it is not possible higher temperatures to be used, as the degradation of polyester begins. Probably, this temperature constitutes the highest limit. The reactions that take place during these stages and

Table 1
Properties of PESu samples with different molecular weights

a/a	T_{pol}[a] (°C)	IV (dL/g)	M_n	M_w	T_m (°C)	T_g (°C)	T_c (°C)	ΔH_m (J/g)	X_c[b] (%)	[–COOH] (equiv./10^{-6})
1		0.08	–	–	77	−43.5	6.5	62.7	34.7	942
2	170	0.15	3560	9820	101	−16.7	40	67.7	37.6	178
3	200	0.28	6810	17980	102	−11.1	41	67.7	37.6	80
4	220	0.41	11350	29050	103	−11.3	41	61.0	33.8	39
5	230	0.57	17100	43780	105	−11.1	46	59.1	32.7	16
6	250	0.69	21480	53700	105	−10.2	47	54.2	30.0	21

[a] T_{pol}: the polycondensation temperature.
[b] Degree of crystallinity was calculated using 180 J/g heat of fusion for pure crystalline PESu [18].



Scheme 1. Procedures and chemical reactions during preparation of succinate polyesters.

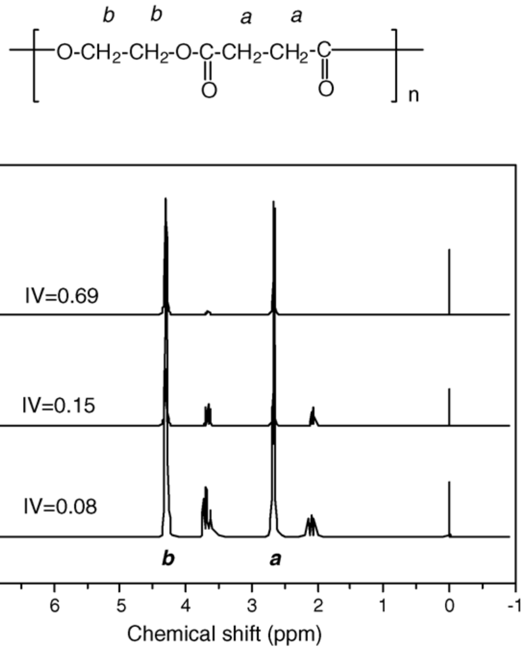


Fig. 1. ^{1}H NMR spectra of PESu samples with different intrinsic viscosities.

the procedure that was used for the synthesis of poly(ethylene succinate) are presented in Scheme 1.

The prepared polyesters have a yellowish-brown colour due to the use of tetrabutyl titanate as catalyst. The colour becomes more intense in samples prepared at higher polycondensation temperatures due to thermal decomposition reactions that take place, resulting in the creation of chromophoric groups. The produced samples have completely different properties, regarding their stiffness. The samples with low molecular weights up to 3560 g/mol are soft and sticky while these with high molecular weight present progressive hardening. Of course, the sample with the highest molecular weight $M_n = 21480$ g/mol (IV = 0.69 dL/g) presents incredible resistance during extension, having tensile strength 48 MPa and elongation at break higher than 700%. The values for there properties are particularly high for biodegradable polymers, while the sample with $M_n = 17100$ g/mol (IV = 0.57 dL/g) results has tensile strength at break 28 Mpa and elongation at break higher than 500%, which are directly comparable with those of polyolefines (HDPE, PP). The carboxyl end groups are gradually decreased from oligomers till intrinsic viscosity 0.57 dL/g revealing the progress of polycondensation reaction. The small increase calculated in the sample prepared at 250 °C with intrinsic viscosity 0.69 dL/g is maybe an indication to degradation reactions that take place, hypothesis that is strengthened from its light brown colour that this sample has.

The ^{1}H NMR spectra of studied PESu samples are shown in Fig. 1. The ^{1}H NMR spectrum of PESu is very simple, containing only two characteristic peaks at 2.55–2.67 and 4.18–4.3 ppm attributed to methylene proton *a* of succinic acid and *b* of ethylene glycol, respectively. Furthermore, in samples having low molecular weight, it can be found additionally some other peaks but with smaller intensity at 1.9–2.2 and at 3.45–3.8 ppm. These can be attributed to the presence of oligomers—due to low molecular weight that the particular polyesters have. As long as the molecular weight increases these peaks tend to be minimized, while in the sample, with intrinsic viscosity 0.69 dL/g they have been, almost, eliminated.

