Thermal degradation kinetics and decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and low molecular weight aliphatic diols

Vasilios Tsanaktsis¹, Evangelia Vouvoudi¹, George Z. Papageorgiou², Dimitrios G. Papageorgiou³, Konstantinos Chrissafis³, Dimitrios N. Bikiaris¹*  

¹Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece  
²Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece  
³Solid State Physics Section, Physics Department, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

Abstract
In the present work three novel aliphatic polyesters, namely poly(ethylene 2,5-furan dicarboxylate) (PEF), poly(propylene 2,5-furan dicarboxylate) (PPF) and poly(butylene 2,5-furan dicarboxylate) (PBF) have been prepared by applying the two-stage melt polycondensation method. The interest for polyesters prepared from renewable resources has increased recently since they can be synthesized using monomers like furfural or hydroxymethylfurfural and aliphatic diols. A systematic investigation of the thermal stability and decomposition kinetics of furanoate polyesters was performed using thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). From TGA curves and activation energies it was found that PBF is less stable thermally, than the other two polyesters. The thorough studies of evolving decomposition compounds along with the isoconversional and model-fitting analysis of mass loss data led to the proposal of a decomposition mechanism for every polyester. The decomposition mechanism of 2,5-furan dicarboxylate polyesters was evaluated with Py-GC/MS and from the identified decomposition products it was found that the decomposition of these polyesters is taking place mainly via β-hydrogen bond scission and in lower extent with α-hydrogen scission. 2,5-Furandicarboxylic acid, furoic acid, allyl- and diallyl-compounds are produced in the first case while aldehydes in the second. Radical decomposition takes also place producing carbonyl compounds.  

Keywords: Poly(alkylene 2,5-furan dicarboxylate); polyesters; thermal degradation kinetics; decomposition mechanism.

* Corresponding author. E-mail: dbic@chem.auth.gr
1. Introduction
The worldwide concern on the shortage of non-renewable petroleum resources over the last decades, has lead the interest of the academic and industrial community towards the development of novel chemicals and materials based on renewable resources [1-5]. Towards this scope, several biobased polymers and polymer nanocomposites have been prepared and are already well-established in commercial uses [6-8]. One of the major problems of such materials is that the prices of the monomers and oligomers which are used as building blocks for those bio-based materials is still high, however the continuously growing research efforts, are expected to contribute to the lowering of those costs.

Among these efforts, polyesters based on furan monomers, constitute a unique family of polymers prepared from vegetable renewable resources. 5-hydroxymethylfurfural (HMF) is already widely available and it is synthesized from sugars and polysaccharides. HMF can be used to synthesize with its turn, 2,5-furandicarboxylic acid (FDCA), which is a member of the furan family, is a biomass-derived product [9,10] and it is considered one of the most promising monomers for the synthesis of polyesters, polyamides and polyurethanes. The key structural feature associated with FDCA is the close resemblance to its aromatic counterparts, which enables it to synthesize polymers via step-growth mechanisms [11]. FDCA can be produced from cellulose or semicellulose through a multistep process [12], its structure is similar to that of terephthalic acid (TA) and in the near future, it is expected to replace the petrochemical-based terephthalic acid on several occasions. Besides their similar structure, some differences in their ring size and their polarity can attribute different characteristics to FDCA and TA-based polyesters. TA 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 TA results in an angle of 180° between carboxylic acid carbons, while the nonlinear structure of FDCA presents an angle of 129.4° [13].

The emerging developments on the synthesis of FDCA [13-15], have led to the preparation of several FDCA based polyesters, such as poly(ethylene 2,5-furan dicarboxylate), poly(butylene 2,5-furan dicarboxylate), poly(propylene 2,5-furan dicarboxylate) and others, along with some FDCA-based copolyesters. Most of the literature reports which present the synthesis procedure, also perform a comparison between the FDCA-based polyesters and the respective TA-based polyesters [12,16-19]. However, there is not a published work concerning the comparative study of the thermal degradation of these polyesters and the evaluation of their decomposition mechanism. As a matter of fact, the temperature window for processing as well as for applications of a polymer is strongly dependent on its thermal stability and for this reason
several reports look into the decomposition of the materials by using thermogravimetric analysis [1-5,13]. To avoid a gradual deterioration of the physical properties of a polymeric product, thermal degradation reactions must be inhibited or retarded. In turn, successful stabilization must be based on an understanding of the precise mechanism by which each type of degradation occurs.

