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Thermal degradation of biobased polyesters: Kinetics and decomposition mechanism of polyesters from 2,5-furandicarboxylic acid and long-chain aliphatic diols

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ABSTRACT

In the present study, biobased furan dicarboxylate polyesters have been prepared using 2,5-furandicarboxylic acid (FDCA) and diols with high number of methylene groups (long chain diols), namely 8, 10 and 12, which are named as poly(octylene 2,5-furanoate) (POF), poly(decylene 2,5-furanoate) (PDeF) and poly(dodecylene 2,5-furanoate) (PDof), respectively. Semi-crystalline polyesters with number average molecular weight ranging from 34,000 to 39,000 g/mol have been prepared and their chemical structure was proved by ¹H NMR spectroscopy. A systematic investigation of the thermal stability and decomposition kinetics of these polyesters was performed, using thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). From TGA curves it was found that all polyesters have high thermal stability since their decomposition starts around 340 °C and completes near 500 °C. The decomposition mechanism of the prepared polyesters was also studied with pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). From the identified decomposition products after pyrolysis at 350 and 450 °C, it was found that the decomposition of these polyesters is taking place mainly via β-hydrogen bond scission and in lower extent with homolytic >C–C< radical decomposition and with α-hydrogen scission.

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1. Introduction

For many years, the exploitation of natural resources and mainly petroleum for the production of petrochemical polymers has as a result the shrinkage of the above. The effort of using renewable resources came to the fore as an alternative option for the production of chemicals and fuels [1,2]. A large number of such monomers traditionally prepared from fossil resources, is currently available using renewable counterparts [3]. Biomass is the main source since it contains a large amount of organic molecules which provide a satisfactory carbon balance for chemical and fuel production. The synthesis of fine chemicals from the platform molecules obtained through the degradation of the cellulose and lignocellulosic biomass is a most widely envisioned approach toward the implementation of renewable feedstock for fuels and chemicals [3].

Furfural and 5-hydroxymethylfurfural (HMF) can be isolated of carbohydrates. The selective oxidation of HMF releases various furan compounds such as 2,5-diformylfuran (DFF) [4], 5-hydroxymethyl-2-furancarboxylic acid (HMFA) [5] and 2,5-furandicarboxylic acid (FDCA) [6]. FDCA can be also produced from cellulose or hemicellulose through a multistep process [7]. FDCA's structure contains two carboxylic acid groups and is similar to the terephthalic acid (TPA) structure. Apart from their similarities, some differences in their ring size and their polarity can attribute different characteristics to FDCA and TPA-based polyesters. TPA exhibits an interatomic distance of 5.731 Å between carboxylic acid groups, while FDCA is shorter, the distance being 4.830 Å. Furthermore, the linear p-phenyl connection in TPA results in an angle of 180° between carboxylic acid carbons, while the non-linear structure of FDCA presents an angle of 129.4° [8]. Within FDCA based polyesters, the furanic-aliphatic family is one of the most heavily investigated in recent years and these efforts have been extensively described by Sousa et al. [9] Poly(ethylene furanoate) (PEF) [10] is the most interesting polyester from this

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series and gains ground against poly(ethylene terephthalate) (PET) due to renewable sourcing of the monomers and the largely improved barrier, mechanical, and thermal properties compared to PET [11,12]. Other furan based polyesters like poly(butylene 2,5-furan-dicarboxylate) (PBF), poly(propylene 2,5-furan dicarboxylate) (PPF) and poly(hexamethylene 2,5-furan-dicarboxylate) (PHF) have also gained high interest and their properties have been recently reported from our group [13–15]. Besides furanoate polyesters synthesized using low carbon number diols, diols with higher carbon number can be also used such as 1,8-octanediol, 1,10-decanediol and 1,12-dodecanediol. Despite their higher melting and boiling point and the problems caused in the synthesizing procedure, in a previous work it became possible to synthesize such biobased furanoate polyesters by high molecular diols using a new strategy of polymerization [16–18].

The thermal stability of a polymer constitutes a very important property which determines firstly the synthetic procedure and afterward the polymer applications. However, in literature, there is only one work which describes study of the thermal degradation and the evaluation of decomposition mechanism of poly(ethylene furanoate) (PEF), poly(propylene furanoate) (PPF) and poly(butylene furanoate) (PBF) [19]. Of course, there are not any published works which study the thermal degradation of furanoate polyesters with long chain diols.

In this study, three long-chain diol furanoate polyesters, poly(octamethylene furanoate) (POF), poly(decamethylene furanoate) (PDeF) and poly(dodecamethylene furanoate) (PDoF) were synthesized by the melt polycondensation method following an innovate polymerization technique [16]. The aim of the present work was the detailed study of the thermal degradation of POF, PDeF and PDoF, including the decomposition kinetics analysis using data from thermogravimetric analysis (TGA) prior to investigate the decomposition mechanism of the polyesters. Also aiming at the understanding of the decomposition mechanism, Py-GC/MS was used on the polyesters for the determination of the fragments from each macromolecule. Thus a series of corresponding experiments were conducted intending to correlate data about the structure with the decomposition mechanism.

2. Experimental

2.1. Materials

2,5-furan dicarboxylic acid (purity 97%), 1,8-octanediol (98%, m.p. = 57–61 °C and b.p. = 172 °C/20 mmHg), 1,10-decanediol (98%, m.p. = 71–75 °C and b.p. = 297 °C), 1,12-dodecanediol (99%, m.p. = 79–81 °C and b.p. = 189 °C/12 mmHg) and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. All other materials and solvents used were of analytical grade.

2.2. Synthesis of 2,5-dimethylfuran-dicarboxylate (DMFD)

15.6 g of 2,5-furandicarboxylic acid, 200 mL of anhydrous methanol and 2 mL of concentrated sulphuric acid was transferred into a round bottom flask (500 mL) and the mixture was refluxed for 5 h. The excess of the methanol was distilled and the solution was filtered through a disposable Teflon membrane filter. During filtration dimethylester was precipitated as white powder and after cooling 100 mL of distilled water was added. The dispersion was partially neutralized by adding Na₂CO₃ 5% w/v during stirring while pH was measured continuously. The white powder was filtered and the solid was washed several times with distilled water and dried. The isolated white methylester was recrystallized with a mixture of 50/50 v/v methanol/water. After cooling, DMFD was precipitated

in the form of white needles. The reaction yield was calculated at 83%.

2.3. Polyester synthesis

The polyesters were prepared by applying a variation of the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [16]. DMFD and the appropriate diols at a molar ratio of diester/diol = 1/2 were charged into the reaction tube of the polyesterification apparatus with 400 ppm TBT. The reaction mixture was heated at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h and finally at 170 °C for 1 h. This first step (transesterification) is considered to complete after the collection of almost all the theoretical amount of CH₃OH, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. After this stage the corresponding bishydroxyalkylene-2,5-furan carboxylate monomers have been formed. In the second stage these monomers reacted with DMFD in a molar ratio 1/1.05 at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h and finally at 170 °C for 1 h. During this stage methanol was also removed as by-product. After that time in the third step of polycondensation a vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min. The temperature increased to 210 °C and the polymerisation continued for 1 h at this temperature, at 220 °C for 1 h and 230 °C for 0.5 h using a stirring speed 720 rpm. After the polycondensation reaction was completed, the polyesters were easily removed, milled and washed with methanol.

2.4. Polyester characterization

2.4.1. Intrinsic viscosity and molecular weight measurements

Intrinsic viscosity [η] measurements of prepared polyesters were performed using an Ubbelohde viscometer at 30 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40 w/w). The sample was maintained in the above mixture of solvents at 90 °C for some time to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter made of Teflon.

The number-average molecular weight (M_n) was measured by Gel permeation chromatography (GPC) using a Waters 150 °C apparatus equipped with differential refractometer as detector and three ultrastyrigel (10³, 10⁴, 10⁵ Å) columns in series. Tetrahydrofuran was used as mobile phase at a flow rate 0.5 mL/min at 40 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

2.4.2. Nuclear Magnetic Resonance (¹H NMR)

¹H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated trifluoroacetic acid (dTFA) 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.

2.4.3. Thermogravimetric analysis (TGA)

Simultaneous TG/DTA (thermogravimetry/differential thermal analysis) measurements were carried out by a STA 449C (Netzsch-Gerätebau, GmbH, Germany) thermal analyzer. The heating range was from room temperature up to 600 °C and four heating rates, i.e., β = 5, 10, 15 and 20 °C/min were employed in N₂ (99.9%) constant flow of 30 mL/min.