In Fig. 2, the DSC thermograms for the studied samples are presented. All polyesters after melting were quenched in liquid nitrogen in order to be taken completely amorphous and their previous thermal history to be erased. From the thermograms, it can be concluded that melting temperatures of the polyesters are shifted to higher temperatures with the increase of the molecular weight till IV = 0.15 dL/g and remain almost stable for polyesters with IV > 0.28 dL/g (Table 1). The oligomers with IV = 0.08 dL/g have the lowest melting point 77 °C while the fusion peak is very broad. Some broadness can be attended also,

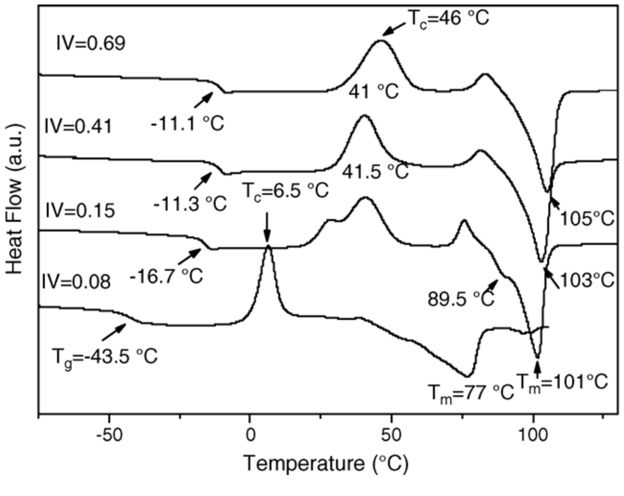


Fig. 2. DSC thermograms of the studied polyesters with different intrinsic viscosities.

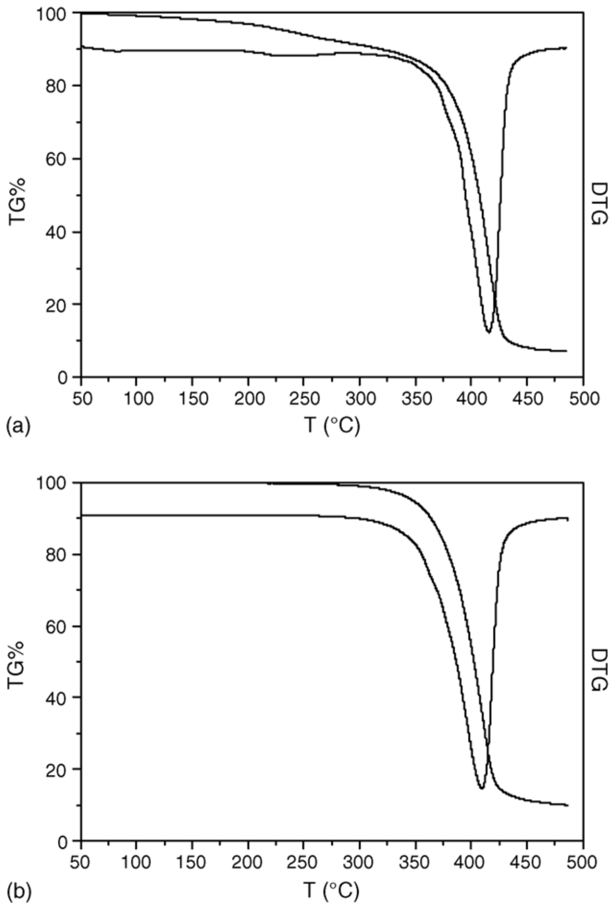


Fig. 3. Mass loss (TG%) and derivative mass loss (DTG) vs. temperature at heating rate $\beta = 10\,^{\circ}\mathrm{C/min}$ for PESu samples with: (a) IV = 0.08 dL/g and (b) IV = 0.69 dL/g.

in the sample with IV = 0.15 dL/g, which beyond the main melting point at 101 °C has also a shoulder at 89.5 °C, due to the presence of crystals with lower perfectness. This was also reflected in the cold crystallization where two peaks are recorded. The cold-crystallization exotherms presented a remarkable shift to higher temperatures by increasing the molecular weight of the polyesters, especially till IV = 0.15 dL/g. This shift is retarded at higher molecular weights, confirming the difficulty that they have for crystallization due to the higher entanglement of macromolecular chains. Furthermore, cold crystallization of all samples is accompanied by recrystallization exotherms, behaviour that is well known for these polyesters. In order to calculate the degree of crystallinity (X_c), 180 J/g heat of fusion for pure crystalline PESu was used [18]. As it can be seen in Table 1, the degree of crystallinity is increased until the sample with IV = 0.28 dL/g, where the highest value achieved, and then it is decreased substantially confirming what was already commented about the crystallization difficulty of samples with high molecular weights.

