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Thermal degradation kinetics and decomposition mechanism of two new aliphatic biodegradable polyesters poly(propylene glutarate) and poly(propylene suberate)

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ABSTRACT

The synthesis, characterization and thermal behavior of two biodegradable aliphatic polyesters poly(propylene glutarate) (PPGlu) and poly(propylene suberate) (PPSub) derived from 1,3-propanediol and glutaric and suberic diacid, respectively, have been studied. These polyesters were characterized using several techniques. Thermal degradation of both polyesters was studied by determining theirs mass loss during heating. From the thermogravimetric curves it can be seen that PPSub present a relatively better thermostability than PPGlu since the maximum mass loss occurred at temperatures 411.2 and 409.1 °C, respectively. The activation energy (E) of degradation was calculated using the isoconversional methods proposed by Ozawa–Flynn–Wall (OFW) and Friedman. From the variation of E with increasing degree of conversion it was found that the polyester decomposition is taking place with a complex reaction mechanism with the participation of at least two different mechanisms. Two combinations of models, nth order and nth order with autocatalysis (Fn–Cn) as well as nth order with autocatalysis in both mechanisms (Cn–Cn) give the better results. Using pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) it is found from mass ions detection that the decomposition of both polymers takes place, mainly, through β-hydrogen bond scission and secondarily by α-hydrogen bond scission. At 410 °C CO_2 is the main gas product of decomposition while allyl, diallyl, carboxylic acids, aldehydes and hydrocarbons are the main liquid products.

1. Introduction

Nowadays biodegradable polymers have attracted an increasing interest. Two classes of polyesters were prepared, based on α- or ω-hydroxycarboxylic acids and on α,ω-alkanediols and aliphatic dicarboxylic acids. Among them aliphatic polyesters like poly(L-lactic acid), poly(ε-caprolactone), poly(3-hydroxy butyrate), poly(3-hydroxy valerate), etc., are prepared by ring-opening polymerization of lactones or other cyclic esters, whereas the second class of polyesters such as poly(butylene succinate), poly(ethylene succinate), etc., are usually prepared by polycondensation of diols and diacids, consisting a very important class due to their favourable features of biodegradability and biocompatibility [1–5]. Till recently dominated polyesters are derived from ethylene-glycol and 1,4-butanediol, due to difficulties in the preparation of 1,3-propanediol (1,3-PD) in sufficient quantities and purity [6,7]. In recent years more attractive processes have been developed for the production of 1,3-propanediol (1,3-PD) from renewable resources; therefore, research on related polymers has attracted interest from both industrial and academic point of view [8–11]. Thus, polyesters of 1,3-PD show excellent properties and poly(propylene succinate) (PPSu) was the first studied biodegradable polyester from 1,3-PD [12–15].

PPSu has gained an increasing interest, since it has high biodegradation rates, which are higher than those of the well known – and commercially available – poly(ethylene succinate) (PESu) and poly(butylene succinate) (PBSu) polyesters. Very few papers has been appeared last years in the literature on other aliphatic polyesters from 1,3-PD like poly(propylene adipate) (PPAd) or poly(propylene sebacate) (PPSeb) [16–18]. Only in one paper a comparative study of poly(propylene dicarboxylate)s has been presented, but it was, also, limited in just four polymers of the family namely PPSu, PPGlu, PPAd and PPAz [19]. All the above mentioned polyesters were prepared using the well known two-stage melt polycondensation method (esterification and polycondensation) at elevated temperatures (230–250 °C). However, as the polycondensation temperature increases, the rate of side degradation reactions increases, also [20–22]. Quite recently, it was found

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that new catalysts can catalyze the polycondensations of diols and dicarboxylic acids at very low temperatures such as 80 °C in bulk, so that molecular weights up to 30,000 Da were obtained [23,24].

In our previous work, synthesis, thermal behavior and enzymatic degradation of a series of seven fast biodegrading aliphatic polyesters, derived from 1,3-propanediol and aliphatic diacids with increasing number of methylene units (x) from $x = 2$ (succinic acid) to $x = 8$ (sebacic acid), were reported [25]. It was found that the melting points of the studied polyesters decreased from that of poly(propylene succinate) (PPSu) ($x = 2$) to that of poly(propylene adipate) (PPAd) ($x = 4$) and then increased again up to poly(propylene azelate) (PPAz) ($x = 7$) and poly(propylene sebacate) (PPSeb) ($x = 8$). A maximum in heat of fusion was also found for PPAz. Furthermore, crystallization rates increased steadily with increasing x. It was found that all these polyesters can be disintegrated within 36 h during enzymatic degradation in the presence of mixture of *Rhizopus delemar* and *Pseudomonas cepacia* lipases. The hydrolysis rate was much faster than that of poly(ε-caprolactone) (PCL), which is one of the most used aliphatic polyester. Poly(propylene suberate) (PPSub) ($x = 6$) exhibited the faster enzymatic hydrolysis rates while PPAz and PPSeb the slowest. Beyond the high enzymatic hydrolysis rates such aliphatic polyesters are appropriate as drug carriers for controlled release applications [26,27].

In this work, a comparative study on thermal decomposition kinetic of two aliphatic polyesters namely poly(propylene glutarate) (PPGlu) and poly(propylene suberate) (PPSub) is presented. This is very important in such polyesters in order to choose the appropriate conditions for the preparation of polyesters with high molecular weight and thus with increased mechanical properties during the melt polycondensation. The mechanism of thermal decomposition is also evaluated and discussed.

2. Experimental

2.1. Materials

The polyesters were synthesized from 1,3-propanediol and the respective glutaric or suberic diacids (purum 99%) which were purchased from Aldrich Chemical Co. (Stainheim, Germany). 1,3-Propanediol (CAS Number: 504-63-2, purity: >99.7%) was kindly supplied by Du Pont de Nemours Co. Tetrabutyl titanate catalyst of analytical grade and polyphosphoric acid (PPA) used as heat stabilizer were purchased from Aldrich Chemical Co. All the other materials and solvents which were used for the analytical methods were of analytical grade.

2.2. Synthesis of polyesters

The aliphatic polyesters were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. The procedure was the same with that presented in our previous publication [25]. In brief, the proper amount of diacid and propanediol in an acid/diol molar ratio 1/1.1, and the catalyst $Ti(OBu)_4$ 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 180 °C under argon atmosphere and with stirring at a constant speed (500 rpm). During this first step (esterification) H_2O was formed and it was removed from the reaction mixture by distillation.

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol SA), which is believed to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was slowly increased to 230 °C while stirring speed was increased at 720 rpm. The polycondensation continued for about 90 min for all prepared polyesters. After the polycondensation reaction was completed, the polyesters were easily removed, milled and washed with methanol.

2.3. Measurements

^{1}H NMR spectra of polyesters were obtained with a Bruker AMX 400 spectrometer. 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.

Intrinsic viscosity measurements on the isolated polymers were performed using an Ubbelohde viscometer cap. Oc at 25 °C in chloroform at a solution concentration of 1 wt%.

Gel permeation chromatography (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.

