Unravelling the *para-* and *ortho-*benzene substituent effect on the glass transition of renewable wholly (hetero-)aromatic polyesters bearing 2,5-furandicarboxylic moieties

Sami Zaidi [a,b], Maria J. Soares [a], Abdelkader Bougarech [b], Shanmugam Thiyagarajan [c],
Nathanael Guigo [d], Souhir Abid [e,b], Majdi Abid [e,b], Armando J.D. Silvestre [a],
Andreia F. Sousa [a,f,*]

[a] *CICECO – Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Faculté des Sciences, Laboratoire de Chimie Appliquée HCGP, Université de Sfax, Sfax 3038, Tunisia*
[c] *Wageningen Food & Biobased Research, P.O. Box 17, 6700 AA Wageningen, the Netherlands*
[d] *Université Côte d'Azur, Institut de Chimie de Nice, UMR CNRS 7272, Nice Cedex 2, France*
[e] *Chemistry Department, College of Science and Arts, Jouf University, P.O. Box 756, Al-Gurayyat, Al Jouf, Saudi Arabia*
[f] *CEMMPRE, Department of Chemical Engineering, University of Coimbra, 3030-790 Coimbra, Portugal*

ARTICLE INFO

ABSTRACT

High-glass transition thermoplastic polymers have dawned much attention in recent years due to their typical stiffness, enhanced thermal properties, and more importantly the emerging need to replace commercial fossil-based products by more sustainable alternatives, derived from renewable resources. In this regard we engineer here for the first time the design of wholly (hetero-)aromatic polyesters based on a key-platform chemical-2,5-furandicarboxylic acid (FDCA) and commercially-available catechol, or hydroquinone, whose structures were characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). Both polymers had a high glass transition (T_g up to 167 °C) detected by differential scanning calorimetry (DSC) and has excellent thermal stability according to thermogravimetric analysis (TGA). The *para-* and *ortho-* substitution in hydroquinone and catechol, respectively, affected crystallinity, which was typically higher for poly (1,4-phenylene-2,5-furandicarboxylate) (PHQF) favouring a stiffer and close packing structure. Also, the thermal properties were higher for PHQF.

1. Introduction

In the last decades some of the most interesting developments on polymer science and technology were aimed at a transition from polymers derived from fossils into more sustainable alternatives from renewable resources, such as compounds derived from biomass [1–3]. The main drivers of such a transformation are essentially the announced depletion of fossil resources and the yearning for renewable and more sustainable functional materials [3,4]. In particular, as pointed out on a timely review paper of Miller's group [5], a quest for high-glass transition (T_g) thermoplastic polymers based on renewables is one of the main research topics being carried out by both academy and industry.

This quest for high – T_g thermoplastic polymers from renewables is fuelled by the important properties of the commercially available fossil-based counterparts, namely typical stiffness, thermal stability, thermal fire resistance, and related commercial relevance. One examples of such polymers is acrylonitrile butadiene styrene (ABS), with a T_g of approximately 105 °C, used in the production of uncountable stiff product parts, including the well-known LEGO bricks. However, their replacement by renewable alternatives is still hindered, since today the most important renewable-based commercial polymers are essentially poly (lactic acid) (PLA) and poly(butylene succinate) (PBS) but they are limited by their relatively modest T_g (54 °C and −30 [6], respectively).

One of the most effective ways to achieve high – T_g polymers is by introducing rigid components into polymers' backbone, namely (hetero-)aromatic moieties to enable reducing the chain mobility. In this regard, poly(dihydroferulic acid), derived from renewable vanillin, was introduced as a replacement for poly(ethylene terephthalate) (PET) with a T_g

---

at approximately 73 °C [7]. In the same vein, also hydroxyethylvanillic acid and hydroxyethylsyringic acid were used through their copolymerisation with lactide and caprolactone to enhance the glass transitions of poly(lactic acid) (PLA) or poly(caprolactone) (PCL) homopolyesters [8]. The ensuing copolymers had a T_g of *ca.* 70–79 and 33–77 °C, respectively, whereas the same parameter for neat PLA and PCL is much lower (55 and −60 °C, respectively).

Considerable progress has been achieved, yet, by other polyesters bearing in their backbone the hetero-aromatic sugar derivative 2,5-furandicarboxylic acid (FDCA). The furan homologue of PET, poly(ethylene 2,5-furandicarboxylate) (PEF) has a glass transition above 70 °C, besides having superior gas barrier properties [1,9,10]. Other semi-aromatic polyesters derived from FDCA, namely poly(butylene 2,5-furandicarboxylate) (PBF) also shows interesting properties (T_g *ca.* 46 °C) [11], whereas those based on FDCA and long-chain aliphatic diols (*e.g.* poly(dodecylene 2,5-furandicarboxylate) (PDoF) [12–16] typically have much lower transition temperatures mainly attributed to the high flexibility of the aliphatic moieties. Despite the progress achieved, a question arises: *how can we still increase the T_g of bio-based polyesters and, more generally, how can we tune the structure to increase their chain stiffness?*

Several studies further improved the polymers chain stiffness to expand the range of application fields, by developing entirely renewable polyesters bearing both FDCA and cyclic aliphatic compounds, namely 1,4:3,6-dianhydrohexitols isomers [17–25] or cyclohexylene moieties [26,27].

A few other studies addressed, instead, the possibility of using FDCA with other (hetero-)aromatic compounds. The pioneering work of Gandini *et al.* [18] reported the polycondensation of FDCA derivative with the following (hetero-)aromatic diols: 1,4-di-(hydroxymethyl)-benzene, bis(2,5-hydroxymethyl)furan and hydroquinone. The ensuing poly(1,4-phenylbismethylene-2,5-furandicarboxylate) displayed a T_g slightly above that of PEF (at 87 °C), whereas for poly(1,4-phenylene-2,5-furandicarboxylate) (PHQF) and poly(2,5-furandimethylene 2,5-furandicarboxylate) no thermal events were reported, remaining unknown until the present study. Among the few existing studies, two addressed the possibility of polymerising FDCA with aromatic moieties based on lignin derivatives. In 2015, Llevot *et al.* [28] studied the combination of FDCA with a vanillin derivative (methylated divanillyl diol) to originate a polyester with a T_g of 139 °C. Furthermore, aromatic thermotropic polyesters based on FDCA and vanillic acid exhibited interesting rigidity with a T_g of up to 109 °C [29].