4.2. *Thermogravimetric analysis*

Thermal degradation of PESu was studied by following its mass loss during heating. In Fig. 3 (TG% and Derivative TG versus T) are presented assembled, the results for samples having different molecular weights. From the thermograms in Fig. 3a, it can be seen that sample with IV = 0.08 dL/g presents three stages in the mass loss curve. These stages are distinguishable in the diagram of mass loss (TG%) during heating as well as—more clearly—in the diagram of derivative mass loss (DTG). These stages are: first in the region of temperatures up to the 180 °C, second roughly up to the 290 °C and the third stage is completed before the 500 °C. On the contrary, in TG-thermograms of the other samples with IV = 0.15–0.69 dL/g, which behave similar (Fig. 3b) one clear stage of mass loss can be observed, at temperature higher than 290 °C. However, as it can be seen in the curves of DTG, in the early stages of the decomposition, there is a small shoulder probably due to a slight difference in the slope of decomposition curve of TG. Such a pre-major weight loss stage was also mentioned in poly(propylene terephthalate), where this first decomposition step corresponding to small weight loss was attributed to the volatilization of small molecules, residual catalysts, 1,3-propanediol and carbon dioxide that devaluated from chain ends [19].

From preliminary studies of the monomers used for synthesis of PESu, it was found that succinic acid degrades at temperatures close to 200 °C [20] and ethylene glycol volatilizes at slightly higher temperatures. However, both are fully decomposed or volatilized at temperatures lower than 300 °C. These data strengthens our hypothesis that the first decomposition step is due to oligomer degradation. Comparing the TG and DTG thermographs of the samples with intrinsic viscosity higher than that of 0.15 dL/g, it can be concluded that these have similar thermal behaviour, as was already discussed above and can be characterized as one group. One difference that can be mentioned is a small dependence of final mass loss percent from molecular weight (Fig. 3a,b). It is obvious that increasing the molecular weight is followed by a—rather small—progressive reduction of the total decomposed mass.

Examining more carefully the TGA thermograms (Fig. 3), it can be seen that in the sample with IV = 0.08 the mass loss starts immediately with the beginning of heating at temperatures just above its melting point thus, presenting no thermal stability. Similar melt instability in aliphatic biodegradable polyesters was mentioned in poly(hydroxyalcanotes) and mainly in poly(3-hydroxybutyrate). This instability restricted its uses for commercial applications for item production via melt processing techniques [21]. However, in our case, there is no interest for such a case since sample with so low molecular weight cannot find industrial applications for large-scale productions. On the contrary, the samples with IV higher than 0.15 dL/g, present a relatively good thermostability, since no significant weight loss is recorded. Thus, for the samples containing IV = 0.15 and 0.69 dL/g mass loss occurred at 250 °C was only 0.7 and 0.2%, respectively. This finding constitutes a confirmation that the temperature of 250 °C may be inadequate for the production of PESu while the temperature of 240 °C should be considered as the lower limit for the polycondensation since at that temperature begins, even in limited degree, a progressive degradation of polyester. A temperature T_d (−2 wt.%), at which 2.0 wt.% of the original polyester sample has already been thermally degraded and lost, is hereby taken as an index expressing its thermal stability. This temperature is 163 °C for IV = 0.08 and from 308 to 326 °C for IV = 0.15 to IV = 0.69 dL/g samples.

From the mentioned findings, apart from the highest temperature that can be safely used for the polycondensation reactions of PESu, one more valuable conclusion can be extracted, that was not acquainted for aliphatic polyesters up to today. That important parameters for the production of polyesters with a high molecular weight are also the intrinsic viscosity or better the molecular weight of the oligomers that are prepared in the first stage of esterification. The lower this is the smaller the molecular weight of the produced polyesters will be since the reactions of the thermal decomposition dominates over those of polycondensation. Thus, it appears that there exists a limitation on the molecular weight of the oligomers, which corresponds to a molecular weight of 3000–3500 mol/g or an intrinsic viscosity higher than 0.15 dL/g.