Differential scanning calorimetry (DSC) study was performed on a Perkin Elmer, Pyris Diamond DSC differential scanning calorimeter, calibrated with high purity standards. Function of the system at low temperatures (down to −65 °C) was achieved using a Perkin Elmer Intracooler 2P cooling accessory. Samples of 5 ± 0.1 mg were sealed in aluminium pans and scanned in the instrument. For each one of the samples a cyclic scanning procedure was followed to record the thermal behavior of the polyesters. The procedure involved: (a) heating from 0 to 40 °C above the melting point of the sample at a heating rate 20 °C/min and holding at this temperature for 2 min in order to erase any thermal history of the sample, (b) rapid cooling to −65 °C and equilibration, (c) reheating at a heating rate 2.5 °C/min from −65 to 40 °C above the melting temperature and holding for 2 min, and (d) final cooling, at a cooling rate 10 °C/min, down to −50 °C. Slow heating allows even amorphous samples of slowly crystallizing polyesters, like most of the studied polymers, to crystallize during the scan. All experiments were carried out in nitrogen atmosphere to avoid decomposition of the samples.

Thermogravimetric analysis (TGA) was carried out with a SETARAM SETSYS 16/18 TG–DTA. Samples (6 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 600 °C in a 50 ml/min flow of N_2. Heating rates of 5, 10, 15 and 20 °C/min were used and continuous records of sample temperature, sample weight, its first derivative and heat flow were taken.

2.4. Py–GC–MS

The pyrolysis experiments were carried out in a bench scale fixed bed reactor (12.1 cm height and 1.25 cm ID), made of stainless steel 316 and heated by a 3-zone furnace. The temperature of each zone was independently controlled using temperature controllers. A specially designed piston system was used to introduce the polymeric feedstock into the reactor. A constant stream of N_2 was fed from the top of the reactor during the pyrolysis experiments for the continuous withdrawal of the products and the maintenance of the inert atmosphere during pyrolysis.

For all tests performed in this study a fixed quantity of 1.5 g of the polymer was pyrolyzed at selected temperatures under nitrogen flow (i.e., at a flow rate of 100 cc/min for 15 min at the reaction temperature and at a flow rate of 30 cc/min for additional 30 min during cooling of the reactor). Pyrolysis temperatures were selected for both polymers at 375 and 410 °C, since at the first temperature starts the decomposition while at the second temperature the maximum decomposition rate was recorded from TGA thermographs.

The liquid products were collected in a liquid bath (−17 °C) and quantitatively measured in a pre-weighted glass receiver, while the gaseous products were collected and measured by water displacement and the amount of the solid residue (consisting mainly of unconverted polymer) was measured by direct weighting. Gas chromatography (GC) and GC–MS was used for the analysis of both liquid and gaseous products. The gaseous products were analyzed in a HP 6890 GC, equipped with four columns (precolumn: OV-101; columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30 m × 0.53 mm ID) and two detectors (TCD and FID)). The chromatograph signals were calibrated with standard mixtures of known concentrations of gases. The liquid products were analyzed by GC/MS analysis in a HP 5989 MS ENGINE (electron energy: 70 eV; emission: 300 V; helium flow rate: 0.7 cc/min; column: HP-5MS (30 m × 0.25 mm ID × 0.25 μm)). Separation of the individual compounds was based on their polarity. Internal libraries were used for the identification of the compounds that can be found in the liquid product and their categorization into main functional groups.

3. Kinetics

The transformation rate for a solid-state reaction is generally assumed as the product of two functions, one depending only on the temperature *T* and the other depending only on the fraction transformed α [28]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, *T* the temperature and $f(\alpha)$ the conversion function (reaction model). $k(T)$ is a temperature dependent function given by the Arrhenius equation so that Eq. (1) takes the form

$$\frac{d\alpha}{dt} = A\ \exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

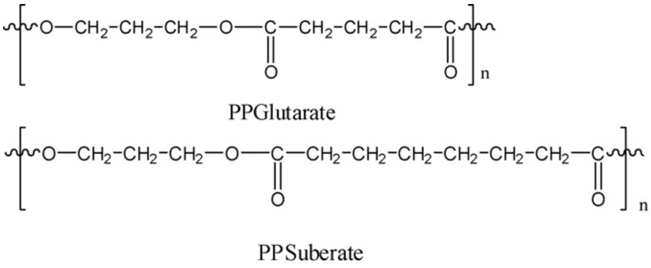
with *A* being the pre-exponential factor, *E* the activation energy and *R* the gas constant. The reaction model may take various forms. For non-isothermal experiments, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the Arrhenius parameters (A and *E*), together with the reaction model $f(\alpha)$, are sometimes called the kinetic triplet [29].

In order to determine this triplet, various methods, for example the isoconversional ones, have been worked out. The isoconversional method, is in fact, a “model-free” method [30] which assumes that the conversion function $f(\alpha)$ does not change with the variation of the heating rate for all values of α. It involves the measurement of the temperatures corresponding to fixed values of α by experiments at different heating rates β [31]. Isoconversional methods are considered to give accurate values of the activation energy [32]. The pre-exponential factor usually cannot be determined without the assumption of the reaction model ($f(\alpha)$). Few of these methods were proposed by Ozawa–Flynn–Wall (OFW) [33], Friedman [34].

The Ozawa–Flynn–Wall (OFW) method involves the measurement of the temperature *T*, corresponding to a fixed value of the degree of conversion α, from the experiments at different heating rates β. The OFW method is based on the following equation:

$$\ln\ \beta = -1.052\frac{E}{RT} + \text{const} \tag{3}$$

The plot of $\ln\beta$ versus $1/T$ gives the slope $-1.0516E/R$ by which the activation energy has been evaluated. 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 [35]. These complications are significant, especially in the case that the total reaction involves competitive mechanisms.



Scheme 1. Chemical structures of PPGlu and PPSub.

The differential isoconversional method suggested by Friedman is based on Eq. (2) that leads to:

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{4}$$

For a constant α, the plot of $\ln(\beta(d\alpha/dT))$ versus $(1/T)$ obtained from curves recorded at several heating rates, should be a straight line whose slope gives the value of *E*. It is obvious from Eq. (4) 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.

The reaction mechanism of polymer decomposition is a very complex radical chain mechanism, including initiation, propagation and termination reactions. As it is well known, two main types of reaction models are, generally, applied on the thermal degradation of polymers: the *n*th-order model with only one parameter, the reaction order, and the first-order model. Other models have, also, been used occasionally, but they are complex containing several fitting parameters [36,37].

4. Results and discussion

4.1. Characterization of prepared polyesters

Poly(propylene glutarate) and poly(propylene suberate) (PPSub) were synthesized following direct polyesterification of 1,3-propanediol and the appropriate dicarboxylic acids according to the two-step melt polycondensation method and their chemical structures are presented in Scheme 1. In the first step the esterification reactions of diacid and diol monomers result in the formation of oligomers. In the second step, the polycondensation of the oligomers at high temperatures and the application of vacuum give polymers of high molecular weight. The preparation of the polyester samples was followed by their molecular characterization, including intrinsic viscosity and GPC measurements, as well as collection of ^{1}H NMR spectra. Both, intrinsic viscosity and GPC measurements proved the high molecular weight values of the prepared polyesters. The intrinsic viscosities of both polyesters are almost similar, 0.581 dL/g for PPGlu and 0.607 dL/g for PPSub while their molecular weights are 14,000 and 15,000 Da, respectively (Table 1).

