Improving the Thermal Properties of Poly(2,5-furandicarboxylate)s Using Cyclohexylene Moieties: A Comparative Study

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The search for new polymers from renewable origin is a sparkling field in polymer chemistry, especially those having promising properties, for example, in terms of their thermal performance. In this vein, in this study, an original renewable 2,5-furandicarboxylic acid-based cycloaliphatic homopolyester, poly(1,4-cyclohexylene 2,5-furandicarboxylate) (PCdF), is synthesized from dimethyl-2,5-furandicarboxylate and 1,4-cyclohexanediol. Poly(1,4-cyclohexanediylene 2,5-furandicarboxylate) is also prepared for comparison purposes, since it is the direct renewable substitute of poly(1,4-cyclohexanediethylene terephthalate) and they are structurally related. The resulting homopolymers are characterized in detail by using attenuated total reflectance Fourier transform infrared, $^1$H, $^{13}$C and 2D NMR, X-ray and elemental analysis, and thermal properties are assessed by thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical thermal analysis. PCdF shows to have a semicrystalline character, exhibiting an extremely high glass transition temperature around 175 °C. Moreover, this polyester also shows to be a high thermally stable material with a degradation temperature of 380.0 °C.

1. Introduction

Polyesters, well-known as highly versatile materials, have a high importance in a broad range of commodity applications spanning from packaging plastics, typically for soft drinks, water, and alcoholic beverages as well as textiles; to films; sheeting; and resins for molding up including sophisticated precision pieces for medical and electronic applications.[5]

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are the most applied thermoplastics with a wide range of applications, mostly due to their well-known good mechanical properties and excellent chemical resistance, as well as their electrical insulation properties.[2] Furthermore, the fact that these polymers show a combination of high glass transition ($T_g$) and high melting temperatures ($T_m$) (75 and 250 °C for PET, and 35 and 225 °C for PBT, respectively)[3,4] enables them to maintain their shape and mechanical properties at high temperatures, positioning them into a privileged position among all thermoplastic materials.[5] Another relevant example, which had some commercial relevance as fibers (Kodel fibres),[1] is also based on terephthalic acid (TPA) but incorporating the rigid cycloaliphatic monomer, 1,4-cyclohexanediimethylene (CHDM). The ensuing poly(1,4-cyclohexanediethylene terephthalate) (PCT) is a high performance polyester with a $T_m$ between 278 and 318 °C, much higher than that of PET or PBT.[6]

Many other polyesters based on TPA have a spotlighted importance in polymer scene, however in recent years, concerns regarding fossil feedstock availability, price instability, as well as environmental issues associated...
with their massive consumption, CO₂ emissions, and improper disposal, lead to an increasing research activity
find sustainable and environmentally friendly alternatives, mainly using plant biomass as the primary raw material.[7–10] In fact, within the biorefinery concept, biomass is expected to be efficiently converted (calling upon sustainable and environmentally friendly processes) into fuels, energy, chemicals, and materials.[11] In this context, 2,5-furandicarboxylic acid (FDCA), that can be easily obtained from hexoses, has been considered as one of the most important platform chemicals for a panoply of applications,[8] among which polyester synthesis is probably one of the most promising.[12] In fact, a significant number of FDCA-based materials have already been successfully synthesized, showing often similar properties to those of the TPA counterpart,[13] and in the case of poly(ethylene 2,5-furandicarboxylate) already produced at pilot scale.

However, oppositely to the increasing number of FDCA-based polyesters using linear short-chain aliphatic alcohols,[13–33] the studies involving cycloaliphatic monomers are scarce. In fact, only a few studies were dedicated to this specific domain, apart from the pioneering work of Moore and Kelly, in the late 1970s[34,35] where the direct polycondensation of 2,5-furandicarbonyl dichloride with 2,5-bis(hydroxymethyl) tetrahydrofuran was reported. It was only several decades later that the synthesis of FDCA-based homopolymers with other cyclic diols, mainly 1,4:3,6-dianhydrohexitols[36–40] several other results have also been patented, focusing the synthesis or specific applications of FDCA-based polyesters, using dianhydrohexitols[39,40] and other cyclic monomers, such as, dichloro-2,3-ο-isopropylidene L-tartrate,[41] 1,4-cyclohexanediolmethanol,[42–44] or 2,2,4,4-tetramethylcyclobutane-1,3-diol,[45] as well as combinations of both,[46] with ethylene glycol[47] or 1,4-butanediol.[43]

Recently, Sousa et al.[48] reported the synthesis of FDCA-based copolymers incorporating isosorbide and different number-average molecular weight poly(ethylene glycol) (PEG200, PEG400 or PEG2000). The resulting materials have shown better or comparable Tₘ to their petro-based counterparts.