In order to be analyzed more deeply the degradation mechanisms of PESu with different molecular weights, it is important the kinetic parameters (activation energy E and pre-exponential factor A) and conversion function $f(\alpha)$ to be evaluated. The relationship between kinetic parameters and conversion (α) can be found by using the mass loss curves recorded in TG dynamic thermograms. From these diagrams presented before, it appears that the studied samples can be divided in two groups depending on the number of mass loss stages. In the first group, belongs the sample with IV = 0.08 dL/g and in second all other samples. Thus, a complete kinetic study will be performed in one member of each group, in the sample with IV = 0.08 and in the sample with IV = 0.69 dL/g. The samples of second group appear to have negligible differences and for this reason the results of kinetic study for the sample IV = 0.69 dL/g could be considered for all others. The results from the kinetic study of sample with IV = 0.28 dL/g are directly comparable [11].

4.3. Kinetic analysis of PESu degradation with IV = 0.08 dL/g

The thermogravimetric curves of PESu with IV = 0.08 dL/g heated in N_2 atmosphere, at different heating rates are shown in Figs. 4 and 5. It is clear from the DTG plots that the peak temperature, T_p that corresponds in the region with the biggest mass loss shifts to higher values with increasing heating rate; an increase of 27.9 °C is recorded for the examined heating rates.

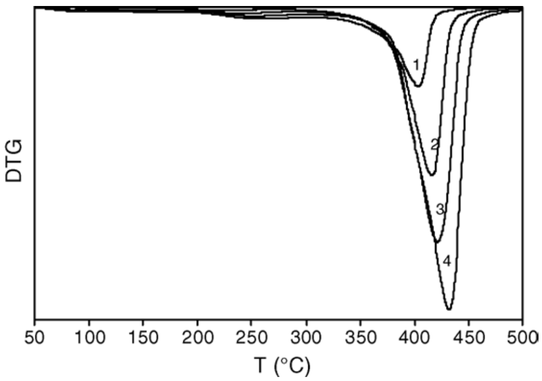


Fig. 5. DTG curves of PESu with IV = 0.08 dL/g at different heating rates β. 1: 5 °C/min, 2: 10 °C/min, 3: 16 °C/min, 4: 22 °C/min.

As it has already be mentioned and it is clear from Figs. 4 and 5, the mass loss follows at least three stages in all heating rates, not completely separated. Therefore, for the precise kinetic description of mass loss at least three different mechanisms have to be considered. Really, in the region of main mass loss (Fig. 5) it appears, that at the first stages considerably overlapped peaks exists, so that in order to describe completely the total mass loss maybe not three but at least four different mechanisms would be required. The activation energy of degradation of the polyester under study for the whole mass loss area was estimated using Ozawa, Flynn and Wall (OFW) and Friedman methods. Firstly, the isoconversional Ozawa method was used to calculate the activation energy for different conversion values by fitting the plots of log β versus $1/T$. Secondly, Friedman method was used by plotting $\ln(d\alpha/dT)$ against $1/T$ for a constant α value and the activation energy is calculated. The results are shown in Fig. 6.

It is followed from Fig. 6 that the dependence of E on α value, as calculated with Friedman and Ozawa methods presents the same tendency. The difference in the E value calculated by the two methods can be explained by a systematic error due to improper integration. The method of Friedman employs instantaneous rate values being, therefore, very sensitive to experimental noise. In Ozawa method, the equation used is

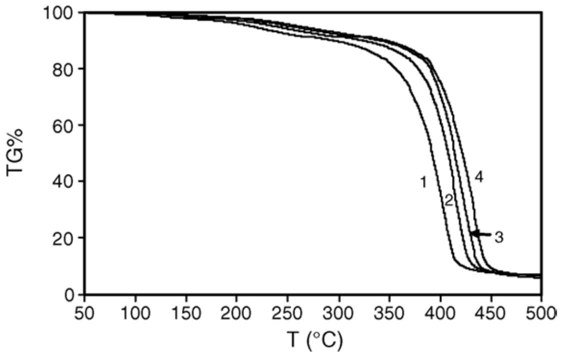


Fig. 4. TG curves of PESu with IV = 0.08 dL/g at different heating rates β (5, 10, 16, 22 °C/min).

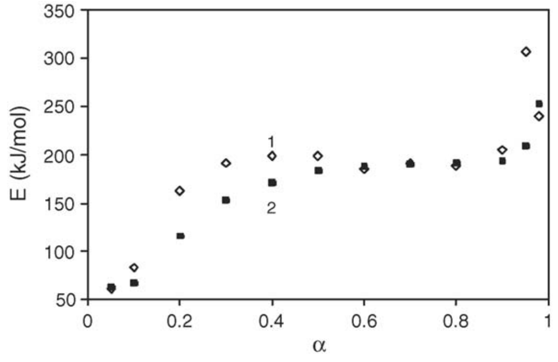


Fig. 6. Friedman (1) and Ozawa (2) plots of PESu with IV = 0.08 dL/g.