In the current manuscript, a set of furan based polyesters [poly(ethylene 2,5-furan dicarboxylate) (PEF), poly(propylene 2,5-furan dicarboxylate) (PPF) and poly(butylene 2,5-furan dicarboxylate) (PBF)] has been synthesized by melt polycondensation under mild conditions using 2,5-furandicarboxylic acid and aliphatic diols with 2-4 methylene groups (ethylene glycol, 1,3-propanediol and 1,4-butandiol). The aim of the present work is to study the thermal degradation of these polyesters along with a decomposition kinetics study, which was implemented on the experimental data from thermogravimetric analysis (TGA), in order to reveal similarities and differences on their decomposition mechanism. Furthermore, pyrolysis-gas chromatography/mass spectroscopy (PY-GC/MS) was employed on the polyesters in order to identify the individual fragments from each sample and obtain structural information concerning the decomposition mechanism of these polyesters.

2. Experimental

2.1 Materials

2,5-furan dicarboxylic acid (purum 97 %), 1,2-ethylene glycol (EG, anhydrous 99.8%), 1,3-propanediol (PD, ≥99.6%), 1,4-butandiol (BD, 99%) 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 sulfuric acid was transferred into a random flask (500 mL) and the mixture was refluxed for 5 hours. 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 2,5-dimethylfuran-dicarboxylate (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 the melt polycondensation method as shown in Scheme I in a glass batch reactor [20, 21] using the proper amounts of DMFD/diols=1/2.2, which were charged into the reaction tube of the polyesterification apparatus. TBT (400 ppm) was added as catalyst.

2.4. Polyester characterization
2.4.1. Intrinsic viscosity measurement
Intrinsic viscosity \([\eta]\) measurements 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 from Teflon.

2.4.2. Nuclear Magnetic Resonance (NMR)
\(^1\text{H}-\text{NMR} \) spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. A mixture of deuterated trifluoroacetic acid (DTFA) and chloroform in a ratio 3/1 w/w (DTFA/CDC\(_3\)) 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.

2.4.3. Wide angle X-Ray diffraction patterns (WAXD)
X-ray diffraction measurements of the samples were performed using a MiniFlex II XRD system from Rigaku Co, with CuK\(_\alpha\) radiation (\(\lambda=0.154 \text{ nm}\)) in the angle 2\(\theta\) range from 5 to 60 degrees.

2.4.4. Thermogravimetric Analysis
Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 16/18 instrument. Samples (5.0 ± 0.3 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. The FDCA-based polyesters were heated from ambient temperature to 550 °C in a 50 mL/min flow of N\(_2\) at heating rates of 5, 10, 15 and 20 °C/min. Continuous recordings of sample temperature, sample weight and heat flow were taken.
2.4.5. 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” 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 sample was retained at 100 °C for 2 min and heated with a rate 200°C/min to its decomposition temperature. The pre-selected pyrolysis temperatures were 340, 390, 500°C and the GC oven temperature was programmed from 50 to 300°C at 20°C/min. The three temperatures were selected based on the TGA experiments and represent the sample prior, during and after thermal decomposition. The 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 53.6kPa and the remaining portion exited the system via the vent. The pyrolyzates are separated using temperature programmed capillary column of a Shimadzu QP-2010 Ultra Plus (Japan) gas chromatograph and analysed 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 10-1000 amu and scan speed 10.000. The chromatograph and spectra retrieved by each experiment are subject to further interpretation through Shimadzu and Frontier post-run software.

3. Results & Discussion

3.1. Synthesis and characterisation of polyesters

The studied furan dicarboxylate polyesters were synthesized by applying the melt polycondensation method, as was described in the experimental section and in Scheme 1. In the first stage esterification of 2,5-furandicarboxylic acid (FDCA) with methanol was necessary since due to its decomposition it is very difficult to prepare polyesters with high molecular weight by direct esterification of FDCA with diols. Using the dimethylester of FDCA and excess of diols, transesterfication took place and the corresponding bis(hydroxyalkyl 2,5-furan dicarboxylate)s were prepared as intermediate for the preparation of polyesters. After that
procedure, at the last stage (polycondensation) the temperature was increased gradually from 220 to 250°C in order to remove the excess of the used diols and let condensation take place by increasing the molecular weight of polyesters. The polyester yield is ranged between 83% for PBF and 87% for PEF, while for PPF is 86%.