2.4.4. Pyrolysis-gas chromatography–mass spectroscopy (Py-GC/MS)

For Py-GC/MS analysis of polyesters a very small amount of each material is “dropped” initially into the “Double-Shot”

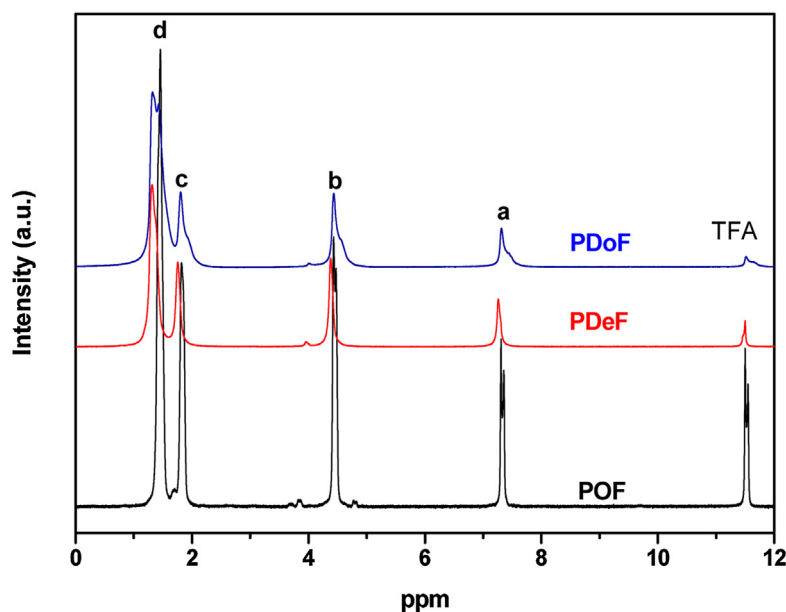
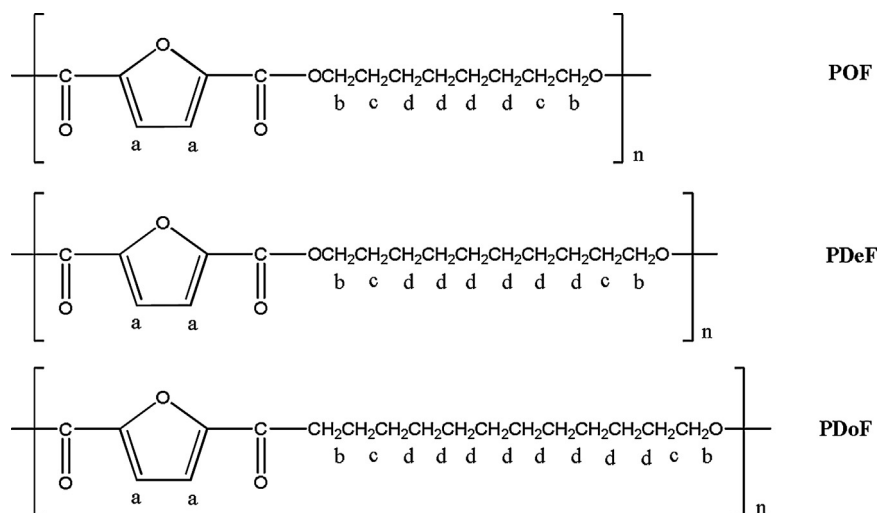


Fig. 1. ^1H NMR spectra of POF, PNF, PDeF and PDoF in dTFA.

EGA/PY-3030D Pyrolyzer (Frontier Laboratories Ltd., Fukushima Japan) using a CGS-1050Ex (Japan) carrier gas selector. For EGA analysis the furnace temperature is programmed from 50 to 700 °C with a heating rate 20 °C/min using He as purge gas and air as cooling gas. For pyrolysis analysis (flash pyrolysis) each sample was placed into the sample cup which afterwards fell free into the Pyrolyzer furnace. The pre-selected pyrolysis temperatures were 350 and 500 °C and the GC oven temperature was heated from 50 to 300 °C at 20 °C/min. Those two temperatures were selected based on the EGA pyrogram and represent the sample prior and after thermal decomposition. Sample vapors generated in the furnace were split (at a ratio of 1/50), a portion moved to the column at a flow rate of 1 mL/min, pressure 53.6 kPa and the remaining portion exited the system via the vent. The pyrolyzates were separated using temperature programmed capillary column of a Shimadzu QP-2010 Ultra Plus (Japan) gas chromatogram and analyzed by the mass spectrometer MS-QP2010SE of Shimadzu (Japan) use 70 eV. Ultra ALLOY® metal capillary column from Frontier Laboratories

LTD (Fukushima Japan) was used containing 5% diphenyl and 95% dimethylpolysiloxane stationary phase, column length 30 m and column ID 0.25 mm. For the mass spectrometer the following conditions were used: Ion source heater 200 °C, interface temperature 300 °C, vacuum 10^{-4} – 10^0 Pa, m/z range 10–500 amu and scan speed 10,000. The chromatogram and spectra retrieved by each experiment are subject to further interpretation through Shimadzu and Frontier post-run software.

3. Results and discussion

3.1. Synthesis and characterization of polyesters

The polyesters were prepared by applying a variation of the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [16]. This procedure was used in order to avoid the difficulty to distill the extent of used diols, which due to their high molecular weight have also high boiling

Table 1
Intrinsic viscosity (IV), number and weight average molecular weights and polydispersity of the molecular weight distribution of POF, PNF, PDeF and PDoF.

Sample	IV (dL/mg)	M_n (g/mol)	M_w (g/mol)	PD
POF	0.43	34556	62085	1.80
PDeF	0.47	36710	57025	1.55
PDoF	0.49	39371	68965	1.75

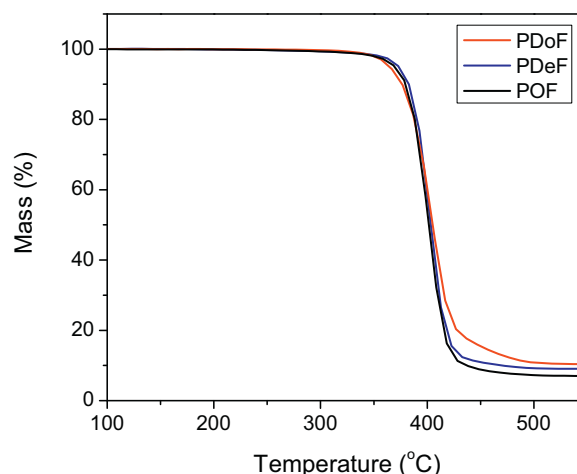
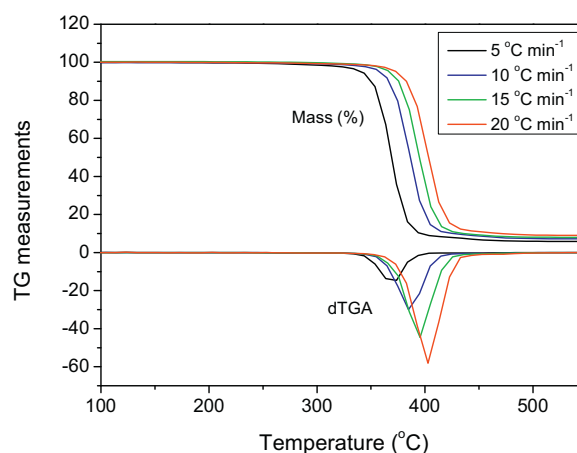
points. According to this polycondensation procedure, which was described with details in experimental part, after the end of esterification and the formation of oligomers, DMFD was added again and the procedure was continued for some time. In this case methanol is the byproduct of the reaction and not the high boiling point diols. At the end polycondensation was applied and polyesters with intrinsic viscosity values ranging from 0.43 to 0.49 dL/g are obtained (Table 1). This is because the used polycondensation time was identical in all polyesters (i.e., 1 h at 210 °C and 220 °C and 0.5 h at 230 °C). The molecular weights of the prepared polyesters measured by GPC are also presented in Table 1. It can be seen that the number average molecular weights ranged from 34,500 to 39,400 g/mol, not depending on the number of methylene groups of the used diols. The polydispersity (PD) index is also satisfactory (i.e., around 1.8) for the polymers. This proves that the used procedure is appropriate for synthesis of furan polyesters with high molecular weight, using high boiling point diol monomers.