DSC study of the polyesters revealed that both polyesters are semicrystalline since PPGlu has a melting point at 45.9 °C while PPSub, although with higher number of methylene groups, has a similar melting point, at 46.7 °C. Such low melting points were also mentioned in similar aliphatic polyesters prepared from 1,3-propanediol and dicarboxylic acids like poly(propylene succinate) and poly(propylene adipate) [15,16]. After melting and quenching they can be taken completely amorphous with glass transitions

Table 1
Intrinsic viscosity [η], average molecular weight (M_n), melting point (T_m), glass transition temperature (T_g), crystallization temperature (T_c), cold-crystallization temperature (T_{cc}) and heat of fusion (ΔH_m) of the studied polyesters.

Sample	[η] (dL/g)	M_n (Da)	M_w/M_n	T_m (°C)	T_g (°C)	T_c (°C)	T_{cc} (°C)	ΔH_m (J/g)
PPGlu	0.581	14,000	2.13	45.9	−53.3	–	–	46.0
PPSub	0.607	15,000	2.09	46.7	−57.8	−17.5	−50	55.2

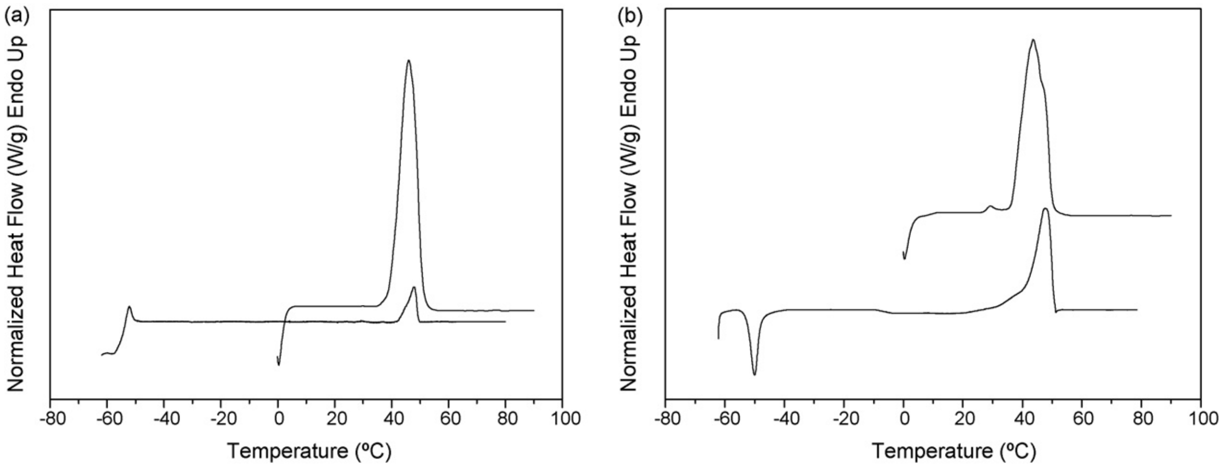


Fig. 1. DSC traces of as received (heating rate 20 °C/min) and amorphous (heating rate 2.5 °C/min) samples of: (a) poly(propylene glutarate) and (b) poly(propylene suberate).

at −53.3 and −57.8 °C, respectively. As can be seen from Fig. 1 PPGlu does not exhibit a cold-crystallization temperature during heating from the amorphous state and only PPSub presents a cold-crystallization temperature at −17.5 °C.

4.2. Thermal degradation kinetic

Thermal degradation of PPSub and PPGlu was studied by determining their mass loss during heating. In Fig. 2 the mass loss and the derivative mass loss (DTG) curves of the two studied polyesters are presented together, at a heating rate of 10 °C/min. From the mass loss curves it can be seen that PPSub present better thermostability than PPGlu since the 2% mass loss occurred at 331.5 °C for PPSub and at 296.5 °C for PPGlu. This difference exists for all the same values of mass loss of the two materials; for example the 50% mass loss occurred at 413.1 °C for PPSub and at 405.7 °C for PPGlu. Furthermore, as it can be seen from the peak of the first derivative, the temperature at which the PPSub decomposition rate is highest is at 411.2 while for PPGlu is at 409.1 °C. Although this difference seems to be negligible it can be better understood if we examine its origin that is due to the different slope of mass loss of the two materials. Additionally, it is more obvious if we compare the values of the mass loss at this point, which are: 53.9% for PPSub and 43.0% for PPGlu.

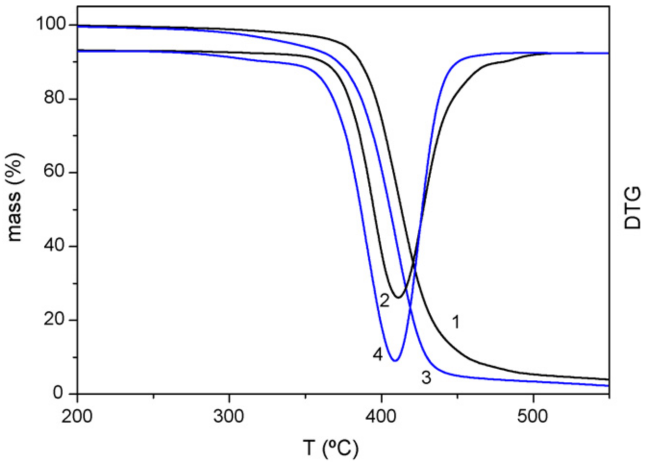


Fig. 2. Mass loss (%) and derivative mass loss (DTG) versus temperature with heating rate $\beta = 10$ °C/min: (1) TG (%) – PPSub, (2) DTG – PPSub, (3) TG (%) – PPGlu, and (4) DTG – PPGlu.

In order to analyze thoroughly the degradation mechanism of PPSub and PPGlu it is important that the kinetic parameters (activation energy E and pre-exponential factor A) and the conversion function $f(\alpha)$ to be evaluated. The relationship between kinetic parameters and degree of conversion (α) – partial mass loss – can be found using the mass loss curves recorded in the TG measurements. The degradation for these polyesters was studied through non-isothermal measurements at different heating rates (5, 10, 15, 20 °C/min). In Figs. 3a and b and 4a and b the mass loss and the derivative mass loss at different heating rates for PPSub and PPGlu are presented.

For the determination of the activation energy by using multiple heating rates the above analyzed isoconversional methods are used. Since every isoconversional method has different error, the use of more than one method can give a range of values for the activation energy at every particular value of α. The plots of $\ln \beta$ versus $1/T$ of the Ozawa–Flynn–Wall (OFW) method, for PPGlu as an example, are given in Fig. 5. The straight lines fitting the data, are nearly parallel, which is an indication that the activation energies at different degrees of conversion are almost similar. Friedman method was also used by plotting $\ln(d\alpha/dT)$ versus $1/T$ for a constant α value and the activation energy was calculated (Fig. 6). The straight lines fitting the data are nearly parallel except those for $\alpha = 0.05$ and 0.1.