The progress achieved highlights the ability of (hetero-)aromatic compounds to tailor thermal properties, but their availability is still limited. Therefore, in the present study, we started a quest for: *which promising aromatic monomer could offer i) rigidity to the ensuing polymer, being simultaneously ii) renewable-based and, above all, could provide the competitive advantage of being iii) commercialised in large-amounts?* This search underscored catechol, a reactive *ortho*-benzene diol, naturally occurring in some eucalyptus species, onion, as well as in tea [30,31], and industrially produced from phenol. Though phenol is today derived from fossil resources, the introduction of the biorefinery concept and the progress achieved, stresses the opportunity of preparing this compound, in high yields, from *e.g.* pyrolysis of ubiquitous cellulose biomass [32]. Nevertheless, to the best of our knowledge, catechol has never been used before on FDCA-polyesters synthesis.

On the basis of these evidence this study addresses the synthesis of wholly (hetero-)aromatic polyesters based on FDCA and catechol or using instead the *para*-isomer, hydroquinone, aiming at synthesising extremely high-glass transition polymers. Structure-properties relationships about the different effect of the *ortho*- and *para*- positions on thermal and crystallinity has been reported for the first time.

2. Experimental

2.1. Materials

2,5-Furandicarboxylic acid (FDCA, >98%) and catechol (Ct, >99%) were purchased from TCI Europe NV. Acetic anhydride (Ac$_2$O, 99,5%), benzyltriethylammonium chloride (TEBAC, 99%), thionyl chloride (SoCl$_2$, 97%), trifluoroacetic acid (TFA, 99%), dimethylformamide (DMF, 99.8%), deuterated dimethyl sulfoxide (DMSO-d_6, 99.5% D) and titanium(IV) *tert*-butoxide (TBT, 97%) were acquired from Sigma-Aldrich Chemicals Co. Hydroquinone (HQ, 99.9999%) was purchased from Riedel-de Haën and anhydrous sodium acetate (NaOAc) was purchased from Fluka. All solvents used were of analytical or higher grade. All chemicals were used as received, without further purification.

2.2. Poly(1,2-phenylene-2,5-furandicarboxylate) (PCtF) and poly(1,4-phenylene-2,5-furandicarboxylate) (PHQF)

2.2.1. Bulk polycondensation

The reactions were carried out using FDCA (1.0 g, 6.4 mmol, 1.0 eq.); Ct or HQ (0.7 g, 6.4 mmol, 1.0 eq.); Ac$_2$O (4.0 mL) and, NaOAc (6.5 × 10^{-2} g) as catalyst; and with/without TBT (400 ppm) as co-catalyst. The mixtures were progressively heated up to 200 °C and kept at that maximum temperature for 5 h. Acetic acid was continuously removed as by product. Then, vacuum was applied, and the temperature was further raised to 220 °C and kept at that maximum temperature for 3 h. Afterwards the reaction was stopped, and the ensuing reaction products were purified by pouring a chloroform/trifluoroacetic acid solution (12/1 V/V) of this product into an excess of cold methanol. Subsequently, the polymer was filtered, washed with methanol, Soxhlet extracted also with methanol for 12 h, and vacuum dried at 45 °C, for 3 days.

2.2.2. Interfacial polycondensation

First, 2,5-furandicarbonyl dichloride (FDCDCl) was synthesised in solution following a procedure reported elsewhere [19], by refluxing FDCA (6.0 g) with an excess of SOCl$_2$ (12.0 mL) in the presence of DMF (0.12 mL), at 80 °C for 4 h. The ensuing monomer was isolated and purified as small white crystals (yield ~ 71%), by double distillation under vacuum. FTIR (λ / cm^{-1}): 3145 (=C—H); 1677 (C=O); 1567 (C=C); 958, 810, 759 (C—H). ^{1}H NMR (Fig. S1 of Supplementary material) (300 MHz, DMSO-d_6, δ/ppm): 7.29 (s; H3, H4; furan ring).

Subsequently, interfacial polycondensation reactions were carried out at room temperature, with mechanical stirring (700 rpm) for 3 h, using a biphasic system [18]: NaOH aqueous solution of HQ or Ct (0.6 g, 5.2 mmol, 1.0 eq.) and TEBAC (72.4 mg), as phase transfer catalyst; and a dichloromethane solution of FDCDCl (1.0 g, 5.2 mmol, 1.0 eq). Afterwards, the medium was acidified to pH 2 and the polyesters were isolated by filtration, rinsed thoroughly with water and/or ethanol and vacuum dried at 45 °C.

2.3. Characterisation

Attenuated total reflection Fourier transform infrared (ATR FTIR) spectra were taken with a PARAGON 1000 PerkinElmer FTIR spectrophotometer equipped with a single horizontal Golden Gate ATR cell. The spectra were recorded after 128 scans, at a resolution of 8 cm^{-1}, within the range of 500–4000 cm^{-1}.

[1]H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy analyses of samples dissolved in DMSO-d_6 were performed using a Bruker AMX 300 Spectrometer operating at 300.13 and 75.47 MHz, respectively. All chemical shifts (δ) were expressed in parts per million (ppm) and downfield from tetramethylsilane (TMS), used as the internal standard.

[13]C cross-polarized magic-angle spinning NMR (^{13}C CP-MAS NMR) spectra were obtained using BRUKER AVANCE III 400 Spectrometer operating at a carbon frequency of 400 MHz, using a 2.5 mm double-

bearing MAS probe with proton 90° pulses. Chemical shifts are given in ppm from TMS.

^{1}H MAS NMR spectra were obtained using a BRUKER AVANCE III − 400 MHz wide-bore Spectrometer ([1]H Larmor frequency of 400.1 MHz) using a double-resonance 4 mm Bruker MAS probe, with a spinning rate of 12 kHz. The spectra were recorded using single-pulse experiment, with a pulse of 3.65 us and a recycle delay of 5 s. Chemical shifts are given in ppm from TMS.

Intrinsic viscosity measurements were carried out on an Ubbelohde type viscometer maintained at 25 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (50/50) (wt%/wt%). PCtF polyester was dissolved in that solvent mixture (0.1 g per 20 mL). The intrinsic viscosity ([η]) was determined by the ratio of specific viscosity and sample solution concentration ((η_{sp}/c, where $\eta_{sp} = (t_1 - t_0)/t_0$ and t_0 and t_1 are the solvent mixture elution time of the solvent mixture and polyester solution, respectively). The viscosity-average molecular weight (M_v) of PCtF was calculated by the Mark-Houwink equation using the K and α parameters for PET ($[\eta] = 4.68 \times 10^{-4} M_V^{0.68}$) [33–35].