The structure of the prepared polyesters was verified with ^1H NMR spectroscopy. The spectra of POF, PDeF and PDoF are shown in Fig. 1. According to the NMR theory, the protons on and next to the aromatic ring are the most deprotected due to its π electrons. As a result, the 'a' protons of the composed polyesters attributed to the furan ring appear at the highest ppm values, ranging between 7.26 and 7.3 ppm. This is in accordance with our previous studies [12–19]. The aliphatic segment of the carbon chain of POF, PDeF and PDoF contains 16, 20 and 24 protons respectively. The closest to the ring protons ('b' and 'c' protons) are displayed on higher ppm values in comparison with the protons in the middle of the chain ('d' protons). Even the 'd' protons are not equivalent, due to the fact that are located far from the molecular groups which attract electrons, they appear at similar ppm values and differentiation is almost impossible. So, the peak integration concerned that the absorption of all 'd' protons coincides in each polymer spectrum. The observed absorptions were: POF, 'a' protons at 7.32 δ (2 H, s), 'b' protons at 4.45 δ (4 H, t), 'c' protons at 1.80 δ (4 H, q), 'd' protons at 1.45 δ (8 H, s), PDeF, 'a' protons at 7.26 δ (2 H, s), 'b' protons at 4.38 δ (4 H, t), 'c' protons at 1.75 δ (4 H, q), 'd' protons at 1.31 δ (12 H, s), PDoF, 'a' protons at 7.31 δ (2 H, s), 'b' protons at 4.43 δ (4 H, t), 'c' protons at 1.80 δ (4 H, q) and 'd' protons at 1.37 δ (16 H, s). The absent of any other peaks indicates that polyester with high purity have been prepared.

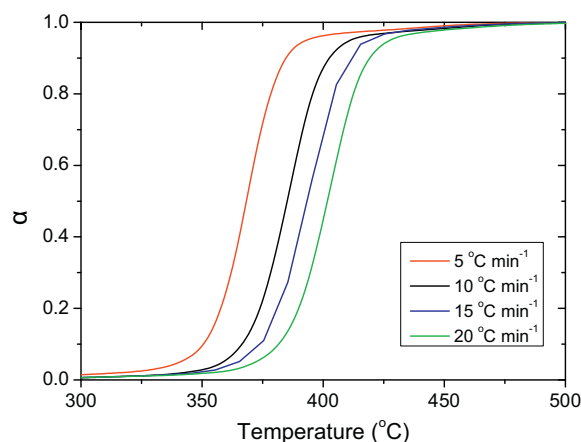
All prepared polyesters are semicrystalline materials as was verified by XRD and DSC [16]. POF showed a T_m of 140 °C, while the T_m values for PDeF and PDoF were 116 and 111 °C, respectively. The recorded T_m for PDoF is very close to that reported from Grosshardt et al., and is 109.0 °C [20], while that for POF is slightly lower than the value reported by Jiang et al. ($T_m = 148.6$ °C) [21].

3.2. Thermogravimetric analysis and kinetics

Thermal stability of furan dicarboxylate polyesters was studied by TGA. The recorded TG scans of the three samples obtained at 20 °C min⁻¹ are illustrated in Fig. 2. It is seen that degradation starts almost at the same temperature for the three polymers, i.e., around 340 °C and completes again at approximately the same value, near 450 °C. The main difference between different polyesters observed was that the residue was higher with increasing num-

**Fig. 2.** TG measurements of PDoF, PDeF and POF at 20 °C min⁻¹.**Fig. 3.** Effect of the heating rate on the percentage of mass loss and its derivative with respect to temperature as a function of temperature for PDeF.

ber of methylenes in the glycol used. Thus, it was almost 7, 9 and 10.3% for POF, PDeF and PDoF, respectively. From Fig. 2, although the shape of the curves seems to be similar for the three polyesters, some characteristic details appear. Thus, PDeF presented the steepest change, while, the degradation seems to last longer for PDoF. Compared with the other furan dicarboxylate polyesters it can be

**Fig. 4.** Variation of the extent of degradation, α with temperature for PDeF at different heating rates.

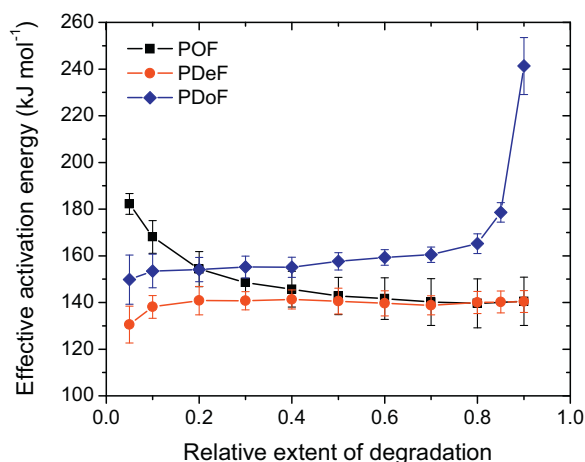


Fig. 5. Variation of the activation energy with the extent of degradation for the three polyesters POF, PDeF and PDoF estimated with the KAS method.

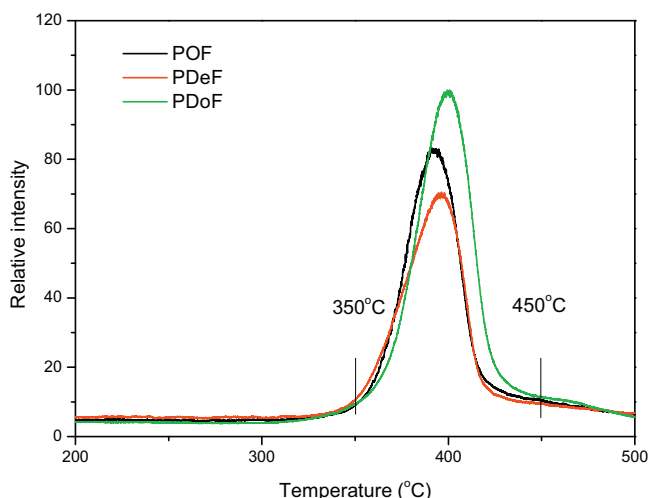


Fig. 6. EGA pyrograms for POF, PDeF and PDoF.

seen that they have similar thermal stability with PEF, PPF and PHF but slightly higher than PBF [15,19]. In order to identify these differences in the degradation mechanism of the three polymers, a kinetic analysis was further performed.

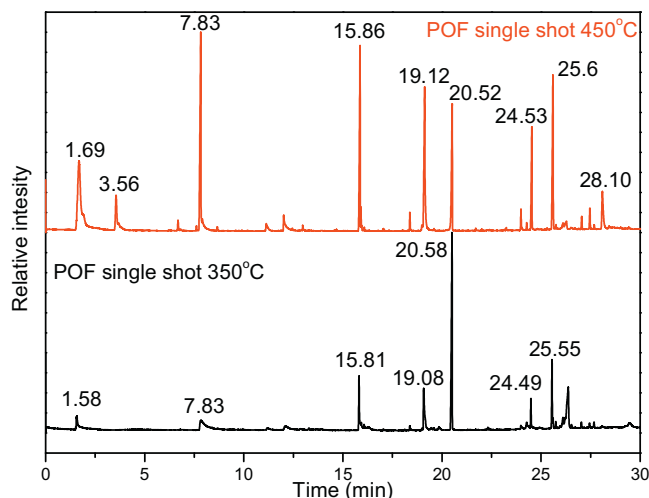


Fig. 7. Gas chromatographs of POF at different decomposition temperatures.

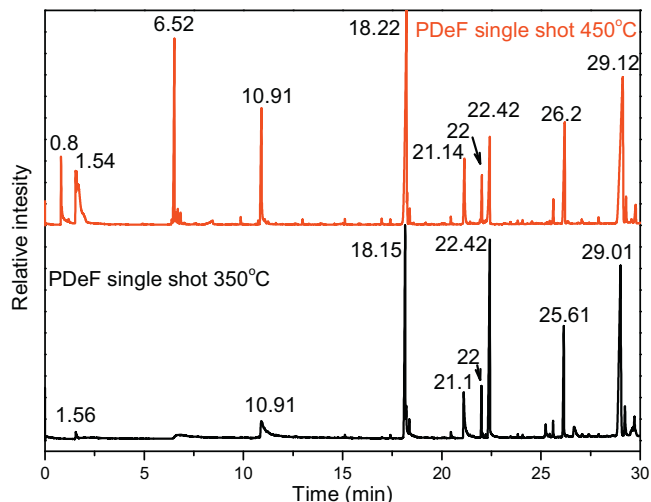


Fig. 8. Gas chromatographs of PDeF at different decomposition temperatures.