**Scheme I.** Synthetic route for 2,5-furan dicarboxylate polyesters.
The intrinsic viscosities of the polyesters were 0.45 dL/g for PEF, 0.39 dL/g for PPF and 0.47 dL/g and for PBF, indicating that the used procedure was appropriate for the preparation of these polyesters. The number average molecular weight of these polyesters, as was measured by gel permeation chromatography using a Waters 150°C and hexafluoroisopropanol as solvent is 11200 g/mol (PDI:1.9) for PEF, 10700 g/mol for PPF (PDI:2.1) and 11500 g/mol for PBF (PDI:1.8). These polyesters have carboxyl end-group content, which was determined according to Pohl’s method, 52 eq/10^6 g for PEF, 61 eq/10^6 g for PPF and 57 eq/10^6 g for PBF, which are very typical values for aliphatic polyesters.

The 1H NMR spectra of the polyesters verified their structure (Figure 1). The protons of the furanoate aromatic ring are the most deprotected in the macromolecules due to the carbonyl groups and the π electron system of the bead and they appear at 7.3 ppm (the a, c and f protons of PEF, PPF and PBF respectively). As for the protons of the aliphatic chain, the most deprotected are those which are located next to the ester bond and appear at the area of 4.5-4.8 ppm (b protons for PEF, d and g protons for PPF and PBF respectively). The e and h protons are located in the middle of the carbon chain and recorded only in PPF and PBF polyesters, they are less deprotected and appear at 2.2 and 2.0 ppm respectively.

![Figure 1. 1H NMR spectra of PEF, PPF and PBF. The corresponding peaks can be found in Scheme I.](image-url)
The WAXD patterns of PEF, PPF and PBF are shown in Figure 2 and they confirmed that all polyesters are semicrystalline materials with characteristic peaks in the range of 15-28°. In more detail, the PEF spectrum presents sharp peaks at $\theta=15.1^\circ$, 16.9°, 19.7°, 22.4° and 25.5°, the PPF spectrum at 16.3, 18.5, 22.6, 24.5, 26.6 and 28.4°, while the PBF spectrum at 17.6, 23.8 and 24.1° which indicate quite high degree of crystallinity. Similar XRD patterns have been reported also in earlier works [22-24].

![WAXD pattern of PEF, PPF and PBF.](image)

**Figure 2.** WAXD pattern of PEF, PPF and PBF.

### 3.2. Thermogravimetric Analysis

The thermal stability of the synthesized polyesters was studied by means of thermogravimetric analysis. The samples were heated from ambient temperature up to 550°C and the thermogravimetric curves can be seen at Figure 3a. It is obvious that PBF presents the lowest thermal stability, while the other two polyesters present similar behaviour, with the PEF sample presenting its main degradation step at temperatures slightly higher than PPF (Figure 3b). The results are consistent with previous reports on polyesters by our group and others, according to which, the thermal stability decreases with increasing methylene units [13,25-29]. The beginning of thermal decomposition (mass loss>1%) follows the same trend as with the
maximum rate of decomposition, indicating the stable behaviour of the prepared polyesters (Table 1) during the heating procedure.

![Graphs](image)

**Figure 3.** a) Mass loss (TG %) curves and b) DTG curves for the studied polyesters PEF, PPF and PBF.

**Table 1.** Thermogravimetric analysis results for the synthesized polyesters

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{1%} ) (°C)</th>
<th>( T_{50%} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBF</td>
<td>299</td>
<td>362</td>
</tr>
<tr>
<td>PPF</td>
<td>333</td>
<td>395</td>
</tr>
<tr>
<td>PEF</td>
<td>337</td>
<td>415</td>
</tr>
</tbody>
</table>
3.3. Kinetic analysis based on thermogravimetric data – Isoconversional methods

Thermogravimetric analysis can provide information not only on the thermal stability but also on the reactions taking place during the decomposition process and the mechanisms which can describe it. The general directions for the performance of such analysis methods have been given by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [30,31] and they involve the implementation of experimental procedure under multiple heating rates. In the present work, the heating rates that were used were 5, 10, 15 and 20 °C/min (Figure 4).