In this vein, the incorporation of more rigid cycloaliphatic monomers into the polyesters backbone could be a very interesting approach to obtain materials with enhanced thermal and mechanical properties. To achieve this goal it is expected that the incorporation of 1,4-cyclohexanediol (CHD) in FDCA-based polyesters could lead to materials with enhanced thermal properties and at same time with good processability. Thus, in this study poly(1,4-cyclohexylene 2,5-furandicarboxylate) (PCfD) was synthesized using two approaches, namely, the two-step polytransesterification procedure (transesterification followed by a polytransesterification), and the direct polycondensation reaction. Moreover, the synthesis of poly(1,4-cyclohexanediethylene 2,5-furandicarboxylate) (PCF) was also performed for comparison, since this polyester is the direct furanic-renewable substitute of PCT and they are structurally related.

Finally, the ensuing polyesters were fully characterized by size-exclusion chromatography (SEC), attenuated total reflectance Fourier transform infrared (ATR FTIR), 1H, 13C and HSQC NMR, elemental analysis, as well as by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and X-ray diffraction (XRD) techniques.

2. Experimental Section

2.1. Materials

CHD (99.99%, cis/trans 43/57), CHDM (99.99%, cis/trans 46/54), 1,1,2,2-tetrachloroethane (TCE, 98.0%), anhydrous pyridine (99.8%), thionyl chloride (97.0%), dimethylformamide (DMF, 99.8%), trifluoroacetic acid (TFA, 99%), deuterated trifluoroacetic acid (TFA-d5, 99 atom % D), titanium (IV) butoxide (TBT, 97%), and zinc acetate (ZnAc, > 99.99%) were purchased from Sigma-Aldrich Chemicals Co. FDCA (98%) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, >99%) were purchased from TCI Europe N.V. Concentrated hydrochloric acid (37%) was purchased from Panreac, and methanol, chloroform, dichloromethane, among other solvents (pro-analysis and HPLC grade) were purchased from Fisher Scientific. Polystyrene standards with molecular weights between 4290 and 66 350 Da were supplied by Polymer Laboratories. All chemicals were used as received, without further purification.

2.2. Synthesis of Furanic Monomers

2.2.1. Synthesis of Dimethyldifuranic Monomer (DMFDC)

The synthesis of DMFDC followed a previously reported procedure.[14] Typically, DMFDC was prepared by reacting FDCA with an excess of methanol, under acidic conditions (HCl). The final product was isolated in 71% yield as a white powder. FTIR (v/cm⁻¹): 3168 (═C−H); 2965 (C−H); 1706 (C=O); 1578, 1522 (C=C); 1288 (C−O); 1024 (furan ring breathing); 969, 825, 757 (2,5-disubstituted furan ring). 1H NMR (300 MHz, CDCl₃, δ/ppm): 7.2 (s, H₃/H₄ furan ring); 3.9 (s, 2,5-COOCH₃). 13C NMR (75 MHz, CDCl₃, δ/ppm): 158 (2,5-COOCH₃). 1H NMR (75 MHz, CDCl₃, δ/ppm): 158 (2,5-C=O); 147 (C2/C5 furan ring); 118 (C3/C4 furan ring); 52 (2,5-COOCH₃).

2.2.2. Synthesis of 2,5-Furandicarboxyl Dichloride (FDCDCl)

The synthesis of FDCDCl followed a previously reported procedure.[17] Typically, FDCDCl was prepared in solution using FDCA (~2 g) dissolved in DMF (~50 µL) and an excess of SOCl₂ (~5 mL). The mixture was refluxed at 80 °C for 6 h, with constant stirring. Subsequently, the excess of SOCl₂ and DMF was removed under vacuum at room temperature and finally the pure dichloride monomer was isolated by vacuum sublimation, at ~60 °C.
The final product was isolated in 60% yield as a white powder. FTIR (v/cm⁻¹): 3141, 3109 (=C–H); 1731 (C=O); 1046 (furan ring breathing); 977, 829, 767 (2,5-disubstituted furan ring). ¹H NMR (300 MHz, CDCl₃, δ/ppm): 7.5 (s, H3/H4). ¹³C NMR (75 MHz, CDCl₃, δ/ppm): 156 (2,5-C=O); 149 (C2/C5); 123 (C3/C4).