Gel Permeation Chromatography (GPC) measurements were performed using a Omnisec HP-SEC system on 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (model CHR6000 sn. MAL 1202615) provided with a (standard) injection volume of 100 μL, flow of 0.7 mL min^{-1} and oven temperature of 35 °C and HFIP effluent + 0.02 M KTFA. Accurately weighted samples were dissolved overnight in 3.0 mL of effluent in 4 mL HPLC vails. Concentrations were 3–4 mg/L of polymer (dependent of expected molecular weight). Filtering is done before measuring through 0.45 um PFTE syringe filters. Narrow standard PolyCal PMMA 50kD (from Viscotek) was used for absolute calibration of the system.

Thermogravimetric analyses (TGA) were carried out with a Shimadzu TGA50 analyser equipped with a platinum cell using platinum pans to encapsulate the samples (ca. 5 mg). Thermograms were recorded under a nitrogen flow of 20 mL min^{-1} at a constant heating rate of 10 °C min^{-1} from 25 to 800 °C.

X-ray diffraction (XRD) patterns were acquired using a Philips X'pert MPD diffractometer operating with CuKα radiation (λ = 1.5405980 Å) at 45 kV and 40 mA. Samples were scanned in the 2θ range of 3–60 °C, with a step size of 0.026° and a time per step of 67 s.

DSC thermograms were obtained with a Setaram DSC92 calorimeter. Scans were carried out under dry 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. The first heating scan was used to erase the thermal history of the polymers, and the second heating scan was performed after rapid cooling from the melted polymers.

Dynamic mechanical thermal analyses (DMTA) of a small amount of powder samples, dispersed in a foldable stainless-steel sheet with a rectangular shape (30.0 × 7.5 mm^2), acquired from Materials Pocket of Triton Technology, were performed with a Tritec 2000 DMTA Triton equipment operating in the bending (single cantilever) mode. Tests were performed at 1 and 10 Hz and the temperature was varied from −100 to 200 °C, at 2 °C min^{-1}.

3. Results and discussion

Two wholly (hetero-)aromatic polyesters, the poly(1,2-phenylene 2,5-furandicarboxylate) (PCtF) and poly(1,4-phenylene-2,5-furandicarboxylate) (PHQF), possessing very rigid structures, were synthesised either by interfacial polycondensation using the diacyl chloride of FDCA and the selected aromatic diol (catechol or hydroquinone) in the presence of a phase transfer catalyst; or by a greener approach, not using the irritant benzyltriethylammonium chloride or the diacyl chloride of FDCA, but reacting instead, in the bulk, equimolar amounts of FDCA with the diol, using sodium acetate as catalyst, and titanium(IV) butoxide as co-catalyst (up to 220 °C) (Scheme 1). Both synthetic routes provided the corresponding polyesters in similar yields (after purification), ca. 60% for PHQF and lower to PCtF, ca. 30%. Each
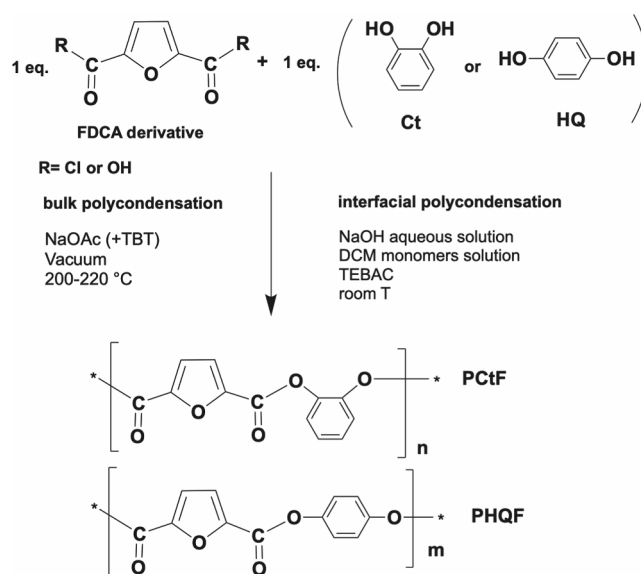
Scheme 1. Synthesis of poly(1,2-phenylene-2,5-furandicarboxylate) (PCtF) and poly(1,4-phenylene-2,5-furandicarboxylate) (PHQF) by bulk and interfacial polycondensation approaches.

experiment was reproduced at least twice with similar yields. As expected PHQF displayed no solubility in common organic solvents (e.g. chloroform, dichloromethane, 1,1,2,2-tetrachloroethane, 1,1,1,3,3,3-hexafluoro-2-propanol, dimethylsulfoxide, propanone, among others) as already previously noticed [18]. This fact precluded PHQF analysis through liquid NMR spectroscopy, GPC and intrinsic viscosity analyses. Oppositely, PCtF revealed to be a more tractable polymer, in this regard, being partially soluble in e.g. 1,1,1,3,3,3-hexafluoro-2-propanol or dimethylsulfoxide.

The soluble part of PCtF polymer has an intrinsic viscosity of ca. 0.10 dL g^{-1} (viscosity-averaged molecular weight of 2.66×10^3) and a weigh-average molecular weight (M_w), determined by GPC, equal to 3.50×10^3 (Fig. S2 of Supplementary material). These preliminary assays are in accordance with the much less crystalline structure of PCtF polymer (discussed below), in which molecules can solvate the polymer more easily. Also, this suggests a way to increase these polymers processing by prompting amorphous domains formation. Nevertheless, one cannot rule out the possibility of the existence of an oligomeric soluble fraction in the case of PCtF, and thus real molecular weights are probably underestimated.

3.1. Structural characterisation

The expected molecular structure of the wholly (hetero)aromatic poly(1,2-phenylene-2,5-furandicarboxylate) bearing both furan and benzenic rings was confirmed by ATR FTIR and ^{1}H, ^{13}C, ^{13}C CP-MAS and ^{1}H MAS NMR spectroscopies and compared to the related poly(1,4-phenylene-2,5-furandicarboxylate).