![Figure 4. Application of multiple heating rates on the PBF sample](image)

The initial part of the kinetic analysis based on thermogravimetric data, involves the calculation of activation energy (E) as a function of the degree of conversion (α) with isoconversional methods. Those methods are generally considered accurate for the treatment of thermoanalytical data [32] and besides the E-α dependence, they can provide additional indications regarding the second step of the kinetic analysis, the model-fitting procedure and the reaction mechanism. The importance of isoconversional methods is reflected on the basis of the absence of any assumptions regarding the reaction mechanisms that take place during the decomposition of the samples. In the current work, the differential method of Friedman [33]
and the integral method of Kissinger-Akahira-Sunose (KAS) \[34,35\] were applied on the experimental set of data.

Friedman’s method was developed by taking the logarithm of the general form of the basic rate equation:

\[
\frac{da}{dt} = k(T) f(a)
\]  

(1.1)

where \(t\) is the time, \(T\) is the temperature, \(k(T)\) is the rate coefficient which is generally given by the Arrhenius law \[36\] \(k(T) = Ae^{-E/RT}\), \(\alpha\) is the extent of conversion and \(f(\alpha)\) is the mathematical function which represents the reaction mechanism. Thus Friedman’s equation takes the form:

\[
\ln \left( \beta_i \frac{da}{dT} \right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha,i}] - \frac{E_{\alpha,i}}{RT_{\alpha,i}}
\]  

(1.2)

where \(A\) is the pre-exponential factor and \(\beta\) is the heating rate. The index \(i\) denotes the different heating rates that were applied on the experimental data. From the above equation it can be realized that if the conversion function is constant, then the activation energy values can be calculated from the slope of the straight lines of the plot \(\ln[\beta_i (da/dT)_{\alpha,i}] vs 1/T_{\alpha,i}\). Differential methods are considered versatile due to the fact that they make no approximations, in contrast to integral methods. However, they can present numerical instabilities regarding to integral ones \[37\], while their accuracy can be limited due to errors in baseline and calibration of the thermal analysis equipment \[38\].

The integral method of Kissinger-Akahira-Sunose was also applied on the current set of data and it is based on the following equation:

\[
\ln\left( \frac{\beta}{T_{\alpha,i}^2} \right) = \text{const.} - \frac{E_{\alpha,i}}{RT_{\alpha,i}}
\]  

(1.3)

The activation energy values versus the degree of conversion in this method can be obtained by plotting \(\beta/T_{\alpha,i}^2\) vs \(1/T_{\alpha,i}\) and taking the slope of those straight lines for each temperature program. The results from the application of the two isoconversional methods can be seen in Figure 5.
Figure 5. Dependence of the activation energy (E) on the degree of conversion (α), as calculated with Friedman and Kissinger–Akahira–Sunose (KAS) methods for the synthesized polyesters.

From Figure 5, it can be seen that the PBF sample presents significantly lower activation energy values than the other two samples (PPF and PEF) and this can be attributed to its lower thermal stability, as it was shown earlier. The other two polyesters, PEF and PPF do not present significant differences on their activation energy values, while it can be also observed that E increases with increasing degree of conversion, showing a different dependency than the PBF sample which remains almost constant. The differences between the activation energy values calculated with different methods, originates from the variations between E and α, which is also the main source of errors of integral methods [39].

3.4. Kinetic analysis based on thermogravimetric data – Model-Fitting methods

The second part of the kinetic analysis based on the thermogravimetric data involves the model-fitting procedure of the experimental curves with mathematical models, which can describe the decomposition process. For the determination of the reaction model, several theoretical models
and their combinations were tested and the respective kinetic triplets (activation energy $E$, pre-exponential factor $\alpha$ and $f(\alpha)$) were calculated. Generally, the complementary use of model-fitting methods and model-free (isoconversional) methods has been a standard procedure for the accurate evaluation of the kinetic parameters of a decomposition process [40-42].