2.3. Melt Polytransesterification Reactions
Reactions were carried out in bulk using DMFDC (5.45 × 10⁻³ mol) and an excess of either CHD or CHDM (1:1 diol to CHDCl) dissolved in TCE (1.0 mL), were allowed to cool down to about 0 °C using an ice bath, and an equimolar amount of FDCDCl (≈1.81 mmol), dissolved in TCE (1.5 mL), was added dropwise, under nitrogen flux, and with vigorous stirring. The reaction mixtures were dissolved in TFA (≈20 mL), and then the polymers precipitated, by pouring into an excess of methanol (≈1 L) to remove the catalyst, unreacted monomers and the soluble oligomers; the resulting PCdF or PCF were filtered, dried at 40 °C, and weighted.

2.4. Solution Polycondensation Reactions
Reactions were carried out in solution following a previously reported procedure.⁹⁷ Typically, the dried diol monomer, either CHD or CHDM (1.5:1 diol to FDCDCl) dissolved in TCE (1.0 mL), were mixed with anhydrous pyridine (1.7 mL). Then, this mixture was allowed to cool down to about 0 °C using an ice bath, and an equimolar amount of FDCDCl (≈1.81 mmol), dissolved in TCE (1.5 mL), was added dropwise, under nitrogen flux, and with vigorous stirring. The reaction was allowed to proceed at room temperature, while its viscosity increased progressively, during 7 h. The ensuing PCD and PCF polymers were precipitated in an excess of cold methanol, filtrated, dried at 40 °C, and finally weighted.

2.5. Characterization Methods
SEC analyses of homopolysters were performed on a homemade chromatograph equipped with a PL-EMD 960 light scattering detector, using a set of two PL HFIP columns (300 mm × 7.5 mm) and one PL HFIP guard column (50 mm × 7.5 mm), kept at 40 °C, and previously calibrated with poly-styrene standards in the range of 4290 to 66 350 Da. A mixture of CH₂Cl₂/CHCl₃/HFP (70/20/10 v/v/v%) was used as the mobile phase with a flow rate of 0.7 mL min⁻¹. All polymers were dissolved using the mobile phase (≈3 mg mL⁻¹), and filtered through a 0.2 µm PTFE membranes before injection.

Elemental analyses (C and H) were conducted in triplicate using a LECO TruSpec analyzer.

ATR FTIR spectra were obtained using a PARAGON 1000 Perkin-Elmer FTIR spectrometer equipped with a single-horizontal Golden Gate ATR cell. The spectra were recorded after 128 scans, at a resolution of 4 cm⁻¹, within the range of 500–4000 cm⁻¹. ¹H, ¹³C and HSQC (2D) NMR spectra were recorded in TFA-d using a Bruker AMX 300 spectrometer, operating at 300 or 75 MHz, respectively. All chemical shifts (δ) are expressed as parts per million (ppm), downfield from tetramethylsilane (used as the internal standard).

TGA analyses were carried out with a Setaram SETSYS analyzer equipped with an alumina plate. Thermogravimetric analyses were recorded under a nitrogen flow of 20 mL min⁻¹ and heated at a constant rate of 10 °C min⁻¹ from room temperature up to 800 °C. Thermal decomposition temperatures were taken at the extrapolated onset temperature of weight loss step and at maximum decomposition temperatures from the heated samples (Td,on and Td,respectively).

DSC thermograms were obtained with a DSC Q100 V9.9 Build 303 (Universal V4.5A) calorimeter from Texas Instruments, using aluminum DSC pans. Scans were carried out under nitrogen with a heating rate of 10 °C min⁻¹ in the temperature range from 0 to 300 °C. Two heating/cooling cycles were performed. Glass transitions (Tg) were determined using the midpoint approach (second heating trace), crystallization (Tc), and melting temperatures (Tm) were determined as the maximum of the exothermic crystallization peak and the minimum of the melting endothermic peak during the second heating cycle, respectively.