The PCtF and PHQF vibrational spectra of Fig. 1 displayed three weak bands ascribed to the stretching of the ═C—H bond of both furan and benzenic rings, centred at 3149 and 3118 cm^{-1}, and 3075 cm^{-1}, respectively. A small band near 3452 cm^{-1} due to the stretching of unreacted hydroxyl end-groups was also observed (especially evident in the case of PHQF, thus indicating lower molecular weight for this polymer). Additionally, a very intense band near 1740 cm^{-1}, ascribed to the C═O stretching vibration, characteristic of ester groups; a band near 1571 cm^{-1} assigned to the C═C stretching vibration of aromatic and furan rings; and a band near 1270 cm^{-1} arising from the C—O stretching vibration of ester moieties were detected. Importantly, these polymers display a relevant spectral difference in the fingerprint region characteristic of the ortho- or para-disubstitution of the benzene ring, as clearly
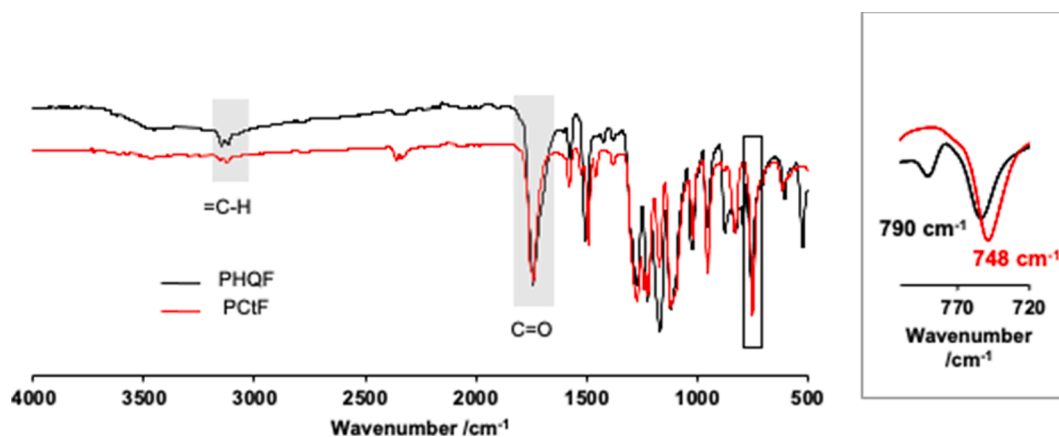
Fig. 1. ATR FTIR spectra of PCtF and PHQF renewable-based polyesters (left) and inset of the expanded fingerprint region highlighting the C—H out-of-plane bending mode of - *para*- and *ortho*-benzene substituent (right).

highlighted in the inset of Fig. 1. While PHQF spectrum displays a band near 790 cm^{-1} arising from C—H out-of-plane bending mode of the *para*-benzene ring and another at 748 cm^{-1} due to the C—H out-of-plane bending mode of the furanic ring; for PCtF these modes (furanic and *ortho*-benzene rings related) are superimposed and centred at 748 cm^{-1}. The week overtone bands expected to appear in the 1800–2000 cm^{-1} range are overlapped with the intense C=O stretching band. All these findings are consistent with PHQF spectrum [18], as well as previously reported FTIR spectra of furanic-benzenic polyesters [36].

The ^{1}H NMR spectrum of PCtF (Fig. 2 and Table S1 in Supplementary material) displays one singlet at $\delta \approx 7.53$ ppm (H3, H4) arising from the furan proton resonances and a multiplet centred at $\delta \approx 7.49$ ppm (H3′, H6′, H4′, H5′) attributed to the catechol aromatic protons resonances. Moreover, there are several minor resonances related to the end-groups protons between $\delta \approx 7.30$–6.83 ppm. The ^{13}C NMR spectrum of PCtF of Fig. S3 (Supplementary material) displays the typical furan ring carbon resonances at $\delta \approx 145.8$ and 121.7 ppm (C2, C5, and C3, C4,

respectively); those associated with the *ortho*-substituted aromatic carbons at $\delta \approx 141.6$, 128.0 and 124.2 ppm (C1′, C2′; C4′, C5′ and C3′, C6′, respectively); and with the 155.4 ppm resonance arising from the carbonyl ester moiety carbon.