The initial step of the model-fitting procedure includes the assumption that the decomposition of the sample(s) can be described by a single step mechanism, that corresponds to the main mass loss. Therefore, the multivariate non-linear regression was applied on the current set of data from the synthesized polyesters and the theoretical model, which fitted more accurately (according to the values of the regression factor) the decomposition process was the $n$-th order model with autocatalysis $Cn$: $f(a) = (1-a)^{n(1+K_{cat})}X$ where $K_{cat}$ is a constant and $X$ are the reactants. The results were satisfying only for the PBF sample, which exhibited quite constant activation energy values during the calculations with isoconversional methods. However, the other two polyesters which exhibited a different $E-\alpha$ dependency, did not present satisfying results, after fitting with a single-step model. The results are presented in Figure 6 and for brevity reasons, only the PBF and PEF samples will be shown.
Figure 6. Mass loss curves and the corresponding fitting curves after fitting with a single-step mechanism and $C_n$ model. (1): $\beta=5^\circ$C/min, (2): $\beta=10^\circ$C/min, (3): $\beta=15^\circ$C/min, (4): $\beta=20^\circ$C/min

It is well known that the decomposition of polymeric materials is a complex procedure including several (overlapping or not) steps, thus the application of two or more consecutive or parallel models should be considered for its description. The initial assumption is based on the fact that the two mechanisms (models) are consecutive and the combination which gave the most accurate fitting results was the $C_n-F_n$ consecutive mechanism, where $F_n$ is an n-th order model $f(a) = (1-a)^n$. The results are presented in Figure 7 and Table 2.
Figure 7. Mass loss experimental data and fitting curves from different heating rates: (1): $\beta=5^\circ$C/min, (2): $\beta=10^\circ$C/min, (3): $\beta=15^\circ$C/min, (4): $\beta=20^\circ$C/min. The fitting model that was used in both cases was the consecutive nth-order model with autocatalysis ($C_n$) and n-order model ($F_n$) ($C_n \rightarrow F_n$).
Table 2. Calculated values of activation energy (E), pre-exponential factor (logA), reaction order (n), branching rate constant (K\text{cat}), and correlation coefficient (R^2) for the synthesized polyesters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (kJ/mol)</th>
<th>logA</th>
<th>n</th>
<th>logK\text{cat}</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBF</td>
<td>121</td>
<td>7.5</td>
<td>1.1</td>
<td>1.7</td>
<td>0.9998</td>
</tr>
<tr>
<td>PPF</td>
<td>159</td>
<td>6.4</td>
<td>0.7</td>
<td>2</td>
<td>0.9999</td>
</tr>
<tr>
<td>PEF</td>
<td>162</td>
<td>9.5</td>
<td>0.9</td>
<td>2.1</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (kJ/mol)</th>
<th>logA</th>
<th>n</th>
<th>logK\text{cat}</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPF</td>
<td>184</td>
<td>5.2</td>
<td>0.9</td>
<td>-</td>
<td>0.9999</td>
</tr>
<tr>
<td>PEF</td>
<td>186</td>
<td>6</td>
<td>0.8</td>
<td>-</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

From the results presented in Figure 7 and Table 2, it can be seen that the correlation quality between PPF and PEF is very high for the \( Cn \rightarrow Fn \) combination, while there is an increase of the activation energy values, as it was expected from the results exported from isoconversional methods. Additionally, the activation energy values from the model-fitting procedure are between the E values calculated with Friedman’s method, indicating the accuracy of the results.

3.5. Evaluation of decomposition mechanism using Py-GC/MS

A general conclusion for the decomposition mechanism of the studied polyesters has been exported from TGA. However, in order to evaluate the way that the decomposition mechanism of 2,5-furan dicarboxylate polyesters proceeds, Py-GC/MS technique was utilized. The results from EGA experiments during pyrolysis of polyesters are shown at Figure 8. As it can be seen, in all polyesters the decomposition starts after 300-330°C which is in good agreement with the TGA data (Table 1). From these curves it can be seen that PBF decomposes first while PPF and PEF exhibit a similar decomposition profile, even though in PPF the decomposition starts at slightly lower temperature, which is also in agreement with the mass loss curves. Another clear difference is that PBF has a broader decomposition temperature range than the other two
polyesters, while the end of decomposition for all the polyesters is almost identical and at the same temperature.