In Figs. 7 and 8, the dependence of the activation energy on the different conversion values is presented for the two polyesters and it is clear that E can be considered as having almost a constant average value for $0.2 < \alpha < 0.8$ in both polyesters. The differences in the values of E calculated by the OFW and Friedman methods can be explained by a systematic error due to improper integration. The method of Friedman employs instantaneous rate values

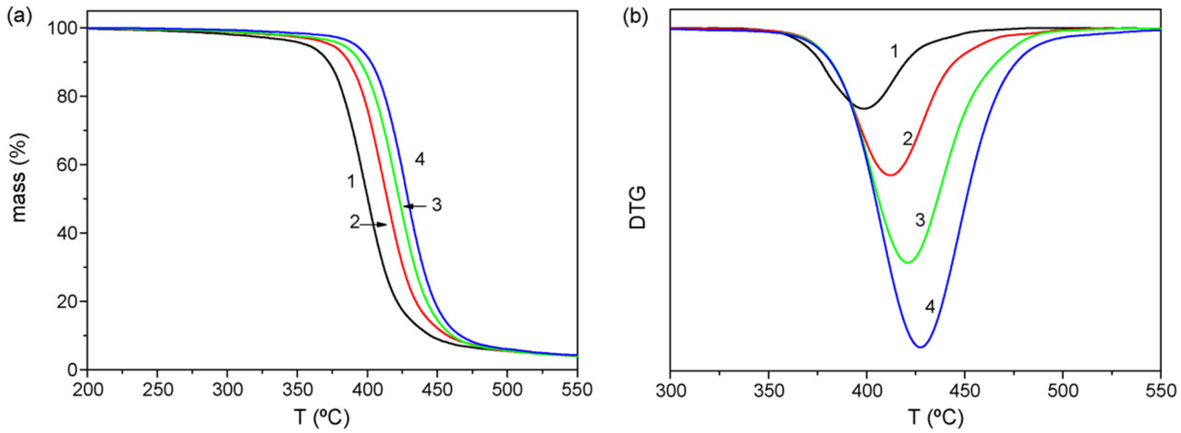


Fig. 3. (a) Mass loss (%) and (b) derivative mass loss (DTG) curves of PPSub at different heating rates: (1) $\beta = 5\,^{\circ}$C/min, (2) $\beta = 10\,^{\circ}$C/min, (3) $\beta = 15\,^{\circ}$C/min, and (4) $\beta = 20\,^{\circ}$C/min.

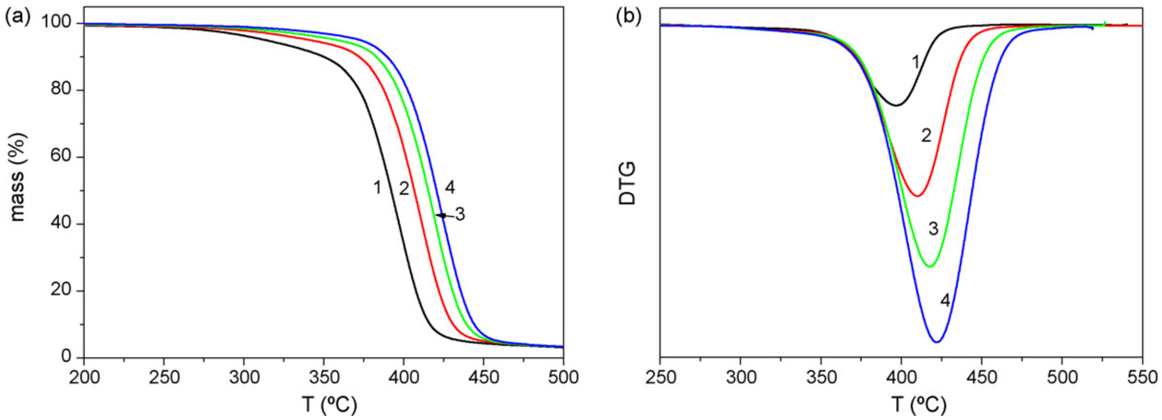


Fig. 4. (a) Mass loss (%) and (b) derivative mass loss (DTG) curves of PPGlu at different heating rates: (1): $\beta = 5\,^{\circ}$C/min, (2) $\beta = 10\,^{\circ}$C/min, (3) $\beta = 15\,^{\circ}$C/min, and (4) $\beta = 20\,^{\circ}$C/min.

being, therefore, very sensitive to experimental noise. With OFW method, the equation used is derived assuming constant activation energy and by introducing systematic error in the estimation of *E* in the case that *E* varies with α, an error that can be estimated by comparison with the Friedman results [38].

Examining more carefully Figs. 7 and 8 it is deduced that the dependence of *E* on α value can be separated in three distinct regions for PPSub and two for PPGlu. For the PPSub sample the first region till α 0.1 where a small increase of the activation energy is observed, the second one for $0.1 < \alpha < 0.75$, where the activation energy can be considered as having the same value and the third region for $\alpha > 0.75$ where a rapid increase of the activation energy is observed. For the PPGlu in the first region is presented, also, a rapid increase for the activation energy till $\alpha = 0.2$ and in the second

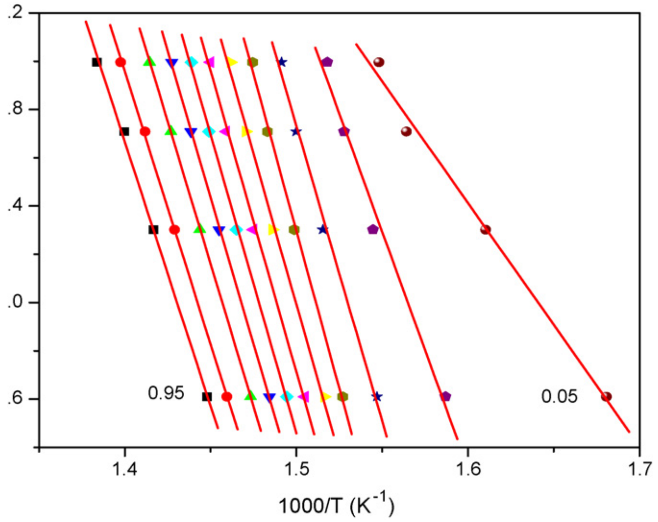


Fig. 5. OFW plots for different degrees of conversion α, from $\alpha = 0.05$ to $\alpha = 0.95$ of PPGlu samples.

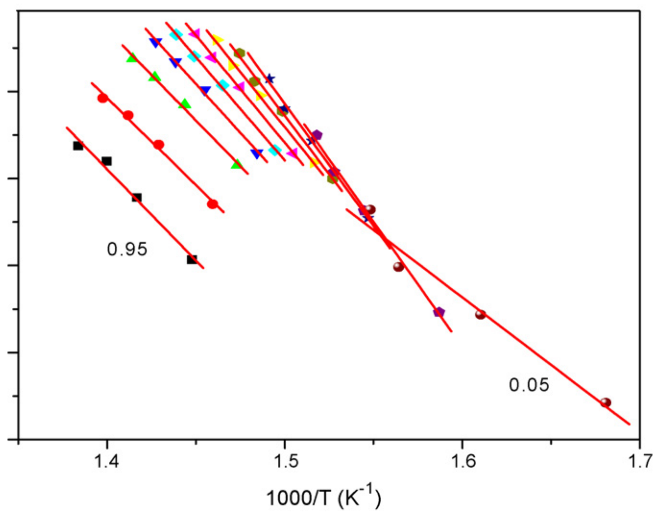


Fig. 6. Friedman plots for different degrees of conversion α, from $\alpha = 0.05$ to $\alpha = 0.95$ of PPGlu samples.