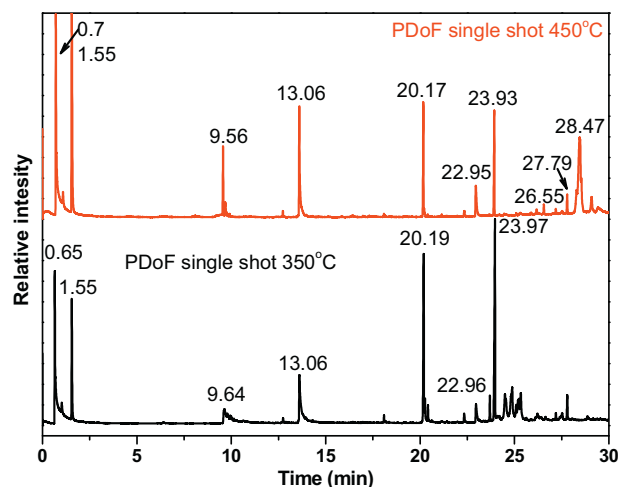


Fig. 9. Gas chromatographs of PDoF at different decomposition temperatures.

According to the ICTAC recommendation, in order, to perform a kinetic analysis on polymer degradation, isoconversional methods are preferred. Isoconversional methods employ multiple temperature programs (e.g., different heating rates) in order to obtain data on varying rates at a constant extent of conversion. Thus, isoconversional methods allow complex (i.e., multi-step) processes to be detected via a variation of the effective activation energy, E_{α} with α [22].

A representative figure showing the effect of heating rate on the percentage of mass loss as a function of temperature for PDeF appears in Fig. 3. As it is common in polymer degradation, increased heating rates results in shifting of the degradation curves in higher temperatures. In the same figure the variation of the derivative TG curves are included. It is interesting to note that all samples exhibit only one degradation peak providing an indication that degradation occurs in one step only.

The kinetics of polymer degradation is usually described by the following single-step kinetic equation [22]:

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

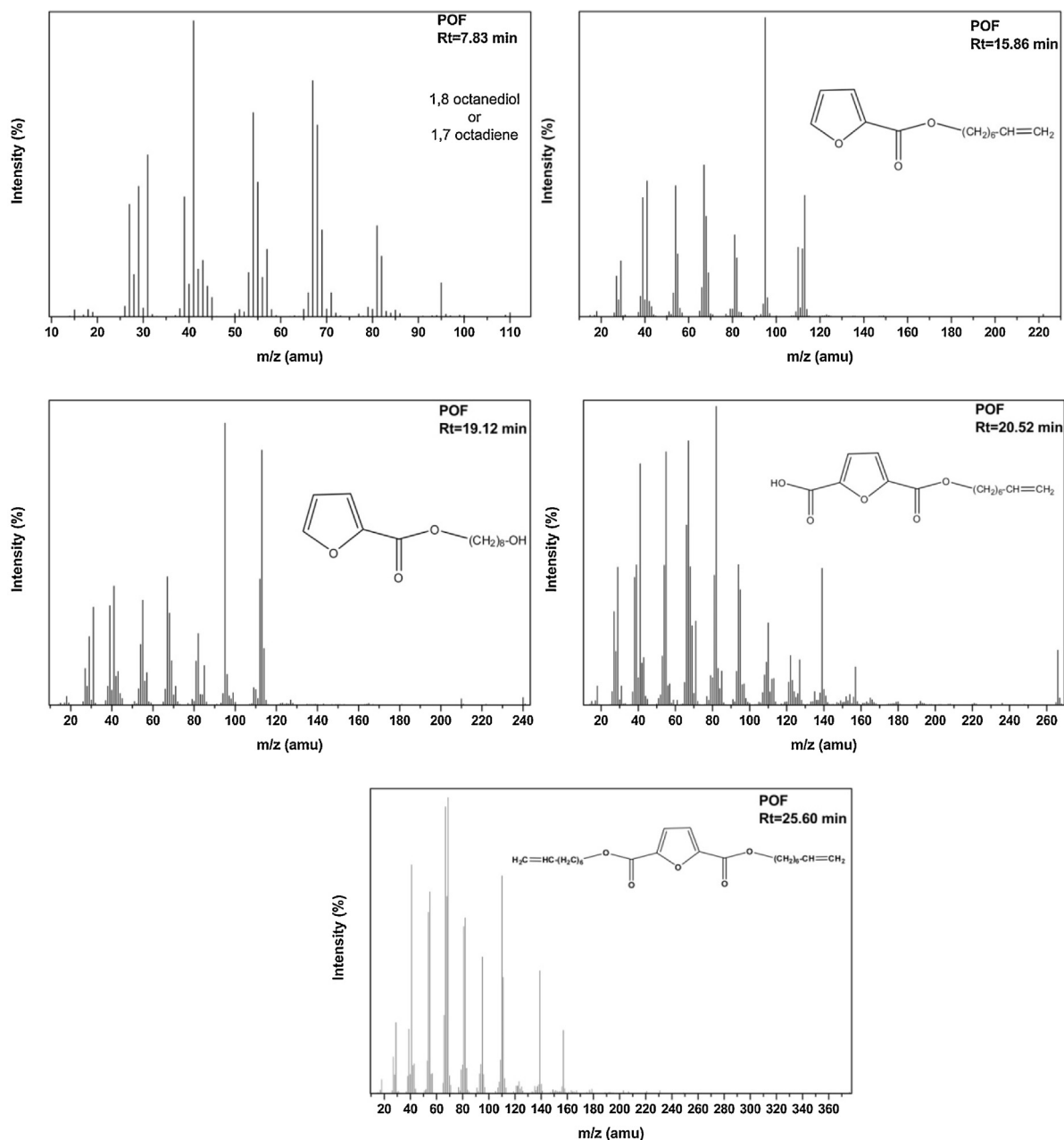


Fig. 10. Mass spectra of decomposition products of POF, pyrolysed at 450 °C.

with t denoting time, $k(T)$ the temperature-dependent rate constant and $f(\alpha)$ the function expressing the reaction model, α represents the extent of reaction ($0 \leq \alpha \leq 1$), given by the quotient:

$$\alpha = \frac{m_t - m_0}{m_\infty - m_0} \quad (2)$$

where mass at the beginning, time t and at the end of the degradation is denoted as m_{600} , m_t and m_∞ , respectively.

Using the definition of Eq. (2) it is ensured that the extent of degradation varies from 0 to 1, as it is needed in the kinetics calculations. The variation of the extent of degradation, α , with temperature for PDeF at different heating rates, appears in Fig. 4.

Using a simple Arrhenius-type form to express the kinetic rate constant, Eq. (1) becomes:

$$\frac{d\alpha}{dt} = A \times \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (3)$$

where A is the pre-exponential factor, E_α the activation energy and R the universal gas constant.

According to the isoconversional principle, at a constant extent of conversion, the reaction rate is a function only of the temperature. So that Eq. (3) can be written as [22]:

$$\left[\frac{d \ln (d\alpha/dt)}{d(1/T)} \right]_\alpha = -\frac{E_\alpha}{R} \quad (4)$$

where the subscript α denotes value at a specific extent of reaction.