DMTA analyses were performed in a material pocket accessory with a Tritic 2000 DMA Triton, operating in the single cantilever

![Scheme 1](image-url) Synthesis of PCdF and PCF via two conventional polymerization approaches: a) bulk polytransesterification reaction, and b) solution polycondensation reaction.
mode. Tests were performed at 1 and 10 Hz and the temperature was varied from −90 to 250 °C, at 2 °C min⁻¹. Tg were determined as the maximum peak of tan δ.

XRD measurements were performed using a Philips X’pert MPD diffractometer operating with CuKα radiation (λ = 1.5405980 Å) at 40 kV and 50 mA. Samples were scanned in the 2θ range of 5° to 50°, with a step size of 0.04°, and time per step of 50 s.

3. Results and Discussion

3.1. From PCdF Synthesis to Its Structural Characterization

The new PCdF homopolyester was prepared by two distinct approaches, namely, melt polyesterification approach (Scheme 1a), or direct polycondensation system (Scheme 1b) (Table 1). In the former case the renewable-based DMFDC and the cycloaliphatic CHD (Scheme 1a) reacted by applying the conventional two-step melt polyesterification approach, in the presence of TBT or ZnAc catalysts. These reactions were circumspectly conducted at relatively moderate temperatures, not exceeding 220 °C, to avoid undesirable side reactions involving the furan moiety (e.g., decarboxylation reactions leading to color problem issues), or the secondary diol CHD decomposition (e.g., through elimination reactions). Reaction time did not exceed 7 h for the same reasons. Direct solution polycondensation of FDCDCl and CHD (Scheme 1b) was also performed at mild reaction conditions to assess their influence on the ensuing reaction products. Additionally, PCF, prepared in this case using CHDM, was also synthesized using similar approaches with the specific aim of providing a comparison point (Table 1). A priori the use of other synthetic approaches could be adopted, including an interesting one recently proposed, however the relatively mild reaction conditions would still have to be applied to avoid side-reaction (vide infra).

The ensuing white PCdF and PCF homopolymers were isolated, after a purification step to remove the catalyst, unreacted monomers, and low molecular weight soluble oligomers, in isolation yields ranging from 33 to 67% (Table 1), being the highest values obtained for the melt polytransesterification approach using TBT as catalyst (50 and 67% for PCdF and PCF, respectively). However, both polyesters obtained with TBT as catalyst had weight-average molecular weight values consistently higher than with the other synthetic conditions (e.g., around 9800 and 4300 for PCdF1 and PCdF2-3, respectively), and the Đ values varied between 1.5–1.7. Therefore, the following characterization results refer to the resulting products polycondensation of FDCDCl and CHD (Scheme 1b) was also performed at mild reaction conditions to assess their influence on the ensuing reaction products. Additionally, PCF, prepared in this case using CHDM, was also synthesized using similar approaches with the specific aim of providing a comparison point (Table 1). A priori the use of other synthetic approaches could be adopted, including an interesting one recently proposed, however the relatively mild reaction conditions would still have to be applied to avoid side-reaction (vide infra).

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### Table 1. Experimental data for all the polymerization reactions carried out in this study.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Experimental conditions</th>
<th>Yield (a) [%]</th>
<th>Mw (b)</th>
<th>Đ (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCdF1</td>
<td>Melt polytransesterification; TBT</td>
<td>50</td>
<td>9800</td>
<td>1.5</td>
</tr>
<tr>
<td>PCdF2</td>
<td>Melt polytransesterification; ZnAc</td>
<td>33</td>
<td>4300</td>
<td>1.2</td>
</tr>
<tr>
<td>PCdF3</td>
<td>Solution polycondensation</td>
<td>43</td>
<td>4300</td>
<td>1.2</td>
</tr>
<tr>
<td>PCF1</td>
<td>Melt polytransesterification; TBT</td>
<td>67</td>
<td>14 100</td>
<td>1.7</td>
</tr>
<tr>
<td>PCF2</td>
<td>Melt polytransesterification; ZnAc</td>
<td>57</td>
<td>11 400</td>
<td>1.7</td>
</tr>
<tr>
<td>PCF3</td>
<td>Solution polycondensation</td>
<td>62</td>
<td>12 100</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(a) Related to the amount of polymer recovered after precipitation in methanol; (b) Weight-average molecular weight (Mw), determined by SEC in DCM/CHCl3/HFP; (c) Polydispersity index (Đ) determined by SEC in DCM/CHCl3/HFP.