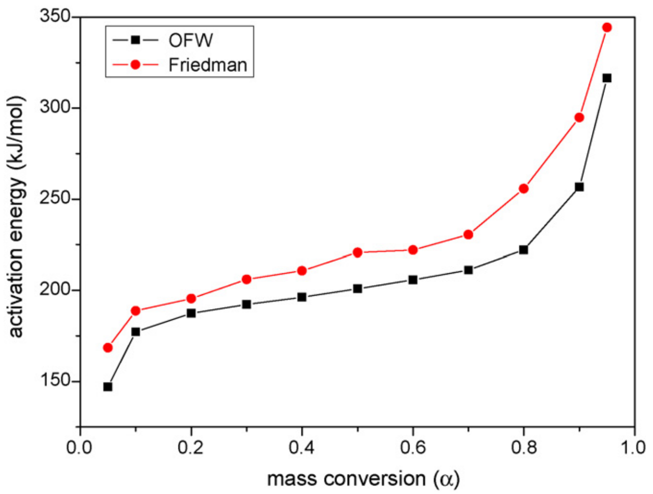


Fig. 7. Dependence of the activation energy (E) on the mass conversion (α), as calculated with Friedman and OFW methods for PPSub.

region, where the activation energy can be considered as having the same value. As it is known, 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, as in the studied polyesters, is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [37]. These complications are remarkable, especially in the case that the total reaction involves competitive mechanisms. From the above it is clear that, according to Figs. 7 and 8, there is an indication of a complex reaction during decomposition with the participation of at least two different mechanisms [39]. The first mechanism 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 mechanism presenting different activation energy. This is very usual in polymers and was reported also in other aliphatic polyesters [21,22,40].

The determination of the reaction model for the multiple heating rates is based on the “model-fitting method”. Different kinetic models were used for the fitting and the conversion range was $0<\alpha<1$. Model-fitting methods involve fitting different models to α versus temperature curves and simultaneously determining the activation energy E and the pre-exponential factor A. It has been demonstrated recently, that the complementary use of the model-free method with the isoconversional methods for one-step reactions is very useful in order to understand the solid-state reaction kinetics [41,42].

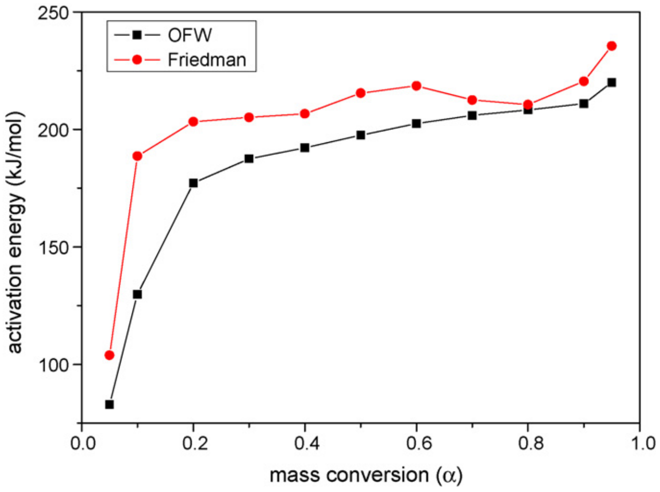


Fig. 8. Dependence of the activation energy (E) on the mass conversion (α), as calculated with Friedman and OFW methods for PPGlu.

Table 2
Kinetic models and their conversion functions $f(\alpha)$.

Kinetic model	Symbol	$f(\alpha)$
First order	F1	$1-a$
nth order	Fn	$(1-a)^n$
Expanded Prout–Tompkins	Bn	$(1-\alpha)^n\alpha^m$
nth order with autocatalysis	Cn	$(1-\alpha)^{n(1+K_{\mathrm{cat}}X)}$

Table 3
Calculated values of E, A of four kinetic models for PPSub and PPGlu samples and its regression coefficient R. Conversion range $0<\alpha<1$.

Model	$\log A$ (s^{-1})	E (kJ/mol)	React. order, n	R
PPSub				
F1	13.18	202.3		0.9985
Fn	16.01	237.1	1.6	0.9990
Bna	13.68	203.1	1.9	0.9996
Cn	12.88	201.4	2.2	0.9997
PPGlu				
F1	13.28	200.8		0.9991
Fn	12.88	195.9	0.9	0.9992
Bna	12.87	197.7	0.9	0.9992
Cn	12.3	189.6	1.2	0.9993

In order to determine the nature of the mechanisms through the comparison of the experimental and theoretical data, initially it is considered that the degradation of the polyester can be described only by a single mechanism that corresponds to the main mass loss, without presuming the exact mechanism. If the result of the fitting cannot be considered as accepted, then we must proceed to fit the experimental data with a combination of two mechanisms. The multivariate non-linear regression method is used for the determination of the kinetic triplet. For this calculation different kinetic models are used. The calculated values of E and A after the fitting for four kinetic models (Table 2), for which the quality of the mathematical fitting depending on the regression coefficient R is at an accepted level, are presented in Table 3.

For the studied polyesters, the best kinetic model is the Cn according to the values of the regression factor R. The values of the activation energy for all these models are in the same area of values that have been calculated with the isoconversional methods. In Figs. 9 and 10 the plots of the fitting with the best models Cn and Fn for the PPSub are presented. Similar are the results for PPGlu aliphatic polyester (data not shown). The results of the fitting with the Fn model are demonstrated since this and F1 model are usually used for the kinetic description of the polymers' degradation.

The quality of the fitting with the Cn and Fn models is good for both studied polyesters. For both models only small divergences appear at the first region which corresponds to the 3–4% of the mass loss and at the end of the degradation. For both samples the divergence at the end of the degradation is a little higher for the Fn model. The regression factors show that the differences between the four models are very small for PPGlu samples and for both samples the F1 model gives the smaller regression factor. Since the differences among the regression factor values are rather small, especially for PPGlu samples, it is very difficult for everyone to choose the real kinetic model from the presented models. This difficulty seems to be greater if it is taken into account that the reaction mechanisms of the polymers are very complex. For this reason, the choice of the appropriate kinetic model, considering one-step reaction, only denotes a possible mathematical form for the conversion function [44]. Comparing the results of the fitting of the two polyesters for every different model we can conclude that the activation energy for PPSub is somewhat larger than that of PPGlu. Also, the bigger values of the reaction order for the PPSub denote the different degradation rates of the two polyesters.

Taking into account that the thermal degradation of the polymers is a very complex reaction, in order to enhance further the quality of the fitting more than one reaction mechanisms must be considered, using the conclusions from the dependence of the activation energy on the partial mass loss.