Generally, isoconversional methods are divided in two categories: differential and integral. The most common differential isoconversional method is that of Friedman [22]. The method is based on the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[Af(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (5)$$

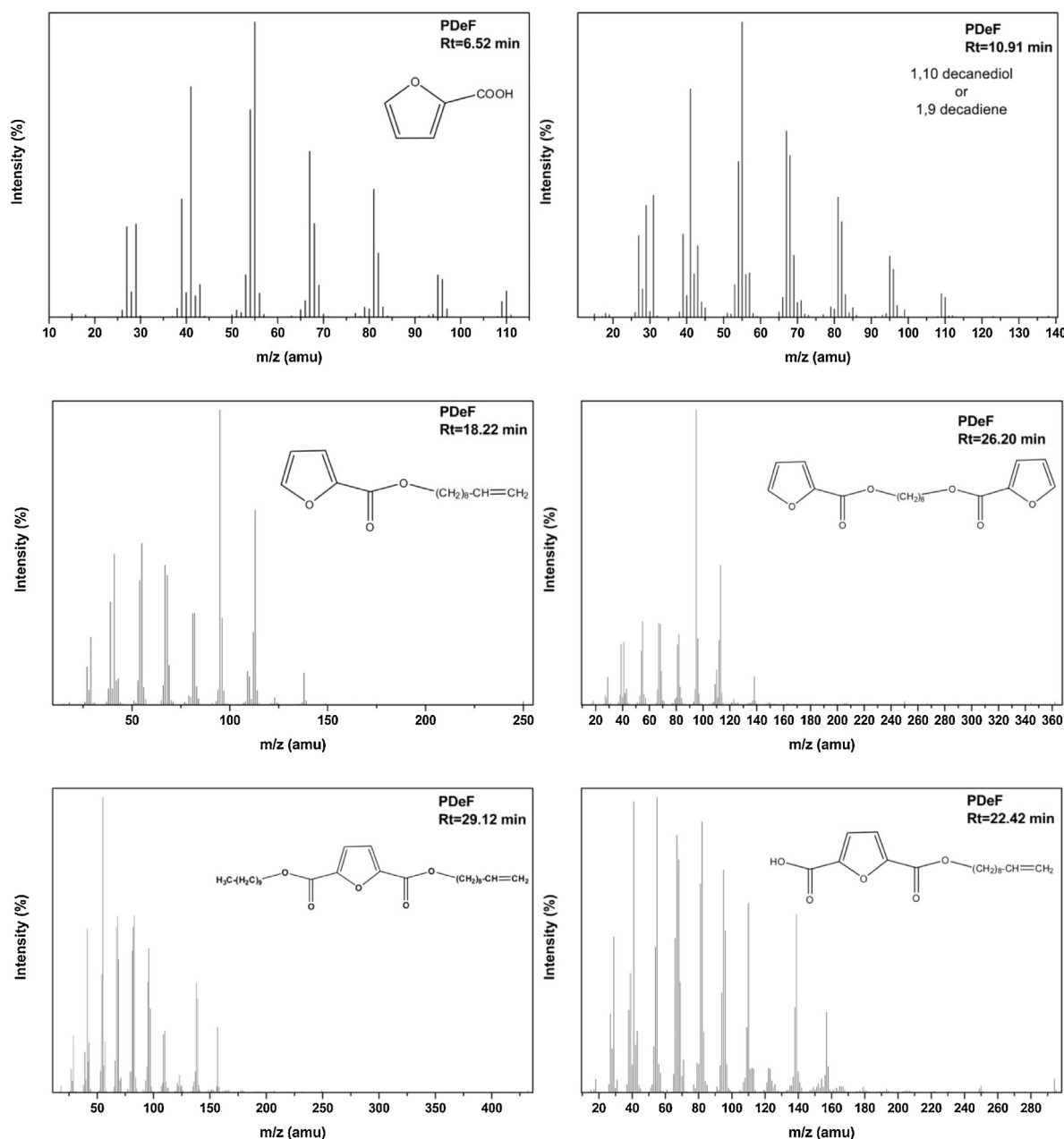


Fig. 11. Mass spectra of decomposition products of PDeF, pyrolysed at 450 °C.

which comes from taking the logarithm of Eq. (3). From the slope of a plot of $\ln(d\alpha/dt)$ vs $1/T$ the activation energy E_α can be calculated [22]. Since this method does not use any approximations, perhaps is more accurate than those following. The differentiation, however, of the experimental data α , carried out by the software of the instrument, often emerges noisy and maladjusted raw data, leading to unstable activation energy values. This problem of numerical differentiation could be avoided by using integral isoconversional methods. One of the most precise methods was described by Coats and Redfern (CR) [23] and leads to the following popular equation that is frequently called the Kissinger–Akahira–Sunose (KAS) equation [22]:

$$\ln \left(\frac{\beta_i}{T_{\alpha,i}^2} \right) = -\frac{E_\alpha}{RT_{\alpha,i}} + \text{constant} \quad (6)$$

where β_i is the constant heating rate ($\beta = dT/dt$)

From the slope of the linear curve obtained after plotting the left-hand side of Eq. (6) with respect to $1/T$, the activation energy E_α can be easily estimated. According to the ICTAC recommendation, Eq. (6) was also employed in this work. It should be pointed here that according to a recent comparative study by Sbirrazzuoli [24], the most precise method, among integral isoconversional ones, is that of Tang et al. [25] which uses an exponent of 1.92 instead of 2 in Eq. (6).

Plots of $\ln(\beta/T^2)$ vs $1/T$ have been created for all different polyesters investigated. The resulted curves followed very good straight lines with correlation coefficients, $R^2 > 0.999$. The activation energies thus estimated as a function of the extent of degradation appear in Fig. 5, together with their corresponding standard deviations. It can be seen that PDeF presented the lower activation energy which was also almost constant during the whole course of degradation, i.e., around 140 kJ/mol. The same also constant value was calculated for POF after 50% degradation. For this

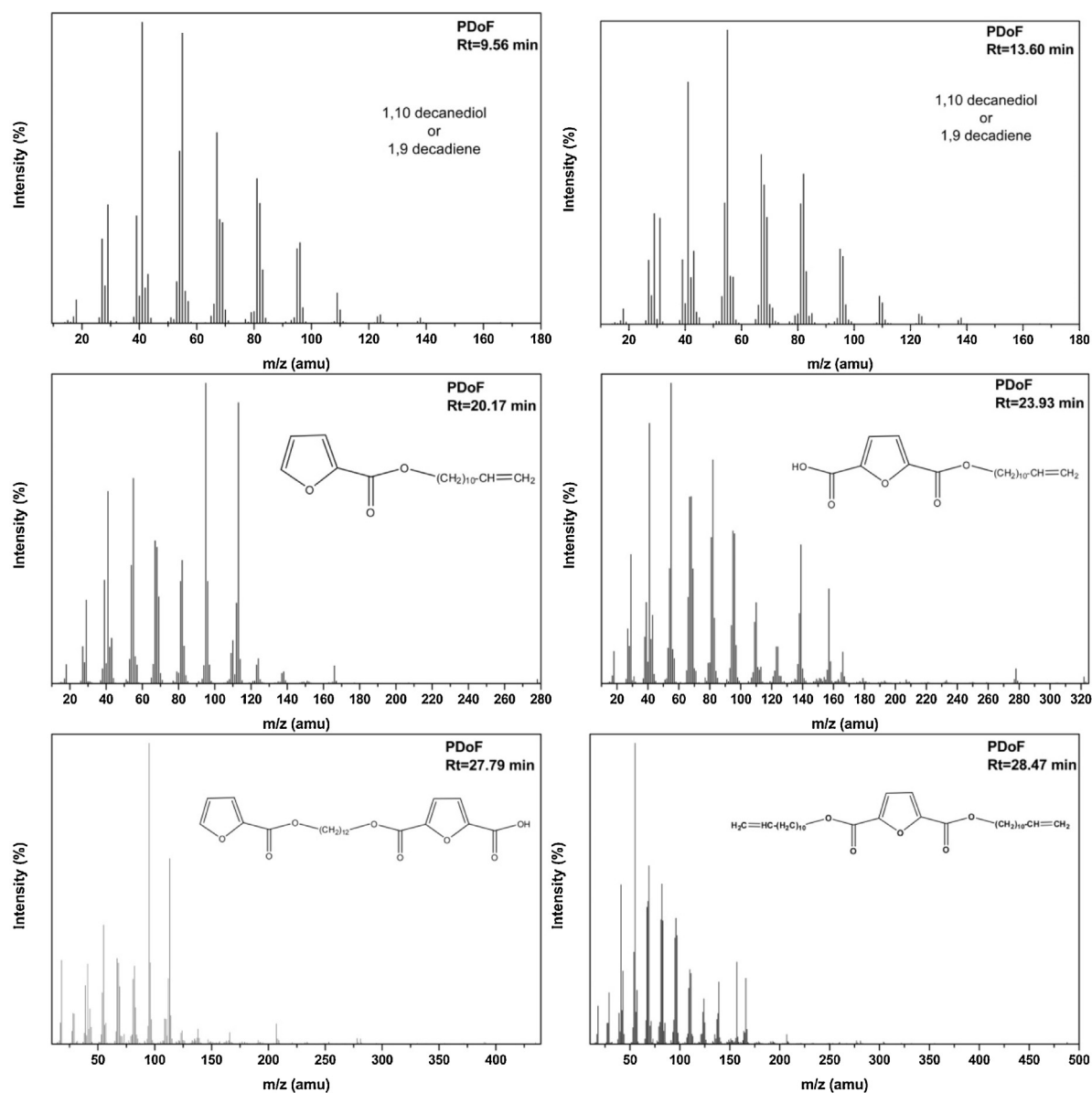


Fig. 12. Mass spectra of decomposition products of PDoF, pyrolysed at 450 °C.