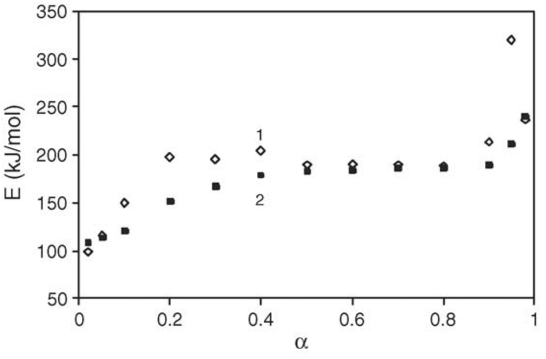


Fig. 7. Friedman (1) and Ozawa (2) plots of PESu with IV = 0.08 dL/g for the region of main mass loss.

derived assuming constant activation energy, introducing systematic error in the estimation of E in the case that E varies with α, error that can be estimated by comparison with the Friedman results [22]. The dependence of E on α value, as calculated with Ozawa method, can be separated in four distinct regions corresponding to the different degradation processes of sample during heating, the first for values of α up to 0.1, in which E presents a slight monotonous increase, the second ($0.1 < \alpha < 0.3$) in which E presents a monotonous but important increase, the third region for $0.3 < \alpha < 0.9$ in which E can be considered as having a constant average value and the fourth region for $\alpha > 0.9$ in which E presents again an important increase. This dependence of E on α is an indication of a complex reaction with the participation of at least four different mechanisms. This has as result the kinetic treatment of total mass loss to be particularly complicated. Thus, since the total confrontation of the subject is particularly questioning it will be presented only the kinetic treatment in the region of main mass loss in equivalence with the kinetic treatment that became also for the other polyesters having different intrinsic viscosities. The activation energy of degradation of the studied polyester, for this region of mass loss, was estimated also using Ozawa and Friedman methods. The results are shown in Fig. 7. As can be concluded from the analysis of the slopes, the dependence of E on α value presents a slightly different tendency from the dependence that was calculated by using the same methods but for the whole mass loss area (Fig. 6). In this second case, the data can be separated not in four but in three distinct regions, the first for values $\alpha < 0.2$, in which E presents a monotonous increase, the second ($0.2 < \alpha < 0.9$) in which E can be considered as having a constant average value and the third region for $a > 0.9$ in which the E presents an important increase. This dependence of E on α confirms that decomposition reaction is very complex with the participation of at least three different mechanisms. The first two steps can be compared with the observed very small divergences from the peak regularity in the DTG-diagram. Although, the "two mechanisms"—as a result of the increasing E with a—is a rather typical phenomenon for many polymers [23], this assumption is based in the multi-step TG curve. This is not clear in our case (for the main mass loss) and the conclusion is extracted through the combined examination of overlapped peak in DTG diagram. From the two mechanisms, the first corresponds to the part where small loss appears while the second part, where the substantial mass loss takes place, is attributed to the main decomposition mechanism, each one mechanism presenting different activation energy.

In order to determine the nature of these mechanisms through the comparison of the experimental and theoretical data, initially, it is considered that the degradation of PESu can be described only by a single mechanism that corresponds to the mass loss, without pre-assuming the exact mechanism. Then, knowing this mechanism ($f(\alpha)$), are determined the data of the other mechanisms, in order the better possible agreement between experimental and theoretical data to be achieved. To determine the conversion function $f(\alpha)$, we used a method referred to as the "model fitting method" [24]. This method that does not assume the knowledge of E and $f(\alpha)$ in advance, was applied simultaneously on the experimental data taken at the heating rates $\beta = 5$, 10, 16 and 22 $^{\mathrm{O}}$C/min. It has been shown that model-fitting to multiple heating rate data gives activation energies similar to the values estimated by the isoconversional methods [25]. For the fitting were used 16 different kinetic models. The form of the conversion function, obtained by fitting is $f(\alpha) = (1 - \alpha)^n$ and the parameters of the mechanisms were: the exponent value $n = 0.61$, activation energy $E = 179.8$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 11.5 and the correlation coefficient was 0.99931. Comparing these results, the nature of mechanism can be evaluated and it can be defined as nth-order reaction mechanism, which coincides with the mechanism that is generally used for the description of mass loss in polyesters [26]. The value of the activation energy is between the limits of the calculated values from the Ozawa and Friedman methods. The fitting to the experimental data is very good for the area where mass loss takes values higher than 20% and lower to 80%. The divergence is important for the regions where the mass loss takes lower values and is exceptionally significant in the area of mass loss higher than 80% (high temperature area).