Due to PHQF high insolubility the characterisation of this polymer comprised only its analysis by solid state ^{13}C CP-MAS NMR (Fig. 3) and ^{1}H MAS NMR spectroscopies (Fig. S3 of supplementary material), while ^{1}H and ^{13}C NMR in DMSO-d_6 were only performed for PCtF (Fig. 2 and Fig. S3 and Table S1 of Supplementary Material). In the case of PHQF the higher symmetry of the *p*-substituted benzene ring originates only the benzene carbon resonances around: 146.7 ppm and at 122.8 ppm ascribed to C2, C5 and C2′, C3′, C5′, C6′, respectively. The typical furan ring carbon resonance are partially overlapped by the former at $\delta \approx 146.7$ and 121.0 ppm (C2, C5 and C3, C4, respectively). The carbonylic carbon resonance typical of esters was detected at 156.2 ppm and an additional C=O resonance at 156.0 ppm was also observed. This latter resonance might arise from C=O of carboxylic acid chain-ends or, from
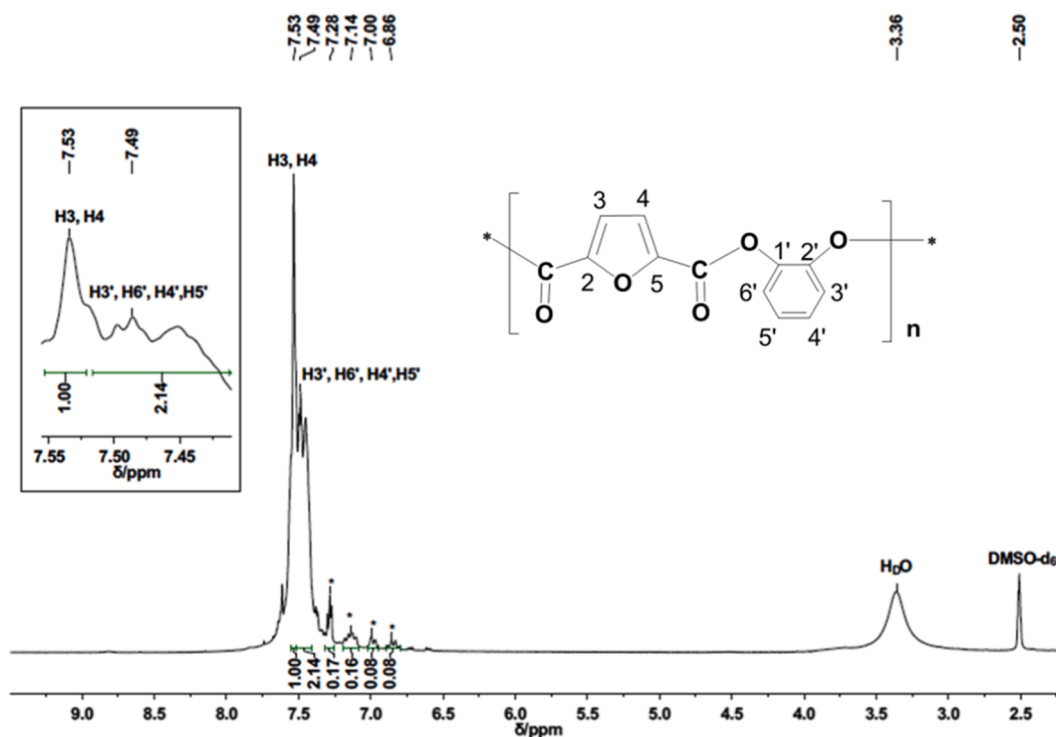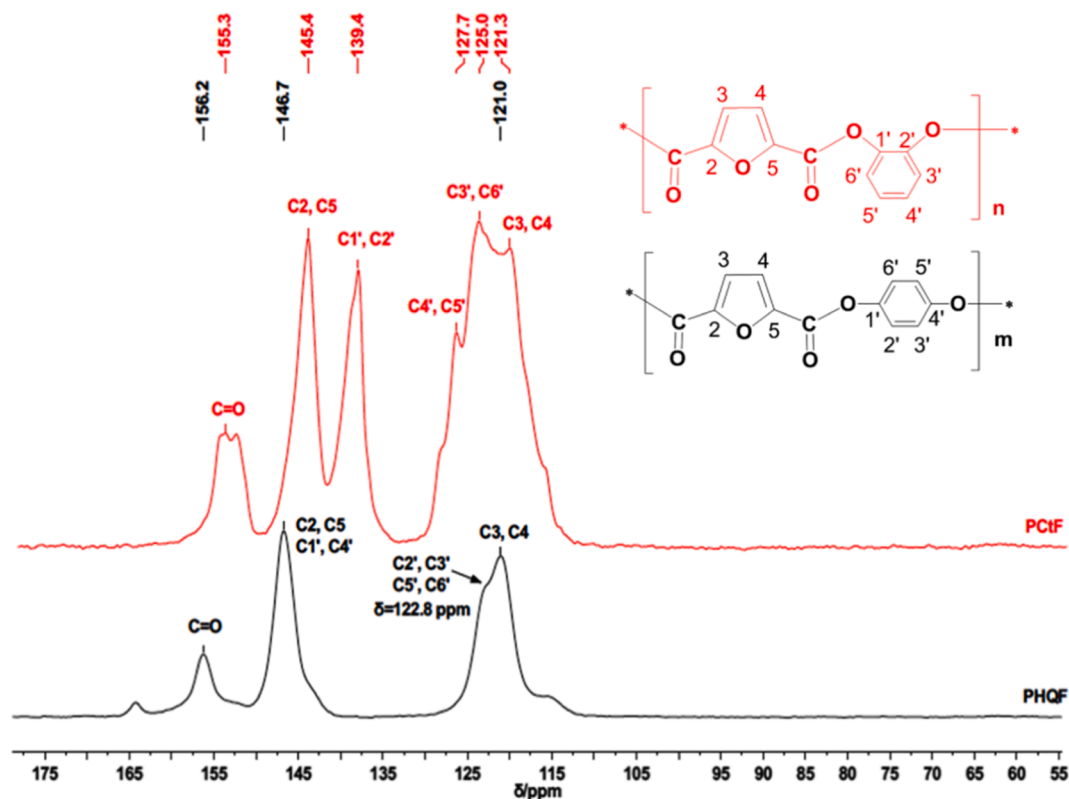

Fig. 2. ^{1}H NMR spectrum of PCtF in DMSO-d_6.

Fig. 3. Solid-state ^{13}C CP-MAS NMR spectra of PCtF and PHQF.

an ester C=O within a crystal (lower mobility). Indeed, PHQF is more crystalline than PCtF (as discussed below).

The ^{13}C CP-MAS NMR spectrum of PCtF (Fig. 3) was also performed for comparison reasons, displaying all resonances observed for PHQF, except the C=O resonance near 165 ppm, plus an additional resonance at $\delta \approx 139$ ppm attributed to C1′, C2′.

3.2. Thermal and X-ray diffraction analyses

In order to pinpoint the expected enhanced thermal properties of these wholly (hetero-)aromatic, TGA analysis of the (hetero-)aromatic polyesters were investigated (Table 1 and Fig. S5 of Supplementary material). PCtF revealed to be thermally stable up to approximately 227 °C; and it degrades in a single step, with a maximum decomposition temperature of *ca.* 379 °C. PHQF exhibited similar T_{on} at 222 °C; but it degrades in a multi-stage process with a major degradation step at a relatively high temperature of 428 °C and two preceding smaller steps ($T_{d,\max}$ 251.0 and 348.6 °C) most probably associated to lower molecular weight chains (in agreement to FTIR). These polyesters degradation can

be described mainly through β scission and most probably less extensively by homolytic scission as reported before for furanic polyesters [37–39].

The X-ray diffractogram of PCtF, as well as that of PHQF, exhibit several reflection peaks consistent with the formation of crystalline domains (Fig. 4). Accordingly, in the case of PCtF, the diffraction pattern shows four broad reflection peaks at $2\theta \sim 7.5°$, $11.5°$, $17.6°$ and $25.0°$, while for PHQF the peaks are sharper and centred at $2\theta° \sim 16.8°$, $25.1°$, $30.1°$ and $35.2°$. The PHQF XRD pattern is in agreement with previously reported results [18]. These results clearly evidence the higher crystallinity of PHQF compared to PCtF, which is most likely associated with the fact that the *para*-substituted benzenic ring in the case of PHQF originates a more symmetric structure that favours a more efficient packing arrangement between polymer chains, thus prompting crystallisation. Also, this can also prompt, in the case of PHQF, hydrogen bonds
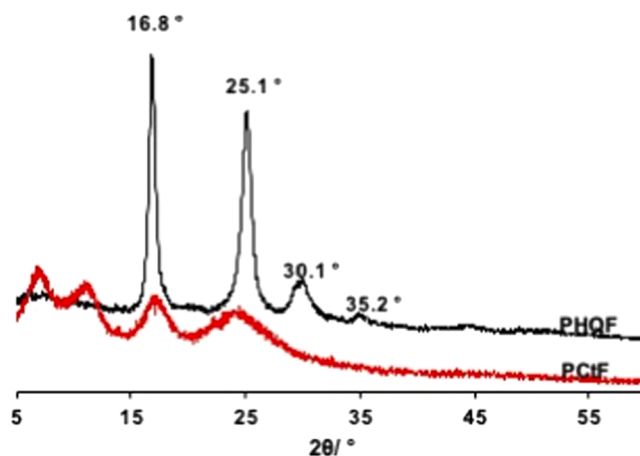
Table 1
Onset of decomposition (T_{on}), maximum decomposition ($T_{d,\max}$), beta (T_β) and glass transition (T_g) temperatures of the wholly (hetero-)aromatic polyesters.