polymer, E_a starts from a high value (i.e., 180 kJ/mol) at low extent of degradation which is constantly decreasing to 140 kJ/mol. In contrast PDoF presented a higher E_a , near 160 kJ/mol, almost constant until 80% degradation, which was further significantly increased to 240 kJ/mol. The above results denote that degradation occurs in one step for PDeF, whereas the same holds for PDoF but only until 80% degradation. The steep increase in the activation energy after that point is in accordance with the observation of the higher amount of residue left for this polyester, meaning that at high degradation conversion a char is formed. Moreover, the constantly higher E_a values estimated for PDoF compared to PDeF is an indication that in this polymer the macromolecular chains are more compact and it is harder to be cleaved. For POF a multi-step mechanism seems to exist until $\alpha = 0.5$, while afterwards the degradation is exactly the same with PDeF.

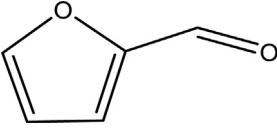
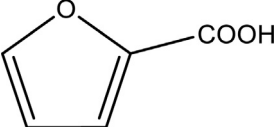
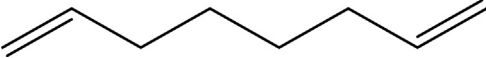
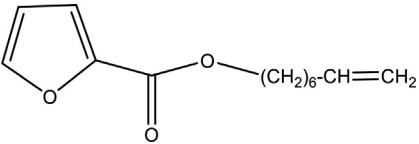
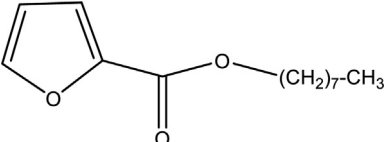
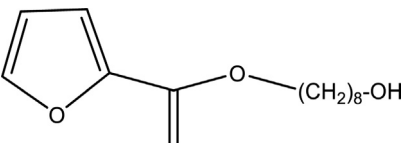
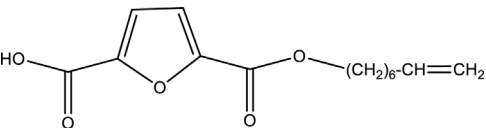
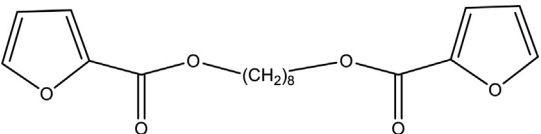
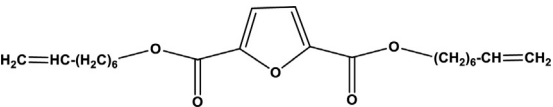
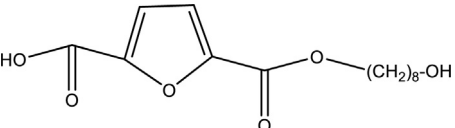
3.3. Py/GC–MS

Decomposition of polyesters has been widely studied with several techniques [26] while in the present study the decomposition

mechanism of the prepared polyesters was evaluated with Py-GC/MS technique. Fig. 6 shows the recorded pyrograms of EGA analysis of all these polyesters. As can be seen, decomposition of all the polyesters starts after 300 °C, exhibits similar profile and is completed at around 450–500 °C. The main peaks of the evolved gases of the polyesters are at temperatures 394.5, 396.5 and 400 °C for POF, PDeF and PDoF, respectively. In accordance with TGA measurements, thermal stability of the polyesters is similar and slightly increases with increasing the methylene groups of the diol.

Pyrolysis of the polyesters was carried out at 350 and 450 °C, corresponding to the start and completion of the decomposition, as concluded from the EGA pyrogram of Fig. 6. The chromatograms of the produced gas compounds of the three polyesters are presented in Figs. 7–9. The main degradation products at each retention time are identified by mass spectroscopy, in order to analyze the possible decomposition mechanism. Mass spectra of the main decomposition products at 450 °C are presented in Figs. 10–12. The possible identified fragments of each polyester are presented in Tables 2–4. Peak areas (%) were calculated with respect to the sum of the area of all components.

Table 2
Compounds identified in the chromatographs of POF.

350 °C		450 °C		M (m/z)	Assigned structure
Retention time (min)	Peak area (%)	Retention time (min)	Peak area (%)		
1.58	2.07	1.69	12.23	44	CO ₂
–	–	3.56	3.04	96	
–	–	6.68	0.55	112	
7.83	5.71	7.83	14.46	202 and/or 146	
15.81	5.51	15.86	11.10	222	
–	–	15.91	0.53	224	
19.08	8.76	19.12	11.36	240	
20.58	32.49	20.52	9.13	266	
24.49	2.74	24.53	5.78	334	
25.55	6.35	25.6	9.97	376	
–	–	28.10	4.20	284	

From the recorded chromatograms it is clear that all studied FDCA polyesters result in fewer decomposition products when pyrolyzed at 350 °C, while a more complex decomposition profile occurs at 450 °C, as revealed by the greater number of peaks in the chromatograms recorded in this temperature. The produced pyrolysis products and therefore the decomposition

mechanism are temperature-dependent. MS analysis revealed that at low retention times (0.5–3 min) gases and volatile compounds such as CO₂, acetaldehyde, furfural and furan are formed. CO₂ and acetaldehyde are reported as products of the decomposition of PET, with acetaldehyde being produced by recombination of vinyl-terminated and carboxyl-terminated units [27]. At greater

Table 3
Compounds identified in the chromatographs of PDeF.

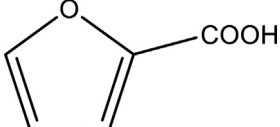

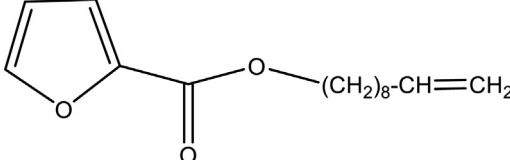
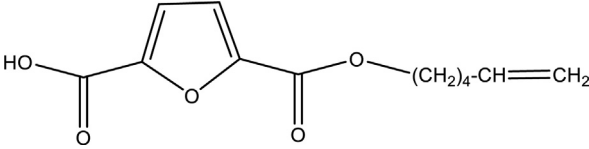
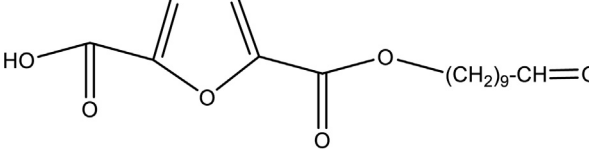
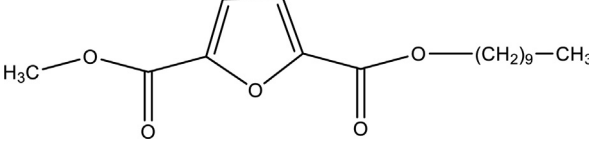
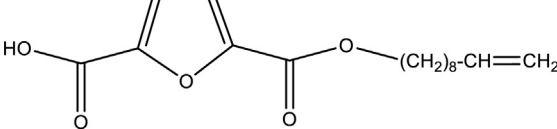
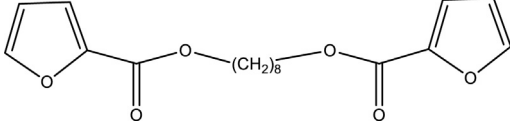
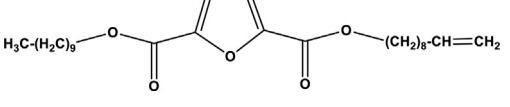
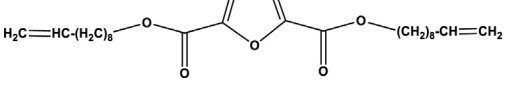
350 °C		450 °C		M (m/z)	Assigned structure
Retention time (min)	Peak area (%)	Retention time (min)	Peak area (%)		
–	–	0.8	1.64	28.44	CO
1.56	0.45	1.54	0.85	44	CO ₂
–	–	6.52	8.11	112	 HO—(CH ₂) ₁₀ —OH and/or
10.91	3.18	10.91	6.26	174 and/or 138	
18.15	13.20	18.22	15.31	250	
21.10	4.04	21.14	3.63	238	 
22.00	2.32	22.00	1.63	310	or 
22.42	16.22	22.42	4.69	294	
26.15	6.88	26.20	6.77	362	
29.01	25.86	29.12	23.22	434	
29.71	0.91	29.28	1.14	432	