For the determination of the mechanism at the first mass loss area for the two studied samples, the following are assumed: (a) the two mechanisms are consecutive and (b) this mechanism, which we try to identify, corresponds to a small mass loss, according to the experimental results. In the process of identification by two different mechanisms, are involved at least six unknown factors with the mathematical problem of identification to be very complex, with several possible solutions. For this reason, at this stage of identification, it is important to limit the scope of the search among all possible combinations of the widely used models. So the models that were used and their combinations were only those which have given satisfactory results from the identification through a single mechanism such as the reaction models Fn, Cn and Bna.

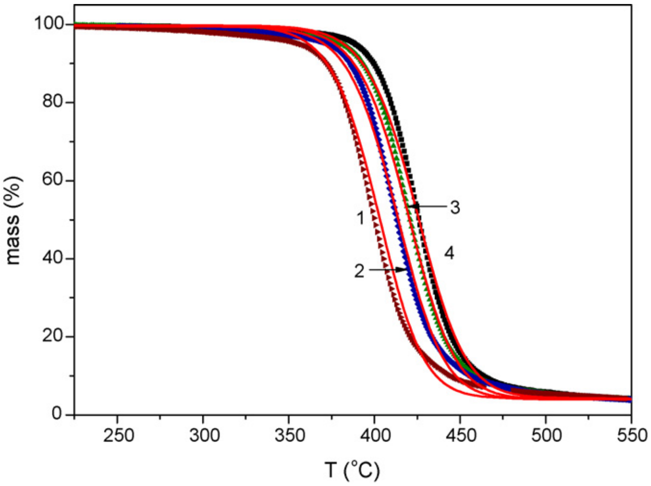


Fig. 9. Mass loss (%) for different heating rates and fitting curves with Fn mechanism versus temperature of PPSub samples: (1) $\beta = 5\,^\circ$C/min, (2) $\beta = 10\,^\circ$C/min, (3) $\beta = 15\,^\circ$C/min, and (4) $\beta = 20\,^\circ$C/min.

Table 4
Activation energy, pre-exponential factor, reaction order and the regression factor of PPSub and PPGlu after fitting with two reaction mechanisms.

Model	Mechanism	E (kJ/mol)	$\log A$ (s^{-1})	n		R
PPSub						
Fn	First	98.9	6.16	1.1		0.99988
Cn	Second	222.3	14.61	2.3	0.78[b]	
Cn	First	97.7	6.09	1.1	−5.49[b]	0.99988
Cn	Second	221.6	14.55	2.3	0.79[b]	
Fn	First	140.2	8.9	1.0		0.99987
Bna	Second	280.9	19.94	2.7	0.28[a]	
Fn	First	144.1	9.19	1.0		0.99987
Fn	Second	292.8	20.79	2.7		
PPGlu						
Fn	First	85.5	4.96	0.7		0.99987
Cn	Second	208.9	13.75	1.5	0.44[b]	
Cn	First	85.1	4.92	0.7	−5.21[b]	0.99987
Cn	Second	208.8	13.74	1.5	0.44[b]	
Fn	First	94.2	5.44	1.1		0.99982
Fn	Second	260.1	18.05	1.3		
Fn	First	93.8	5.44	1.2		0.99982
Bna	Second	257.1	17.81	1.3	0.004[a]	

[a] Exponent m.
[b] $\log K_{cat}$.

In this stage of identification, for the best possible results we left the parameters (E, A and n) of the second mechanism to be recalculated and the results are presented in Table 4. The results of the best fitting are presented in Figs. 11 and 12 for PPSub and PPGlu, respectively, and the fitting to the experimental data is very good for the whole area of mass loss. From Table 4 it is obvious that two combinations of models, nth order and nth order with autocatalysis (Fn–Cn) as well as nth order with autocatalysis in both mechanisms (Cn–Cn) give the better results. Since the calculated value of the $\log(K_{cat})$ has a very large negative value, and therefore the parameter K_{cat} is almost zero, the Cn kinetic model coincides with the Fn model for the first part of mass loss. Another thing must be mentioned. For the other two combinations of models, Fn–Fn and Fn–Bna, which gave the same regression factors the values of the activation energy for both mechanisms, are larger than the ones from the first two models. This can be connected to the different areas of mass loss in which each of the two mechanisms take place. For the first two models the first area of mass loss is around 4% and for the other two greater than 10%.

The necessity of using two different reaction models is due to the not very good quality of the fitting using one reaction model and the

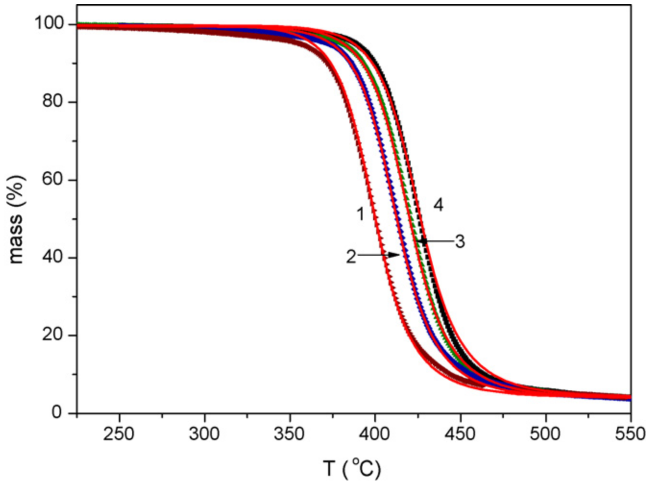


Fig. 10. Mass loss (%) for different heating rates and fitting curves with Cn mechanism versus temperature of PPSub samples: (1) $\beta = 5\,^\circ$C/min, (2) $\beta = 10\,^\circ$C/min, (3) $\beta = 15\,^\circ$C/min, and (4) $\beta = 20\,^\circ$C/min.

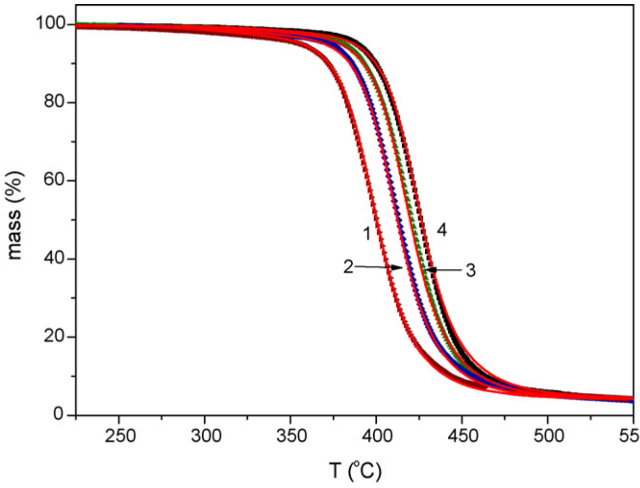


Fig. 11. Mass loss (%) of PPSub and fitting curves for different heating rates and for two reaction mechanisms (Fn–Cn): (1) $\beta = 5\,^\circ$C/min, (2) $\beta = 10\,^\circ$C/min, (3) $\beta = 15\,^\circ$C/min, and (4) $\beta = 20\,^\circ$C/min.