polyester	TGA [a]		DSC [b]	DMTA [c]	
	T_{on} / °C	$T_{d,\max}$ / °C	T_g / °C	T_β / °C	T_g / °C
PCtF	226.6 (5%)	378.7	93	−10.3	136.8
PHQF	221.8 (2%)	251.0; 348.6; 488.3	167 [d]	75.6	184.0

[a] $T_{d,\max}$ and T_{on} were determined by TGA at 10 °C min^{-1}, using the temperature at which the rate of weight loss is maximum (DTG) and ext rapolated onset temperature weight loss step (TG), respectively. In brackets is indicated the % of weight loss at the T_{on}.
[b] T_g was determined by DSC at 10 °C min^{-1} using the midpoint approach.
[c] T_β and T_g were determined by DMTA using the tan δ curve maxima.
[d] from first DSC heating scan.

Fig. 4. XRD patterns of PCtF and PHQF.

formation between the carbonyl oxygens and the furanic hydrogens, as observed previously for PEF [40], thus favouring crystalline domains stabilisation.

The thermal properties of these wholly aromatic polyesters were also investigated by DSC (Table 1 and Fig. S6 of Supplementary material). Despite their semi-crystalline character (XRD results), no melting features were observed in the heating scan between 0 and 300 °C (at a scanning rate of 10 °C min^{-1}). A rough estimative of their melting temperature, based on the empirical rule $T_g/T_m = 2/3$ for melt-quenched glasses [41], indicates a T_m of approximately 387 and 276 °C for PHQF and PCtF, respectively. Hence, quite above the onset of degradation of both PHQF and PCtF. The thermograms only displays a subtle step on the base line ascribed to a glass transition at high temperatures, at approximately 93 °C for PCtF and at 167 °C for PHQF (reported here for the first time). These differences are most probably associated with a higher free volume of the *ortho*-substituted derivative, which is corroborated by a higher Cp variation for PCtF (Fig. S6 of Supplementary material). The scarce studies on FDCA-based wholly aromatic polyesters also show the same trend, for example the polyester prepared from renewable based divanillyl diol and FDCA derivatives showed a T_g value of 139 °C [28]. Homopolyesters derived from hydroquinone and various aryloxyterephthalic acids also have high-T_g values (93–113 °C) but slightly lower than PHQF; and T_m around 325–368 °C [42].

DMTA is a much more sensitive technique to assess glass transition events than DSC [43], however this technique was not used before to characterise PHQF [18] (Fig. 5). In fact, this is the first report on this polymer T_g or even $T\beta$; as well as on PCtF thermal features. Accordingly, the tan δ traces of both polyesters clearly display a T_g, although at higher temperatures (136.8 and 184.0 °C for PCtF and PHQF, respectively). The DSC and DMTA differences are in agreement with previous results [44]. DMTA traces also detected a β transition for both PCtF and PHQF at −10.3 °C and 75.6 °C for PHQF, respectively. This transition is usually ascribed to a gain in free energy, which in the case of a related polymer – PET – is due to the non-cooperative motion of the carbonyl groups and to the cooperative benzenic ring flips [36]; whereas, for PEF this transition is only related to carbonyl motions since the furan ring flipping is suppressed due to ring asymmetry and oxygen polarity, as highlighted in the work of Koros *et al.* [10] and, later, supported also by the Sousa [40], and is related to the enhanced barrier properties of PEF. In the same vein, the β transition of both PCtF and PHQF is most probably related to the carbonyl motion, but the furan ring flipping must be plausibly hindered as observed for PEF. Benzenic ring flipping must be logically more relevant for PCtF than for PHQF, which could also explain the fact that the DMTA trace of PHQF shows much broader transitions with lower tan δ height, rather than PCtF. Another aspect worth considering is the fact that the T_β of PHQF is much higher than that of PCtF. This viscoelastic effect is most probably associated with a stiffer PHQF material prompted by its crystal phases that hinder mobility and energy dissipation.

4. Conclusions

In summary, wholly (hetero-)aromatic polyesters entirely based on renewables, the key-platform chemical- 2,5-furandicarboxylic acid (FDCA) and commercial-available (also potentially produced from renewables) catechol, or hydroquinone were obtained both through bulk and interfacial polycondensations. The progress achieved in this study clearly highlights the ability of (hetero-)aromatic compounds to enhance thermal properties of the polymers thereof. Indeed, the PCtF and PHQF polymers have high thermal properties, with high thermal stability ($T_{d,max}$ higher than 370 °C); high glass transition (above 90 °C, reaching in the case of HQPHQ PHQF 167 °C) and high melting temperature (above 300 °C) prompted by their stiff wholly (hetero-)aromatic nature, bearing both benzenic and furanic rings in their backbone, potentially outperforming high-T_g fossil-based polymers (targeting *e.g.* ABS). Still, differences between the thermal properties and crystallinity of these two polymers were noticed. These differences are most probably prompted by the *para-* and *ortho*-substitution of the benzenic ring affecting stiffness and close packing arrangement between polymer chains and, hence, influencing both amorphous and crystalline domains. Poly(1,4-phenylene-2,5-furandicarboxylate) had a typical higher $T_{d,on}$ and T_g. However, PCtF revealed to be a more tractable polymer in terms of processing due to its higher solubility in organic solvents, paving the way to its more efficient use in high T_g polymer applications among rigid plastics. Furthermore, in the future, copolymerisation with aliphatic moieties will be performed to enhance these (hetero-)aromatic polyesters melting processing properties.