In continuation and taking into account the incomplete fitting in the two regions there will be used the two mechanisms according to the observations from the DTG versus T thermograms. For the determination of these mechanisms are assumed the following: (a) the two mechanisms follow each other; (b) the first mechanism, which we try to identify corresponds to small mass loss, it concerns to the first 20% of mass loss according to the indications that we have from the diagrams DTG versus T and E versus α; (c) this mechanism according to the literature is mechanism of autocatalysis n-order [27,28] that is described by equation $f(a) = (1 - \alpha)^n \alpha^m$.

The agreement of experimental and theoretical results, Fig. 8, leads to a further improvement of fitting that is remarkable mainly in the first stages of mass loss. In this stage of identification for the best possible results, we left the parameters (E, A and n) of the examined mechanisms to be recalculated. Afterwards, the identification the parameters for the two mechanisms are: for first with $f(a) = (1 - \alpha)^n \alpha^m$ the exponent value n is equal to 0.83, activation energy $E = 150$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 9.81 and $m = 4.4\mathrm{E}{-5}$, and for the second with $f(\alpha) = (1 - \alpha)^n$ the exponent value n is equal to 0.66, activation energy $E = 188$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 12.2 and the correlation coefficient was 0.99941. The values of

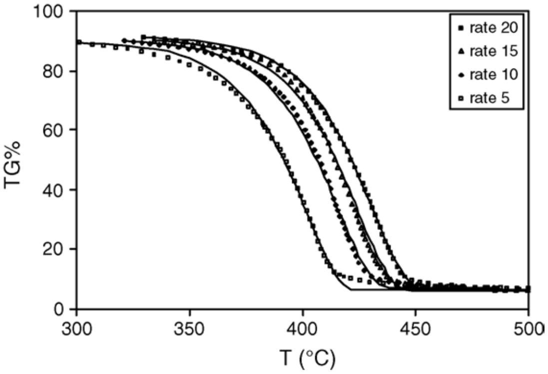


Fig. 8. Fitting and experimental data TG curves of PESu with IV = 0.08 dL/g for all the different heating rates β (5, 10, 16, 22 °C/min) with two reaction mechanisms.

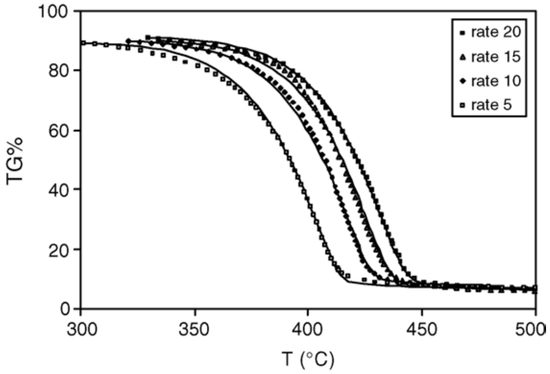


Fig. 9. Fitting and experimental data TG curves of PESu with IV = 0.08 dL/g for all the different heating rates β (5, 10, 16, 22 °C/min) with three reaction mechanisms.

activation energy correspond to the two first stages that are distinguished in the diagram E versus α.

From the comparison of identification that has been achieved with the help of the one or two mechanisms, we can conclude that the use of this second mechanism does not improve the identification in the region of mass loss higher than 80% (high temperatures region). The important differentiation between experimental and theoretical data that are presented for this particular region, in combination with the big increase of activation energy for the particular region as this appears in diagram E versus α, indicates the existence of a possible third mechanism. This mechanism must have as a result the progressive reduction of the decomposition rate of polyester and a substantial shift of decomposition completion in higher temperatures. With the help of diagram E versus a it was designated the regions in which the main mass loss of each mechanism is reported. These regions are differentiated precisely as follows: the first region concerns to the 15% of mass loss, the second to 75% and third to 10%. The form of the conversion function, obtained by fitting for this third mechanism is $f(\alpha) = (1 - \alpha)^n$. Afterwards the identification the parameters for the three mechanisms are: for first with $f(\alpha) = (1 - \alpha)^n \alpha^m$ the exponent value n is equal to 0.74, activation energy $E = 148.4$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 9.69 and $m = 2.4\text{E}{-5}$, for the second with $f(\alpha) = (1 - \alpha)^n$ the exponent value n is equal to 0.54, activation energy $E = 190.8$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 12.4 and for the third with $f(\alpha) = (1 - \alpha)^n$ the exponent value n is equal to 3.9, activation energy $E = 242$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 7.48. The correlation coefficient was 0.99968. The identification is particularly satisfactory, as it appears in Fig. 9, even in the region with mass loss values higher than 80%.