### Table 2. Elemental analysis results (%) of PCdF1 and PCF1.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Element</th>
<th>Calculated [%]</th>
<th>Experimental [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCdF1</td>
<td>C</td>
<td>61.52</td>
<td>61.13</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>4.31</td>
<td>4.25</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>34.17</td>
<td>34.62</td>
</tr>
<tr>
<td>PCF1</td>
<td>C</td>
<td>60.31</td>
<td>61.33</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>5.08</td>
<td>5.30</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>34.61</td>
<td>33.37</td>
</tr>
</tbody>
</table>

Figure 1. ATR FTIR spectra of a) PCdF1 and b) PCF1 homopolymers.
obtained from melt polyesterification reactions using TBT as catalyst, namely PCdF1 and PCF1, since they had shown the highest isolation yields and accordingly also the highest molecular weight values.

Additionally, also in terms of weight-average molecular weights, PCF had always higher values than PCdF counterpart independent of the synthetic method adopted (e.g., 9800 and 14 100 for PCdF1 and PCF1, respectively). This trend was already previously observed in the synthesis of other CHD-, CHDM-based polycondensates, due most probably to a higher chain stiffness of the CHD-related polymers.[50]

The elemental composition of both homopolymers (Table 2) was verified by the elemental analysis of carbon (% C) and hydrogen (% H), while the oxygen content (% O) was assessed by difference to 100% of the former two. The experimental results obtained for both polyesters were found to be in agreement with the calculated elemental composition, excluding a possible presence of low molecular weight oligomers.

**Figure 2.** $^1$H NMR spectra of a) PCdF1 and b) PCF1 in TFA-d.
The ATR FTIR spectrum (Figure 1) of PCdF1 was found to be consistent with its expected macromolecular structure, exhibiting a very intense band near 1720 cm\(^{-1}\), arising from the C=O stretching vibration, typical of ester groups, and the C–O stretching vibration appeared around 1273 cm\(^{-1}\). No significant absorption in the OH stretching region was detected, suggesting that the polymer had reached a possibly reaction yield. Additionally, it was also observed two weak bands near 3150 and 3112 cm\(^{-1}\) arising from the stretching modes of the \(\equiv\)C–H bond of the furan heterocycle, as well as two weak bands near 2923 and 2854 cm\(^{-1}\) assigned to the stretching modes of the C–H bond of cycloaliphatic methylene groups. Moreover, the typical vibration modes of 2,5-disubstituted furans were also observed near 983, 843, and 768 cm\(^{-1}\). The ATR FTIR spectrum of PCF1 (Figure 1) was consistent with the characteristic features of PCdF1 counterpart and also with previously published data for PCF\[^{[43]}\].

The \(^1\)H and \(^{13}\)C NMR spectroscopic analyses have unambiguously confirmed the PCdF1 and PCF1 polyesters' structure (Figure 2a,b and Table 3). The \(^1\)H NMR spectrum of PCdF1 (Figure 2a) displayed in the region of \(\delta = 7.7–4.8\) ppm (dashed square limits of Figure 2a) the typical resonances of H-3 and H-4 of the furan moiety, in the vicinity of cis- and trans-isomers of the CHDM moiety, at around 7.6 and 7.5 ppm, respectively; and the resonances of 2,5-COOCH (H-1) protons attributed to both cis- and trans-isomers of CHD at 5.5 ppm. In the case of PCF1 polymer (Figure 2b) the resonances of CH protons (H-3 and H-4) from the furan ring were also observed at 7.2 ppm, but no distinguishable split related with cis- and trans- isomers of CHDM moiety was detected. Additionally, the spectrum of PCF1 displayed at 4.3 and 4.2 ppm the proton resonances of 2,5-COOCH\(_2\) (H-a) groups attributed to the trans- and cis-isomers, respectively.

The \(^{13}\)C NMR spectra of PCdF1 and PCF1 were in accordance with their \(^1\)H NMR results in the above mentioned region, displaying in both cases the resonances assigned to the furan carbons C-2,5 and C-3,4 at 146.4 and 119.4 ppm, respectively, and the carbonyl carbons at 160.5 ppm.