![Graph](image)

**Figure 8.** EGA comparisons for 2,5-furan dicarboxylate polyesters.

In order to analyse the decomposition mechanism of each polyester, EGA analysis was employed and pyrolysis of all polyesters has been performed at 3 different temperatures, which are characteristic for the different steps that decomposition of polyesters takes place. Initially 340°C was used since it is the temperature where the decomposition of polyesters starts. Also the procedure was performed at 390°C which corresponds to the maximum rate of decomposition and at 500°C, corresponding to the end of decomposition. At each temperature the chromatograms of the produced gas compounds were recorded and for PEF they are presented in Figure 9. As it can be seen, at low decomposition temperatures (340 and 390°C) the chromatograms exhibit fewer peaks, which is an indication that the decomposition mechanism is very simple and thus only limited decomposition compounds are produced. From MS analysis it was found that at low retention times (1-3 min) methanol, CO₂, CO, acetaldehyde and H₂O are the main decomposition products. However, the most characteristic peak in both chromatograms is that recorded at retention time 27 min with m/z=156 and corresponds to the 2,5-furan dicarboxylic acid. The chromatogram recorded at 500°C is
completely different and consisted from a variety of peaks. Therefore, it is clear that decomposition and the produced volatile byproducts are temperature-dependent which is very common in polyesters [43-46]. Using MS data it is possible to identify each one of these decomposition products and for each retention time these are presented in Figure 10.

![Gas chromatographs comparison for PEF at different decomposition temperatures.](image)

**Figure 9.** Gas chromatographs comparison for PEF at different decomposition temperatures.

At low retention times methanol, CO, CO$_2$, H$_2$O, acetaldehyde, dioxane and furan aromatic ring were detected. Similar volatile compounds were reported in decomposition of poly(ethylene terephthalate) from McNeill et al. [47], except from the furan ring. At higher retention times methyl (7.2 min), ethyl (7.7 min), vinyl (11.5 min) and hydroxyethyl (22.34 min) esters of 2-furancarboxylic acid (furoic acid) have been recorded. The main decomposition compound with the higher intensity is 2-furancarboxylic acid, which has been recorded at retention time 18.8 min. Furthermore, compounds with higher ion mass like bis(hydroxyethyl-2,5-furan dicarboxylate) (27.7 min) as well as its mono-vinyl (26.12 min) or its divinyl-derivatives (22.7 min) have been also recorded. These vinyl compounds are produced via $\beta$-hydrogen bond scission of ester groups and this decomposition mechanism is very common in alipharomatic or aliphatic polyesters [7,43,47]. Another compound which was
identified at retention time 27.1 min is 2,5-furan dicarboxylic acid, which is the monomer used for polyester synthesis. Acetaldehyde, which is produced from the unstable vinyl-alcohol and furfural (furan-2-carboxaldehyde) (9.2 min) was also formed but in a lower extent compared to the other compounds. Aldehydes are usually produced via α-hydrogen bond scission of ester bonds instead of β-hydrogen bond scission, but this is not a favorable mechanism. For this reason, the identified byproducts are in low amount. Some carbonyl furan derivatives are also detected at retention times 13.1 and 21.5 min, which cannot be attributed to α- or β-hydrogen bond scission but to radical scission of 2-furancarboxylic acid or furfural, leading to the formation of 2-furancarbonyl and OH or H radicals. A similar decomposition mechanism via radical scission was also reported by Atkinson et al. in poly(lactide-co-glycolide) copolymers [48]. Taking into account all the above facts, some of the identified compounds and the decomposition mechanism of PEF with β-hydrogen, α-hydrogen bond scission and radical chain scission are illustrated in Scheme 2.

![Retention Time vs. % Intensity Chart](image)

**Figure 10.** Chromatograph of PEF at 500°C decomposition temperature with the characteristic decomposition products at different retention times.
Scheme 2. Proposed decomposition mechanism of PEF, as evaluated from the identified compounds using Py-GC-MS technique.