Author statement

Conceptualisation credits is due to AFS. SZ, MJS and AB performed the experimental part. SEC analysis were performed by ST. NG conducted structural and thermal analysis investigations. Supervision was carried out by AFS, AJDS, AB, MA and SA. All authors contributed to writing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
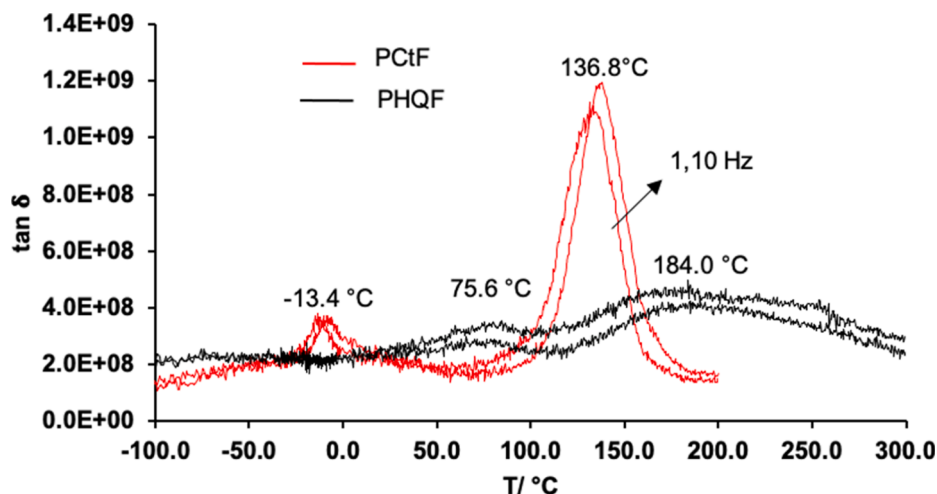

Fig. 5. Tan δ traces of PCtF and PHQF at 1 and 10 Hz.

the work reported in this paper.

Data availability

The raw data required to reproduce these findings are available throughout this manuscript and in the Supplementary material.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2021.110413.

References

[1] K. Loos, R. Zhang, I. Pereira, B. Agostinho, H. Hu, D. Maniar, N. Sbirrazzuoli, A.J. D. Silvestre, N. Guigo, A.F. Sousa, A Perspective on PEF Synthesis, Properties, and End-Life, Front. Chem. 8 (2020) 1–18, https://doi.org/10.3389/fchem.2020.00585.

[2] Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, Nature 540 (2016) 354–362, https://doi.org/10.1038/nature21001.

[3] C. Vilela, A.F. Sousa, A.C. Fonseca, A.C. Serra, J.F.J. Coelho, C.S.R. Freire, A.J. D. Silvestre, The quest for sustainable polyesters-insights into the future, Polym. Chem. 5 (2014) 3119–3141, https://doi.org/10.1039/c3py01213a.

[4] G.Z. Papageorgiou, V. Tsanaktsis, D.G. Papageorgiou, S. Exarhopoulos, M. Papageorgiou, D.N. Bikiaris, Evaluation of polyesters from renewable resources as alternatives to the current fossil-based polymers. Phase transitions of poly (butylene 2,5-furan-dicarboxylate), Polym. 55 (2014) 3846–3858, https://doi.org/10.1016/j.polymer.2014.06.025.

[5] H. Thi, H. Nguyen, P. Qi, M. Rostagno, A. Feteha, S.A. Miller, The quest for high glass transition temperature bioplastics, J. Mater. Chem. A Mater. Energy Sustain. 6 (2018) 9298–9331, https://doi.org/10.1039/C8TA00377G.

[6] M. Matos, A.F. Sousa, A.C. Fonseca, C.S.R. Freire, J.F.J. Coelho, A.J.D. Silvestre, A new generation of furanic copolyesters with enhanced degradability: Poly (ethylene 2,5-furandicarboxylate)-co-poly(lactic acid) copolyesters, Macromol. Chem. Phys. 215 (2014) 2175–2184, https://doi.org/10.1002/macp.201400175.

[7] L. Mialon, A.G. Pemba, S.A. Miller, Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid, Green Chem. 12 (2010) 1704, https://doi.org/10.1039/c0gc00150c.

[8] H.T.H. Nguyen, G.N. Short, P. Qi, S.A. Miller, Copolymerization of lactones and bioaromatics: via concurrent ring-opening polymerization/polycondensation, Green Chem. 19 (2017) 1877–1888, https://doi.org/10.1039/c6gc03238a.

[9] A. Gandini, A.J.D. Silvestre, C.P. Neto, A.F. Sousa, M. Gomes, The furan counterpart of poly(ethylene terephthalate): An alternative material based on renewable resources, J. Polym. Sci. Pol. Chem. 47 (2009) 295–298, https://doi.org/10.1002/pola.23130.

[10] S.K. Burgess, J.E. Leisen, B.E. Kraftschik, C.R. Mubarak, R.M. Kriegel, W.J. Koros, Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) compared to Poly(ethylene terephthalate), Macromolecules 47 (2014) 1383–1391, https://doi.org/10.1021/ma5000199.

[11] J. Zhu, J. Cai, W. Xie, P.-H. Chen, M. Gazzano, M. Scandola, R.A. Gross, Poly (butylene 2,5-furan dicarboxylate), a Biobased Alternative to PBT: Synthesis, Phys. Properties, Cryst. Struct., Macromol. 46 (2013) 796–804, https://doi.org/10.1021/ma3023298.

[12] M. Jiang, Q. Liu, Q. Zhang, C. Ye, G. Zhou, A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources, J. Polym. Sci. Pol. Chem. 50 (2012) 1026–1036, https://doi.org/10.1002/pola.25859.

[13] G.Z. Papageorgiou, V. Tsanaktsis, D.G. Papageorgiou, K. Chrissafis, S. Exarhopoulos, D.N. Bikiaris, Furan-based polyesters from renewable resources: Crystallization and thermal degradation behavior of poly(hexamethylene 2,5-furan-dicarboxylate), Eur. Polym. J. 67 (2015) 383–396, https://doi.org/10.1016/j.eurpolymj.2014.08.031.

[14] J. Deng, X. Liu, C. Li, Y. Jiang, J. Zhu, Synthesis and properties of a bio-based epoxy resin from 2,5-furandicarboxylic acid (FDCA), RSC Adv. 5 (2015) 15930–15939, https://doi.org/10.1039/c5ra00242g.

[15] M.J. Soares, P.-K.K. Dannecker, C. Vilela, J. Bastos, M.A.R. Meier, A.F. Sousa, Poly (1,20-eicosanediyl 2,5-furandicarboxylate), a biodegradable polyester from renewable resources, Eur. Polym. J. 90 (2017) 301–311, https://doi.org/10.1016/j.eurpolymj.2017.03.023.

[16] V. Tsanaktsis, G.Z. Papageorgiou, D.N. Bikiaris, A facile method to synthesize high molecular weight biobased polyesters from 2,5-furandicarboxylic acid and long chain diols, J. Polym. Sci. Pol. Chem. 53 (2015) 2616–2632, https://doi.org/10.1002/pola.27730.