The identification for the two and three mechanisms has been realized considering that these regions of mass loss are independent. However, that is not our case since there is not a constant or clearly separated area before the beginning of each mass loss.

4.4. Kinetic analysis of PESu degradation with IV = 0.69 dL/g

The thermogravimetric curves of PESu with IV = 0.69 dL/g heated in N_2 atmosphere, at different heating rates are shown in Figs. 10 and 11. In order, the achieved data to be comparable with those of sample having IV = 0.08 dL/g, exactly the same heating rates were used.

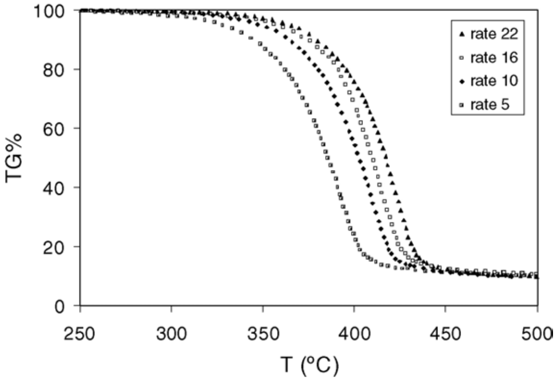


Fig. 10. TG curves of PESu with IV = 0.69 dL/g at different heating rates β (5, 10, 16, 22 °C/min).

The activation energy of degradation of the studied polyester was estimated using also for this sample the Ozawa, Flynn and Wall (OFW) and Friedman methods as in the case of sample with IV = 0.08 dL/g. The results are shown in Fig. 12 revealing that the dependence of E on α value that was calculated with Friedman and Ozawa methods presents the same tendency. The dependence of E on α value, as calculated with Ozawa method,

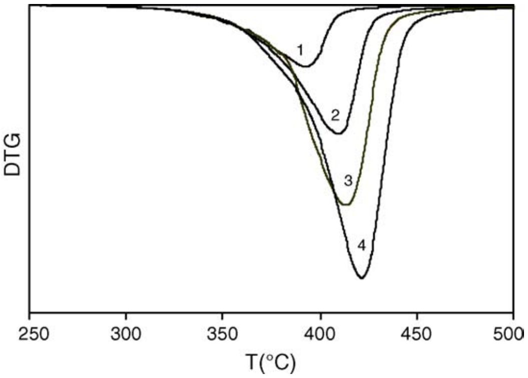


Fig. 11. DTG curves of PESu with IV = 0.69 dL/g at different heating rates β. 1: 5 °C/min, 2: 10 °C/min, 3: 16 °C/min, 4: 22 °C/min.

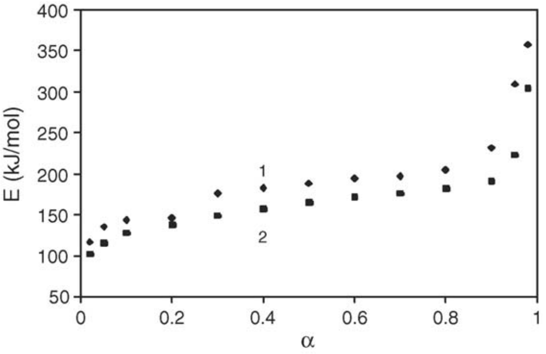


Fig. 12. Friedman (1) and Ozawa (2) plots of PESu with IV = 0.69 dL/g.

can be separated in three distinct regions. The first one for values of α up to 0.2, in which E presents a monotonous increase, the second for values $0.2 < \alpha < 0.8$ in which E can be considered as having a constant average value and a third region for $\alpha > 0.8$ where substantial increase for E can be found. This dependence is similar to the one followed in the sample with IV = 0.08 dL/g. This dependence of E on α is an indication of a complex reaction with the participation, of at least two different mechanisms. This is in accordance with other studies in biodegradable polyesters such as PCL, in which two mechanisms were recorded with different activation energies each other [29–32]. However, such behaviour is not characteristic only for aliphatic polyesters but is also recorded during thermal degradation of other polymers like PE and PP [23]. The activation energies for these polymers are very small at the initial stages of degradation and higher at the final stages. These initial lower values are most likely associated with initiation process that occurs at weak links of PE and PP, which is, however, a limited step of degradation. By increasing the temperature, random scission of macromolecular chains predominates and the activation energy has a greater value.