In the case of PPF, the chromatographs present some differences compared to the ones of PEF. As it can be seen in Figure 11, there are much more peaks recorded at 340°C, which is an indication that more compounds are produced during the decomposition of PPF at this temperature. This is because, as it was verified from TGA and EGA, PPF has slightly lower thermal stability than PEF. Thus, its decomposition starts earlier. The main detected compound at 340°C is recorded at retention time 27.2 min and corresponds to 2,5-furan dicarboxylic acid ($m/z=156$), which was also found among the decomposition products of PEF. Volatile compounds like methanol, CO, CO$_2$, H$_2$O are also detected at low retention times but not acetaldehyde and dioxane, which were detected in the decomposition of PEF and are due to the decomposition of ethylene glycol. However, 2-furancarboxylic acid (18.7 min) and carbonyl furan derivatives (13.1 min) were also detected as in the case of PEF indicating that both
polyesters decompose in a similar manner. Other decomposition products are the hydroxyl-propylene ester of 2-furancarboxylic acid (19.9 min) and its vinyl-derivative (19.6 min) but in lower intensity. Bis-hydroxypropylene ester of 2,5-furan dicarboxylic acid was not detected at 340°C but its divinyl derivative at the retention time of 24.8 min. At higher decomposition temperatures (390 and 500°C) the intensity of decomposition products was increased, as was expected, since according to the TGA the mass loss is much higher than 340°C, while at 500°C the polyester has been completely decomposed. Some new products like furfural was detected at 9.2 min, an anhydride compound produced from the condensation of two 2-furancarboxylic acid with m/z=206 (19.3 min) and the bis-hydroxypropylene ester of 2,5-furanoic acid with m/z=270 and retention time 29.3 min.

Figure 11. Gas chromatographs comparison for PPF at different decomposition temperatures.

According to the identified products the decomposition mechanism of PPF is this of β-hydrogen bond chain scission that was also mentioned in the case of PEF and in a lower extent the α-hydrogen bond chain and radical chain scission take place. Similar mechanisms were also
reported in literature for the poly(propylene terephthalate) [43,49] which has a lot of similarities with PPF since it is also prepared from 1,3-propylene glycol.

In the case of PBF it can be seen that the chromatographs present a lot of similarities in all studied temperatures (Figure 12). This is because PBF has the lowest thermal stability among the studied polyesters and its decomposition is more pronounced even at 340°C. Methanol, CO₂, CO and water are also detected at low retention times. Tetrahydrofuran is also recorded in all temperatures at 1.6 min and butadiene at 2.56 min at 390°C and mainly at 500°C. Both byproducts are produced from the decomposition of 1,4-butanediol and thus they are not detected in the other polyesters. 1,4-Butanediol is also detected at 10.5 min in all decomposition temperatures as well as 2-furancarboxylic acid (18.7 min) and with lower intensity its vinyl-derivative (butylene 2-furancarboxylate, 21.0 min). At higher retention times, products with higher molecular weight are recorded such as 2,5-furan dicarboxylic acid (26.9 min) which is also found in case of the other two polyesters. Bis-hydroxybutylene ester of 2,5-furanoic acid was detected in all decomposition temperatures at 28.6 min, its monovinyl derivative with retention time 24.9 min and its divinyl derivative at 26.4 min. Carbonyl furan derivatives have also been recorded with retention times 13.2 min and 19.9 min, which were also observed in the products of the other two polyesters.

![Figure 12. Gas chromatographs comparison for PBF at different decomposition temperatures.](image-url)
According to the detected compounds, it can be said that the decomposition mechanism of PBF has a lot of similarities with those for PEF and PPF, while the additional detected compounds like tetrahydrofuran and butadiene are due to the different diol moieties. This decomposition mechanism is almost identical to that reported in literature for poly(butylene terephthalate) (PBT), which differs from PBF only in the aromatic ring [50-52].

4. Conclusions
The decomposition of three new aliphatic polyessters, namely PEF, PPF and PBF, has been studied for the first time using TGA and Py-GC/MS, comparatively. It is obvious that the diol used for the synthesis of polyester plays an important role on their thermal stability. From TGA it was found that PBF has the lowest decomposition temperature followed from PPF while PEF has the highest thermal stability. This was proved from the mass loss curves and the calculation of activation energies. Based on these data and the results from decomposition kinetics it was found that the decomposition of PBF takes place in one step which can be described using the n-th order model with autocatalysis \( (Cn) \). PEF and PPF decompose in two steps and their decomposition can be described with an autocatalysis model for the first step and with an n-th order model \( (Fn) \) for the second step \((Cn\rightarrow Fn)\). Py-GC/MS study showed that all the three polyesters decompose mainly via β-hydrogen bond scission producing vinyl compounds and carboxyl derivatives like 2-furoic acid and 2,5-furandicarboxylic acid. Other mechanisms that take place in lower extent are α-hydrogen bond scission producing aldehydes like furfural and radical chain scission producing carbonyl compounds of furoic acid.

References