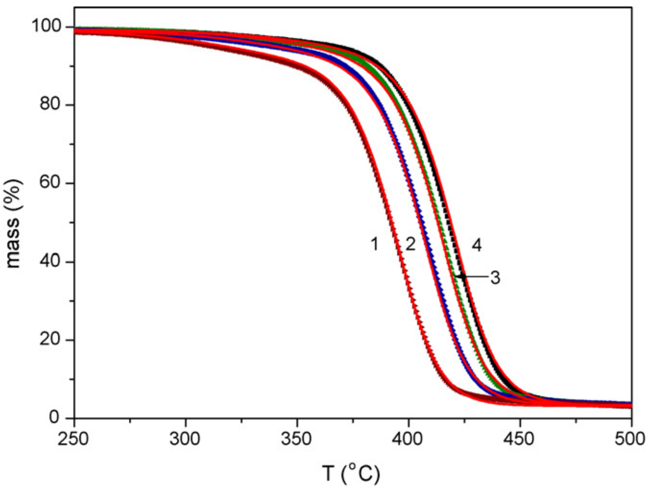


Fig. 12. Mass loss (%) of PPGlu and fitting curves for different heating rates and for two reaction mechanisms (Fn–Cn): (1) $\beta = 5\,^{\circ}$C/min, (2) $\beta = 10\,^{\circ}$C/min, (3) $\beta = 15\,^{\circ}$C/min, and (4) $\beta = 20\,^{\circ}$C/min.

dependence of the activation energy on the mass conversion. The combination of the two mechanisms gives interesting information about the degree of the complexity of the degradation mechanism of the two polyesters. There is no need, for the description of the degradation of every polyester, the use of more than one reaction model: this kind of description is necessary for more complex reactions. Although it is true that when we are using more fitting parameters the correlation coefficients are being better, in this materials we ought to use more than one reaction models for the reasons that we are presenting above. For the same combination of models there are differences, in the activation energy and the reaction order, for the two materials. The activation energy of the PPSub is larger than that of PPGlu for both the reaction models for every combination and this is connected to the better thermal stability of the PPSub. The differences in the values of the reaction order are connected to the different degradation rate of the two polyesters.

4.3. Thermal degradation mechanism

From the determination of activation energies during polyester decomposition it was revealed that two decomposition mechanisms take place corresponding to different mass losses. The first one corresponds to small mass loss and the second to the main mass loss. In order to evaluate chemically these thermal degradation mechanisms Py–GC–MS was used and the collected degradation products at 375 and 410 °C were identified. At the first temperature, according to TG thermograms (Fig. 2), PPSub losses about 5 wt% and PPGlu about 10 wt%, while at the second temperature both polyesters have their maximum decomposition rates.

In gas products collected during decomposition CO_2 dominates with 80.23% in the case of PPGlu and 78.25% for PPSub at 375 °C while H_2 is also produced at amounts close to 6% for both polymers. At 410 °C the evolved CO_2 is in lower amounts, compared with 375 °C, such as 75.2 and 74.6%, respectively, while the production of H_2 has the opposite trend and it is close to 9.5–10% for both polymers. Similar results were also reported in our previous paper by studying poly(propylene succinate) (PPSu) [20] while carbon dioxide was found that can be liberated at small weight loss 2–4% in poly(propylene terephthalate) (PPT) [43]. Other gas products, in both polyesters, at low amounts are hydrocarbons, such as methane (1–2%), ethylene (C_2=) (1.5–3%) and mainly propylene (C_3=) (3.5–4.2% at 375 °C and 6.5–7.2 at 410 °C) compounds. These small differences in the produced gasses at the different temperatures may be attributed to the different decomposition mechanism that takes place, as was already verified by TG analysis. At low temperatures, CO_2 can be produced, mainly, from the decomposition of carboxyl end groups of aliphatic polyester macromolecules. At higher decomposition temperatures this degradation takes, also, place but at lower extent while pyrolysis dominates and the macromolecular chains are degraded, also, by random scission.

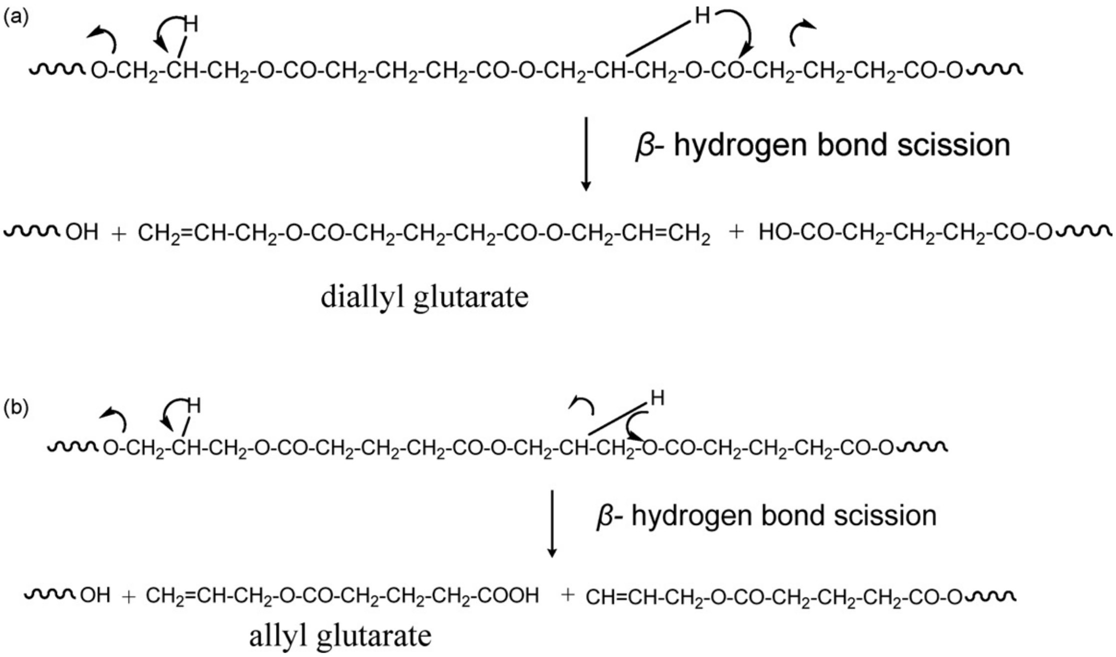
Beyond the gas products, liquid products were also collected and characterized. These are about 26–27 wt% of the whole decomposition mass at 410 °C and only 5–5.5 wt% at 375 °C. The main products as identified by mass spectroscopy are categorized and presented in Table 5.

As can be seen allyl and diallyl compounds with carboxylic acids and anhydrides predominate in both polymers. These can be produced by β-hydrogen bond scission of PPGlu and PPSub as can be seen in Scheme 2. In the case of PPGlu several different ions characterized as allyl and diallyl compounds, were detected corresponding to different ion masses: the first one with retention time 22.6 min and ion mass 124, the second one with retention time 34.5 min and ion mass 172 and the last one with retention time 44.6 min and ion mass 212. The mass spectrum of this diallyl glutarate liquid product (as characterized from mass library) with ion mass 212 is presented in Fig. 13. From the decomposition mechanism presented in Scheme 2 it becomes clear that all these products are produced by the β-hydrogen bond scission of macromolecular chains. With the same mechanism acids and vinyl acid compounds can, also, be produced as presented at Scheme 3. β-Hydrogen bond scission is the main decomposition mechanism in polyesters and the verified products are in good agreement with the already reported studies [44–47].