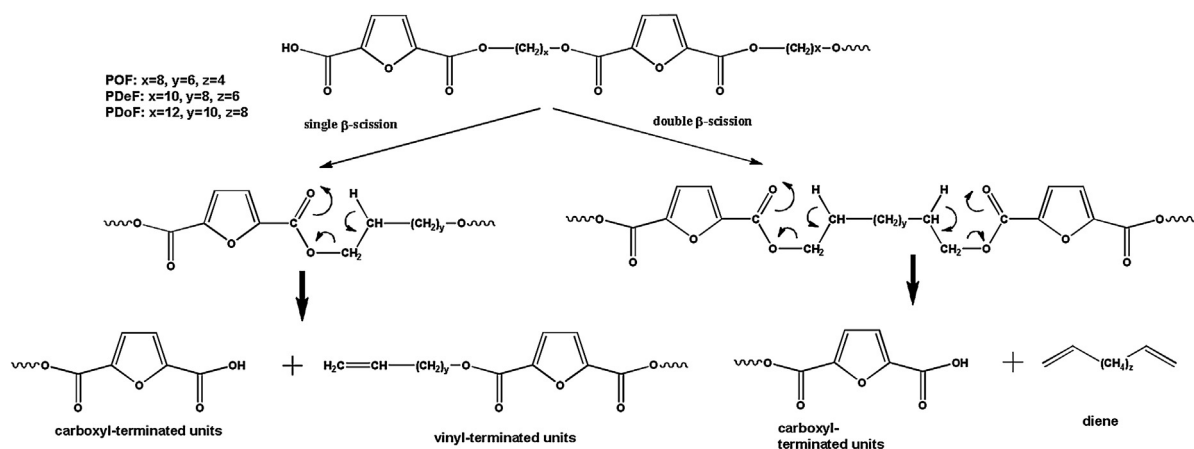
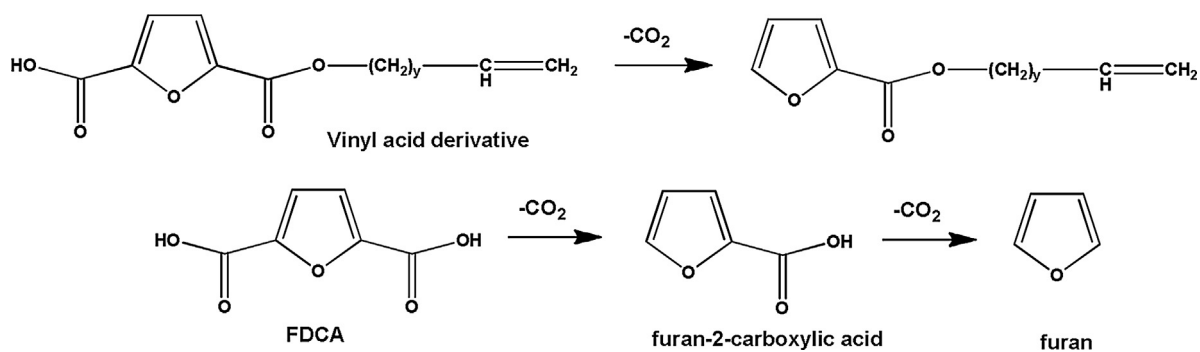
Table 4
Compounds identified in the chromatograms of PDoF.

350 °C		450 °C		M (m/z)	Assigned structure
Retention time (min)	Peak area (%)	Retention time (min)	Peak area (%)		
0.65	7.75	0.7	11.14	28, 44	CO CO ₂
1.55	6.32	1.55	15.63	44	HO—(CH ₂) ₁₂ —OH
9.64, 13.60	1.95, 5.08	9.56, 13.60	3.12, 7.12	202, 166	and/or
20.19	9.11	20.17	5.27	278	
22.96	2.00	22.95	3.03	296	
23.97	14.27	23.93	5.38	322	
–	–	26.55	0.45	492	
27.79	1.44	27.79	1.07	434	
–	–	28.47	12.73	488	

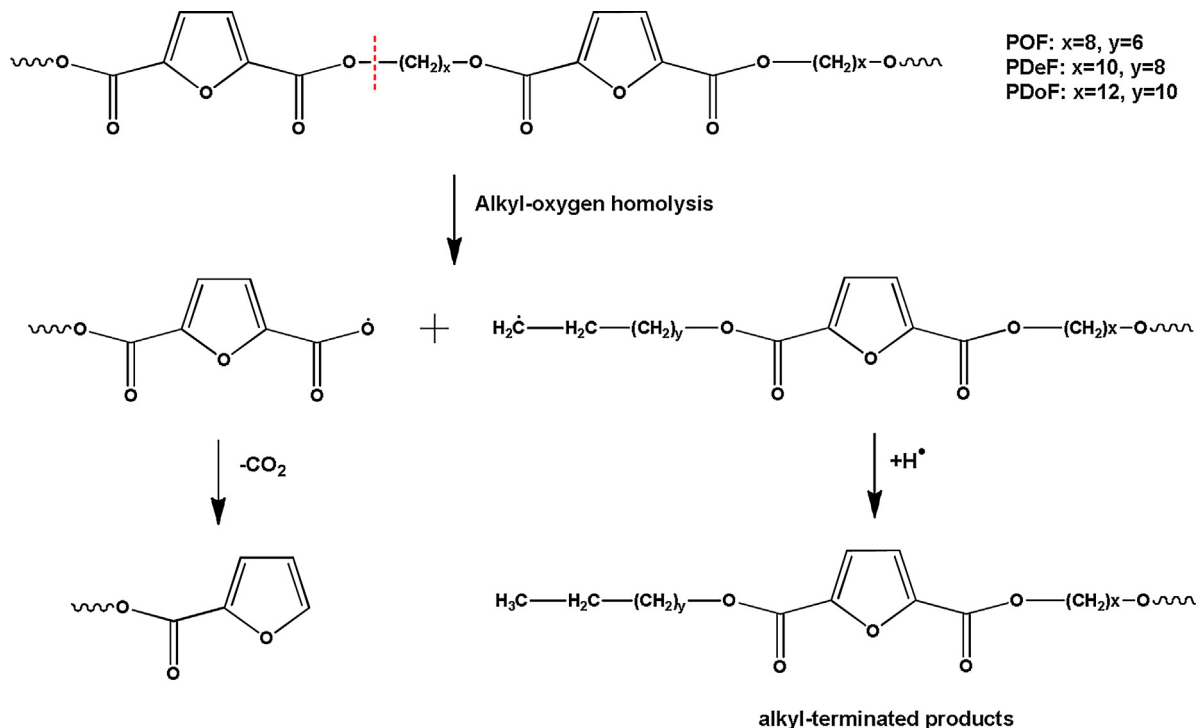
retention times, diols and dienes that correspond to the decomposition of the used monomers for polyester synthesis and several alkyl, vinyl, or hydroxyl terminated esters of FDCA are recorded. Identification of each degradation product can lead to conclusions about the mechanisms that take place during pyrolysis of the polyesters.

Thermal degradation of thermoplastic polyesters occurs via heterolytic and homolytic scission of their aliphatic fragments [26], and an early study by Buxbaum revealed that the primary scission of the ester bond in polyesters with at least one β -hydrogen is β -hydrogen scission rather than homolytic radical scission, since thermal degradation was not inhibited by free radical trapping agents [28]. Furan-based polyesters studied in this work contain 2 β -hydrogens per repeating unit, so it is expected that β -hydrogen scission will be the main degradation mechanism.