Moreover, the \(^1\)H NMR analysis of PCdF1 in the region comprising \(\delta = 2.5–1.5\) ppm (line square limits of Figure 2a) displayed the typical chemical shifts of methylene protons (H-2’ and H-3’) of the cyclohexylene moiety, being, however, impossible to distinguish between the different chemical environments attributed to each protons of cis- and trans-isomers, mostly due to the overlap of their resonances. In the case of PCF1 (Figure 2b), the resonance of ax H-1’and eq and ax H-2’ are displayed at around 1.1 and 1.7–2.1 ppm, respectively, for the trans-isomer. Finally, with the only exception of the resonances displayed at 1.5 and 1.6 ppm, the remaining ones represent the typical resonances of trans-isomer resulting polyester, so the formers are attributed to eq and ax H-1’ and H-2’ in the cis-isomer. These results were in agreement with previously reported results\[^{[43]}\].

In terms of \(^{13}\)C NMR analysis of the latter region, PCdF1 spectrum displayed several resonances at 74.5, 73.9, 26.5, 26.2, and 25.7 ppm attributed to the COOCH\(_2\) and methylenic carbons (C-1’, C-2’, and C-3’) of the cyclohexylene moiety in the cis- and trans-isomers (Table 3). For PCF1 polyester the resonances of COOCH\(_2\), methinic and also methylenic carbons (a, C-1’ and C-2’) of the cyclohexylene moiety were displayed at 71.5, 69.7, 36.4, 33.9, 27.7, and 24.1 in the trans- and cis-isomer, respectively (Table 3).

Furthermore, the NMR results of PCdF1 were also corroborated with the 2D HSQC NMR analysis (Figure 3), showing clearly the overlapping of the proton resonances in the region of 2.0–2.5 ppm.

### 3.1.1. Cis-/Trans-1,4-Cyclohexanediol Isomers Ratio Assessment

A deeper analysis of PCdF1 \(^1\)H NMR spectrum allowed assessing the ratio between the cis- and trans-isomers in the polyester backbone by using the furanic H-3 and

<table>
<thead>
<tr>
<th>Assignment</th>
<th>PCdF1 (\delta) [ppm]</th>
<th>PCF1 (\delta) [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3, 4</td>
<td>7.6, cis-7.5, trans-</td>
<td>119.4</td>
</tr>
<tr>
<td>2, 5</td>
<td>146.4</td>
<td></td>
</tr>
<tr>
<td>2,5-COO (COOCH(_2))</td>
<td>160.5</td>
<td></td>
</tr>
<tr>
<td>1’</td>
<td>5.5, cis- and trans</td>
<td>74.5, trans-73.9, cis-</td>
</tr>
<tr>
<td>2’</td>
<td>26.5, 26.2, 25.7, cis- and trans</td>
<td>1.1, ax, trans-1.6, cis-</td>
</tr>
<tr>
<td>3’</td>
<td>1.7-2.1, ax, eq, trans-1.5, cis-</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Assignment of the \(^1\)H and \(^{13}\)C NMR chemical shifts relative to PCdF1 and PCF1.
H-4 resonances. This ratio was estimated to be 25.8/79.3, instead of 43/57 as the starting feed ratio used, showing that the trans-isomer is clearly more reactive than the cis-counterpart in this polymerization reaction conditions. The modest isolation yields are most plausibly related with this fact. However, in the case of PCF1 polyester (not determined before)[43] the cis/trans ratio was equal to 39.7/60.3 which is relatively closer to the starting monomers feed ratio (46/54).

3.2. Thermal Behavior

The TGA thermograms of PCdF1 (Table 4 and Figure 4) showed that this polyester is thermally stable ($T_{d,\text{on}}$) up to 363.41 °C, a slightly higher value than that obtained for PCF1 (~354.97 °C). The PCdF1 thermogram exhibited a maximum decomposition temperature ($T_d$) at approximately 380.03 °C (~39% weight loss), usually assigned to the degradation of the ester linkages within the polymeric chain.[51] These results are also slightly higher than those obtained for PCF1, which displays a $T_d$ at approximately 377.46 °C (~38% weight loss) which is slightly above a reported value.[43] These results indicate that the incorporation of CHD (or even CHDM moiety) into the backbone of FDCA-based polyesters lead to materials with high thermal stability, presenting a very similar behavior compared to those polymers obtained from TPA, namely, PCdT and PCT, having $T_d$ around 290 and 424 °C, respectively.[5,52,53]