Diallyl glutarate can be further degraded at low decomposition temperatures producing two aldehydes, propenal with retention time 17.25 min and allyl compound with retention time 26.3 min and ion mass 156. Propenal is detected at about 4.2% in 375 °C decomposition temperature while a lower percentage was recorded (1.1%) at 410 °C, maybe because propenal can be

Table 5
Analysis of the liquid products collected during decomposition of PPGlu and PPSub at 375 and 410 °C.

Compounds in liquid product	wt% in liquid product at 375 °C		wt% in liquid product at 410 °C	
	PPGlu	PPSub	PPGlu	PPSub
Hydrocarbons	1.4	2.1	4.3	6.5
Diallyl compounds	2.4	3.9	13.2	8.7
Allyl compounds	7.5	6.2	14.8	12.2
Carboxylic acids	8.3	7.3	12.1	8.6
Anhydrides	10.5	8.7	6.3	4.7
Aldehydes	26.5	28.2	11.9	9.5
Alcohols	2.1	3.3	1.3	0.9
1,3-Propanediol	1.3	0.9	0.4	0.6
Non-identified products	2.5	3.5	1.5	2.6
Heavy compounds (oligomers)	37.5	35.9	34.2	45.7



Scheme 2. β-Hydrogen bond scission mechanism of PPGlu forming (a) diallyl glutarate compounds and (b) allyl glutarate compounds.

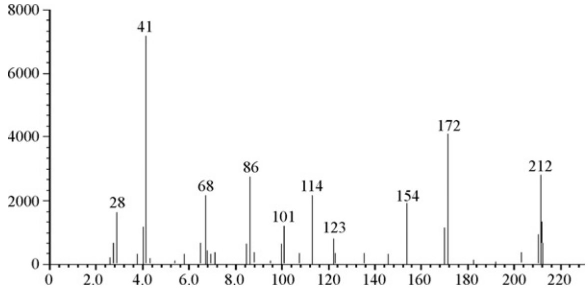
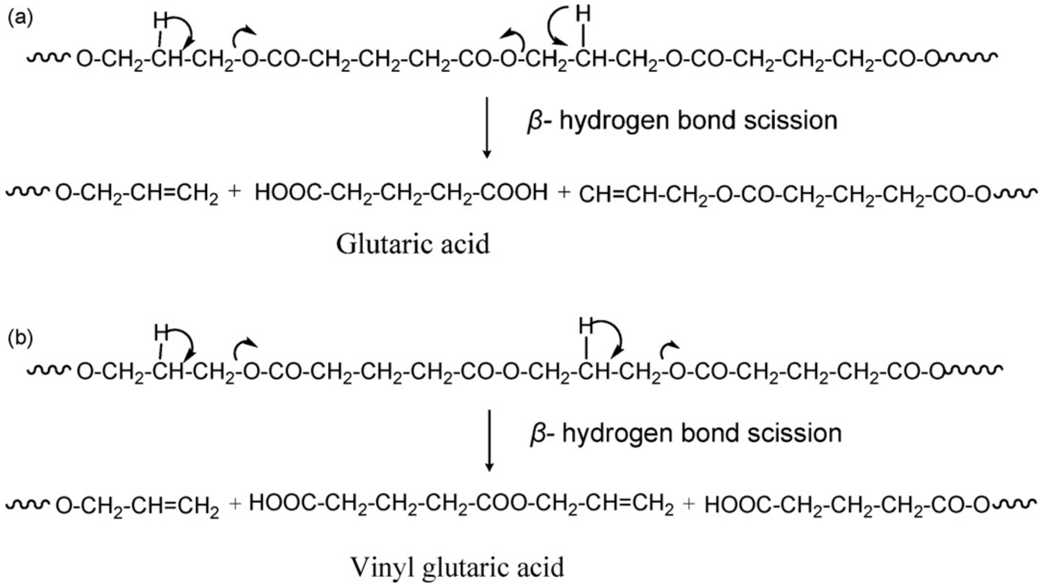


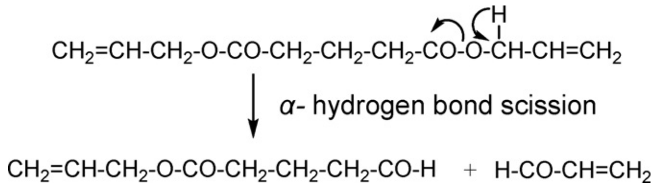
Fig. 13. Mass spectrum of diallyl glutarate liquid product with ion mass 212 obtained during PPGlu decomposition.

further degraded, especially at high temperatures, to ethene and formaldehyde. These aldehydes are produced not by β-hydrogen bond scission but by α-hydrogen bond scission, as is illustrated in Scheme 4.

As can be seen from Table 5 aldehydes are dominating at decomposition temperature 375 °C while at 410 °C allyl and diallyl compounds are the most dominant decomposition products. These are in accordance with our previous study in a similar polyester like poly(propylene succinate) [20], and is a clear proof that both mechanisms are taking place simultaneously (β- and α-hydrogen bond scission) at the studied decomposition temperatures, but to a different extent. Similar results about the decomposition mechanism of an aliphatic polyester like poly(butylene succinate) were also reported recently from Rizzareli and Crroccio [48]. At low temperatures it seems that α-hydrogen bond scission takes place at



Scheme 3. β-Hydrogen bond scission mechanism of PPGlu forming (a) acids and (b) vinyl acid compounds.



Scheme 4. α-Hydrogen bond scission mechanism of PPGlu forming aldehyde compounds.

higher extent while at higher temperatures β-hydrogen bond scission is the most dominant mechanism. These mechanisms may be correlated directly with the findings from TGA study from where also two different mechanisms were found taking place at different decomposition temperatures.

5. Conclusions

PPGlu and PPSub are two semicrystalline aliphatic polyesters and can be prepared with satisfactory molecular weights and melting points at 45.9 and 46.7 °C, respectively.

Both polyesters present a relative good thermostability since the maximum mass loss occurred until 250 °C is 0.5% for PPSub and 1% for PPGlu while the temperature at which the highest decomposition rate takes place is 411.2 °C for PPSub and 409.1 °C for PPGlu.

As far as it concerns to the decomposition kinetics it was found that the decomposition mechanism is very complex and can be described by using at least two different mechanisms. The best fitting of experimental data with theoretical models give *n*th order for the first mechanism and *n*th order with autocatalysis for the second mechanism. *n*th order with autocatalysis gives also very good results for both mechanisms.

From Py–GC–MS studies it was found that both polyesters are decomposing with β- and α-hydrogen bond scission. Both mechanisms are taking place simultaneously. However, β-hydrogen bond scission seems to be more important at higher decomposition temperatures (410 °C).

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