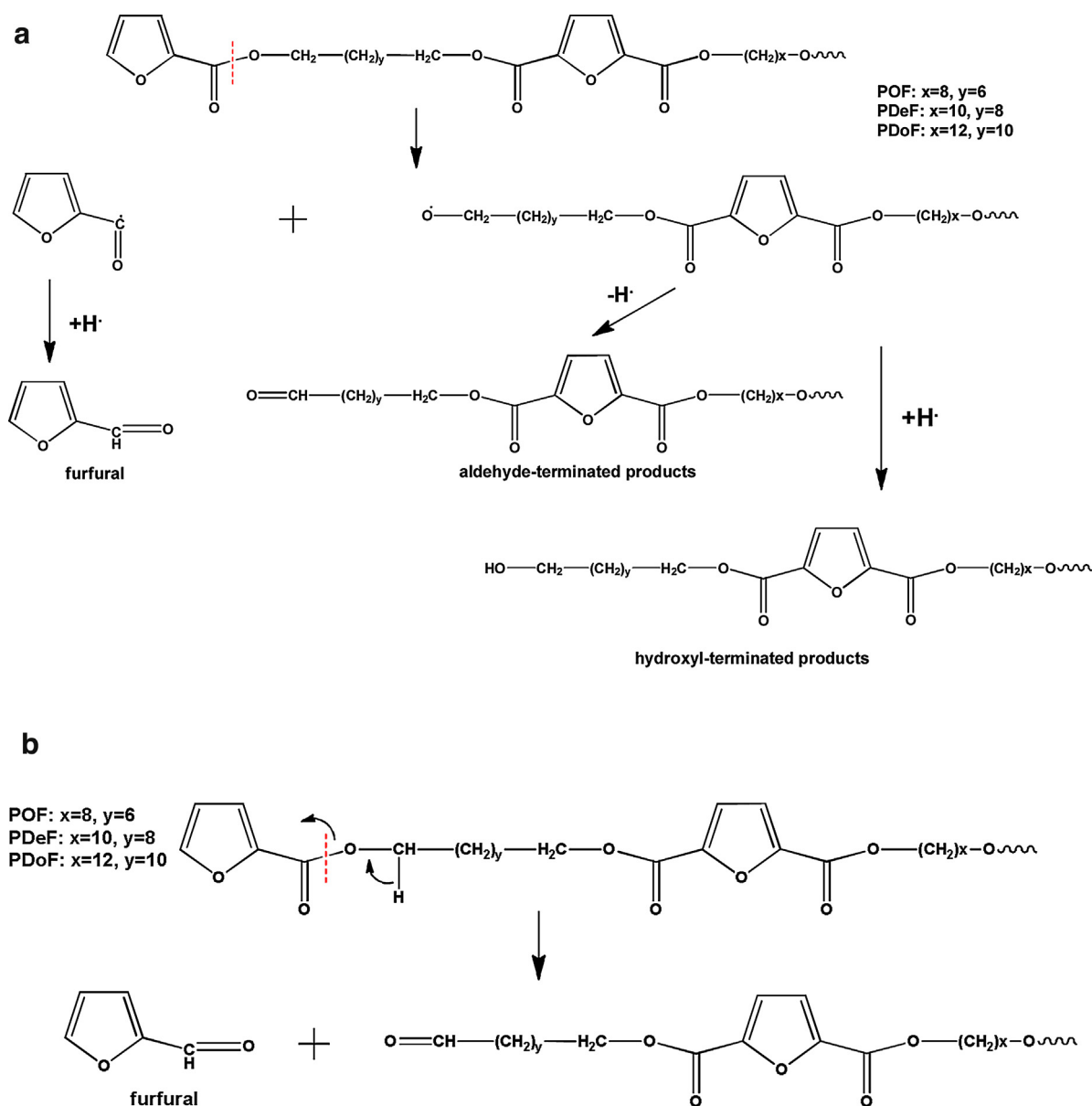
In our study, this hypothesis can be confirmed, since the main degradation products of all 3 polyesters are vinyl- and carboxyl-terminated esters of FDCA, formed by β -hydrogen scission. More specifically, such products were recorded at 15.86, 20.52 and 25.6 min for POF, at R_t = 18.22, 21.14, 22.42, 25.62, 26.2, 29.12 and 29.28 min for PDeF, and at R_t = 20.17, 23.93, 27.79 and 28.47 min for PDoF, when pyrolysed at 450 °C. The main degradation products after pyrolysis at 350 °C were the same vinyl- and carboxyl-terminated compounds too, and the mechanism of their formation is depicted in Scheme 1. Double β -hydrogen scission can lead to the formation of dienes with number of carbon atoms relevant to the diol used in the polymerization (Scheme 1a). 1,7-octadiene, 1,9-decadiene and 1,11-dodecadiene may be pyrolysis products of the polyesters, but the similarity of their mass spectra with those of the corresponding diols makes it impossible to distinguish if the peaks are diene or diol with the same number of carbon atoms.

Scheme 1. Intramolecular β -hydrogen scission process.

Scheme 2. Decarboxylation of polyester pyrolysis products.



Scheme 3. Alkyl-oxygen homolysis mechanism.



Scheme 4. Formation of aldehydes and alcohols by (a) Acyl-oxygen homolysis mechanism and (b) α -hydrogen bond scission.

In the case of PET, divinyl terephthalate is one of its main degradation products [28] and its analogues in the case of polyesters of FDCA are also formed in great relative quantities, at $R_t = 25.6$, 29.28 and 28.47 min for POF, PDeF and PDoF respectively, at pyrolysis temperature 450 °C. Vinyl acid derivatives are also detected in chromatograms of POF at $R_t = 15.86$ and 20.52 min, of PDeF at $R_t = 18.22$, 22.42 and 29.12 min, of PDoF at $R_t = 20.17$ and 23.93 min, at pyrolysis temperature 450 °C. The absence of FDCA from the chromatograms does not rule it out as a pyrolysis products, since furan-2-carboxylic acid, a product of its decarboxylation was intensified. The formation of furan can also be explained by simultaneous decarboxylation of FDCA's carboxyl groups, with the production of CO₂ that was detected in early R_t for all 3 polyesters (Scheme 2). Decarboxylated dimers were also identified, for POF at $R_t = 24.53$ min, for PDeF at $R_t = 26.2$ min and for PDoF at $R_t = 27.79$ min.

CO₂ can also be formed through homolytic reactions, by alkyl-oxygen radical scission (Scheme 3). Increase of the amount of CO₂ produced and new compounds that can only be explained

by homolysis reactions that emerge only at 450 °C suggest that radical scission also takes place at higher pyrolysis temperatures. The formation of alkyl-terminated products can be explained by this radical scission mechanism alkyl-oxygen homolysis.

Several hydroxyl-terminated derivatives were identified, and their formation can be explained by the previous mechanisms, especially by hydrolysis reactions of β -hydrogen scission products and also by acyl-oxygen homolysis (Scheme 4) that leads to alkoxy- and acyl- endcapped radicals. The alkoxy radicals can result in hydroxyl-terminated or aldehyde-terminated molecules. Also, an aldehyde-terminated product was identified for PDeF at 23.46 min. Aldehydes can be usually produced by α -hydrogen bond scission (Scheme 4), as was reported also in our previous studies in polyesters [29–31]. However, the amount of such products that are possibly formed via homolytic routes is small and only formed after pyrolysis at 450 °C and not at 350 °C, indicating that this mechanism is not favoured over β -scission and is also related with higher pyrolysis temperatures.

4. Conclusions

Biobased POF, PDeF and PDoF polyesters have been prepared successfully with appropriate molecular weights using a facile melt polycondensation procedure. These polyesters are semicrystalline materials with melting points to be decreased by increasing the number of methylene groups in the used diol. From TGA analysis it was found that they are very stable materials since their decomposition starts after 340 °C. PDeF and PDoF have the lower activation energy (about 140 kJ/mol) while PDoF presented a higher E_a , near 160 kJ/mol. The decomposition mechanism of studied polyesters was verified by Py-GC/MS. It was found that at low decomposition temperatures (350 °C) β -hydrogen bond scission takes mainly place forming alkylene end group byproducts. This mechanism is also the dominant at 450 °C, at which α -hydrogen bond scission homolytic radical scission take place leading to aldehydes and alkyl end group products.

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