The DSC thermogram of PCdF1 (Table 4 and Figure 5) exhibited only a $T_g$ at an extremely high temperature, around 174.9 °C, corroborated by DMTA results displaying in this case a $T_g$ at ~159.0 °C. Despite some crystallinity of PCdF1 due to its regular structure, and confirmed by XRD studies (discussed below), no melting event was observed in its DSC tracing up to 300 °C, very near where its thermal decomposition begun (~363 °C). Hence, PCdF is expected to have a very high melting temperature which has some practical implications. The processability of PCdF, in similarity to the petro-based PCT must be carried out very carefully,[6,54] since there is a narrow processing window between $T_m$ and the initial degradation temperature. This issue could be attenuated by further increasing the molecular weight of this polymer by applying a third stage of solid state polymerization after conventional two-step polytransesterification. Instead, the narrow temperature range between $T_g$ and $T_m$ could also be, at least in part, circumvented by using lower-molecular weight polymers where, e.g., PCdF2 has a $T_m = 201.9$ °C and a $T_d = 295.4$ °C.

PCF1 DSC trace (Table 4 and Figure 5) also displayed a glass transition but at a lower temperature (104.6 °C), and crystallization and melting accents, viz. around 209.95 and 246.7 °C, respectively. These results are in accordance with the chemical structure of PCdF1 and PCF1, where the absence/presence of the two methylene groups is associated with distinct thermal transition values. For example, the absence of CH$_2$ moieties in PCdF1 results in a more rigid polymer chain backbone, and accordingly it has the highest $T_g$; oppositely, the presence of CH$_2$ groups in PCF provides flexibility to this polymer chains and consequently a lower $T_g$ was reported.

Table 4. Decomposition at onset of weight loss, maximum decomposition, glass transition, melting and crystallization temperatures of PCdF1 and PCF1 homopolymesters.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>$T_{d,\text{on}}$ [°C]</th>
<th>$T_d$ [°C]</th>
<th>$T_g$ [°C]</th>
<th>$T_g$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$T_c$ [°C]</th>
</tr>
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<tbody>
<tr>
<td>PCdF1</td>
<td>363.41</td>
<td>380.03</td>
<td>174.9</td>
<td>159.0</td>
<td>nd$^a$</td>
<td>–</td>
</tr>
<tr>
<td>PCF1</td>
<td>354.97</td>
<td>377.46</td>
<td>104.8</td>
<td>102.9</td>
<td>246.7</td>
<td>210.0</td>
</tr>
</tbody>
</table>

$^a$DSC measurements (nd = $T_m$ was not detected below 300 °C); $^{b}$ $T_g$ was measured by the DMTA tan δ trace.
**Figure 4.** TGA and derivative TGA thermograms of PCdF1 and PCF1.

**Figure 5.** DSC thermograms of a) PCdF1 and b) PCF1.
DSC analysis (Figure S1, Supporting Information) was used to determine the $T_g$ of the homopolymers, and they have corroborated the DSC results. The tan $\delta$ traces of PCdF and PCF homopolymers displayed $T_g$ features at around 159 and 103 °C (Table 4), respectively.

From the previous results for the furan-cycloaliphatic polyesters obtained in this study, we can observe that the thermal properties of these polyesters are typically influenced by the absence/presence of the methylene moieties. Indeed, the restriction in the cyclic ring associated with the absence of methylene moieties in PCdF has resulted in a higher polymer chain rigidity, and subsequently higher thermal behavior in terms of $T_{d,on}$, $T_d$, and $T_g$ as discussed previously.

### 3.3. X-Ray Diffraction Analysis

The XRD pattern (Figure 6) of PCdF1 homopolyester synthesized in this work is in agreement with the DSC results described above, exhibiting a semicrystalline character with peaks at $2\theta \approx 18^\circ$ and $21^\circ$. In general, PCdF1 pattern is very similar to that of the related PCF ($2\theta \approx 17$, 19, and 22°), although with peaks slightly shifted to lower angles indicating not so closer crystallographic packing.

### 4. Conclusions

In summary, the realm of FDCA-based polyesters has been expanded to a new polymer with enhanced thermal properties incorporating 1,4-cyclohexanediol. The ensuing poly(1,4-cyclohexylene 2,5-furandicarboxylate) polymer has shown semicrystalline nature with enhanced thermal stability ($T_g$ around 380.0 °C and $T_g \approx 174.9$ °C). A comparison with the related poly(1,4-cyclohexanediethyl 2,5-furandicarboxylate) showed that the $T_g$ increased with the stiffness of the linkage of furanic and the cyclohexylene ring. Moreover, these materials could find several interesting industrial applications, namely for optical films or for injection molding materials, similar to PCT polymers.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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