In order to determine the nature of these two mechanisms through the comparison of the experimental and theoretical data, the same method as in the sample with IV = 0.08 dL/g was followed [24]. This method was applied simultaneously on the experimental data taken at the heating rates $\beta = 5$, 10, 16 and 22 °C/min. The form of the conversion function, obtained by fitting is $f(\alpha) = (1-\alpha)^n$ and the parameters of the mechanisms were: the exponent value n is equal to 0.62, activation energy $E = 166.2$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 10.6 and the correlation coefficient was 0.99929. Comparing these results, the nature of mechanism can be evaluated and it can be defined as nth-order reaction mechanism, similar to that described extensively before.

With the help of E versus α diagram, we determine the mass loss regions corresponding for each one mechanism, as follows: the first region concerns to a 20% of mass loss, the second 65% and third 15%. The form of the conversion function, obtained by fitting for this third mechanism is $f(\alpha) = (1-\alpha)^n$. Afterwards the identification the parameters for the three mechanisms leads to the following values: for the first with $f(\alpha) = (1-\alpha)^n\alpha^m$ the exponent value n is equal to 0.76, activation energy $E = 140$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 9.04 and $m = 2.1\mathrm{E}{-5}$, for the second with $f(\alpha) = (1-\alpha)^n$ the exponent value n is equal to 0.56, activation energy $E = 182$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 11.96 and for the third with $f(\alpha) = (1-\alpha)^n$ the exponent value n is equal to 3.06, activation energy $E = 290$ kJ/mol, pre-exponential factor $\log A$ (s^{-1}) = 20.72. The correlation coefficient was 0.99976. The identification is particularly satisfactory, as it appears in Fig. 12, even for the region of values with mass loss higher than 80%. Summarizing, the parameters of the mechanisms can be found in Table 2.

Table 2
Calculated parameters of the mechanisms

	Mechanism	n	E (kJ/mol)	$\log A$ (s^{-1})
PESu IV = 0.08 dL/g				
First	$f(\alpha) = (1-\alpha)^n\alpha^m$	0.74	148.4	9.69
Second	$f(\alpha) = (1-\alpha)^n$	0.54	190.8	12.40
Third	$f(\alpha) = (1-\alpha)^n$	3.90	242.0	17.48
PESu IV = 0.69 dL/g				
First	$f(\alpha) = (1-\alpha)^n\alpha^m$	0.76	140.0	9.04
Second	$f(\alpha) = (1-\alpha)^n$	0.56	182.0	11.96
Third	$f(\alpha) = (1-\alpha)^n$	3.06	290.0	20.72

From the comparison of the received results from the fitting of the experimental data of samples with different molecular weights, it can be concluded that the values of the activation energy and the exponent n for the two groups of samples are similar regarding the first two mechanisms, while there is a differentiation in the case of the third mechanism.

5. Conclusions

Synthesis of biodegradable aliphatic polyesters like PESu that are studied in the present work, takes place by the two-stage melt polycondensation method. From the study with thermogravimetric analysis of PESu samples having different molecular weight, it was realized that in both stages—esterification and polycondensation—there exist critical factors that have to be taken into consideration in preparation of polyesters with particularly high molecular weight.

It was concluded that molecular weight above 3000–3500 dL/g has much less effect on thermal decomposition rates. In lower molecular weights, such as the oligomers with IV < 0.15 dL/g, decomposition starts at very low temperatures, close to 200 °C, which may constitute restrictive factor for the essential increase of molecular weight during polycondensation. Thus, in order to achieve high molecular weight polyesters, molecular weight of oligomers in the second stage of polycondensation should be higher than 3500 g/mol while polycondensation temperatures 230–240 °C should be used.

A complete kinetic study has been performed in the sample with IV = 0.08 and in the sample with IV = 0.69 dL/g. In the polyester with IV = 0.08 dL/g, degradation takes place in three stages. For the kinetic description of the mass loss of all samples (main mass loss in sample with IV = 0.08 dL/g), three different mechanisms must be used. The first corresponds to a very small mass loss, the second for the main degradation stage and the third—at elevated temperatures—that has the lowest rate is due to the decomposition of very small mass. These stages are attributed to different decomposition mechanisms and activation energies as are determined with isoconversional methods of Ozawa, Flyn, Wall and Friedman.

The values of the activation energy and the exponent n for the two groups of samples—with different molecular weight—are similar, regarding the first two mechanisms, while there is a differentiation in the case of the third mechanism.

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