[17] Y. Jiang, A.J.J. Woortman, G.O.R. Alberda van Ekenstein, K. Loos, A biocatalytic approach towards sustainable furanic–aliphatic polyesters, Polym. Chem. 6 (2015) 5198–5211, https://doi.org/10.1039/C5PY00629E.

[18] M. Gomes, A. Gandini, A.J.D. Silvestre, B. Reis, N. Gomes, A. Gandini, A.J. D. Silvestre, B. Reis, Synthesis and characterization of poly(2,5-furan dicarboxylate)s based on a variety of diols, J. Polym. Sci. Pol. Chem. 49 (2011) 3759–3768, https://doi.org/10.1002/pola.24812.

[19] A.F. Sousa, J.F.J. Coelho, A.J.D. Silvestre, Renewable-based poly((ether)ester)s from 2,5-furandicarboxylic acid, Polym. 98 (2016) 129–135, https://doi.org/10.1016/j.polymer.2016.06.015.

[20] R. Storbeck, M. Ballauff, Synthesis and properties of polyesters based on 2,5-furandicarboxylic acid and 1,4:3,6-dianhydrohexitols, Polym. 34 (1993) 5003–5006.

[21] Y. Chebbi, N. Kasmi, M. Majdoub, P. Cerruti, G. Scarinzi, M. Malinconico, G. D. Poggetto, G.Z. Papageorgiou, D.N. Bikiaris, Synthesis, characterization, and biodegradability of novel fully biobased poly(decamethylene-co-isosorbide 2,5-furandicarboxylate) copolyesters with enhanced mechanical properties, ACS Sustain. Chem. Eng. 7 (2019) 5501–5514, https://doi.org/10.1021/acssuschemeng.8b06796.

[22] F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J.-P. Pascault, Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review, Prog. Polym. Sci. 35 (2010) 578–622. doi: 10.1016/j.progpolymsci.2009.10.001.

[23] T. Kim, J.M. Koo, M.H. Ryu, H. Jeon, S.M. Kim, S.A. Park, D.X. Oh, J. Park, S. Y. Hwang, Sustainable terpolyester of high Tg based on bio heterocyclic monomer of dimethyl furan-2,5-dicarboxylate and isosorbide, Polym. 132 (2017) 122–132, https://doi.org/10.1016/j.polymer.2017.10.052.

[24] Z. Terzopoulou, N. Kasmi, V. Tsanaktsis, N. Doulakas, D.N. Bikiaris, D.S. Achilias, G.Z. Papageorgiou, Synthesis and characterization of bio-based polyesters: poly(2-methyl-1,3-propylene-2,5-furanoate), poly(isosorbide-2,5-furanoate), poly(1,4-cyclohexanedimethylene-2,5-furanoate), Materials. 10 (2017) 1–19, https://doi.org/10.3390/ma10070801.

[25] N. Kasmi, N.M. Ainali, E. Agapiou, L. Papadopoulos, G.Z. Papageorgiou, D. N. Bikiaris, Novel high Tg fully biobased poly(hexamethylene-co-isosorbide-2,5-furan dicarboxylate) copolyesters: Synergistic effect of isosorbide insertion on thermal performance enhancement, Polym. Degrad. Stab. 169 (2019), 108983, https://doi.org/10.1016/j.polymdegradstab.2019.108983.

[26] M. Matos, A.F. Sousa, A.J.D. Silvestre, Improving the thermal properties of poly (2,5-furandicarboxylate)s using cyclohexylene moieties: a comparative study, Macromol. Chem. Phys. 218 (2017) 1600492 (1–10). doi: 10.1002/macp.201600492.

[27] J. Wang, X. Liu, Y. Zhang, F. Liu, J. Zhu, Modification of poly(ethylene 2,5-furandicarboxylate) with 1,4-cyclohexanedimethylene: Influence of composition on mechanical and barrier properties, Polym. 103 (2016) 1–8, https://doi.org/10.1016/j.polymer.2016.09.030.

[28] A. Llevot, E. Grau, S. Carlotti, S. Grelier, H. Cramail, Renewable (semi)aromatic polyesters from symmetrical vanillin-based dimers, Polym. Chem. 6 (2015) 6058–6066, https://doi.org/10.1039/c5py00824g.

[29] C.H.R.M. Wilsens, B.A.J. Noordover, S. Rastogi, Aromatic thermotropic polyesters based on 2,5-furandicarboxylic acid and vanillic acid, Polym. 55 (2014) 2432–2439, https://doi.org/10.1016/j.polymer.2014.03.033.

[30] M. Weber, M. Weber, V. Weber, Phenol Derivatives, Ullmann's Encycl. Ind. Chem. (2012), https://doi.org/10.1002/14356007.a19.

[31] E. Faure, C. Falentin-daudré, C. Jérôme, J. Lyskawa, D. Fournier, P. Woisel, C. Detrembleur, Catechols as versatile platforms in polymer chemistry, Prog. Polym. Sci. 38 (2013) 236–270, https://doi.org/10.1016/j.progpolymsci.2012.06.004.

[32] Y. Zhang, H. Lei, Z. Yang, K. Qian, E. Villota, Renewable high-purity mono-phenol production from catalytic microwave-induced pyrolysis of cellulose over biomass-derived activated carbon catalyst, ACS Sustain. Chem. Eng. 6 (2018) 5349–5357, https://doi.org/10.1021/acssuschemeng.8b00129.

[33] S.A. Jabarin, Crystallization kinetics of polyethylene terephthalate. I. Isothermal crystallization from the melt, J. Appl. Polym. Sci. 34 (1987) 85–96, https://doi.org/10.1002/app.1987.070340107.

[34] S. Farah, K.R. Kunduru, A. Basu, A.J. Domb, Molecular weight determination of polyethylene terephthalate, in: P.M. Visakh, Mong Liang (Eds.), Elsevier Inc., Oxford, 2015: pp. 143–165. doi: 10.1016/B978-0-323-31306-3.00008-7.

[35] K. Li, X. Song, D. Zhang, Depolymerization of poly(ethylene terephthalate) with catalyst under microwave radiation, J. Appl. Polym. Sci. 109 (2008) 1298–1301, https://doi.org/10.1002/app.28187.

[36] A.F. Sousa, M. Matos, C.S.R. Freire, A.J.D. Silvestre, J.F.J. Coelho, New copolyesters derived from terephthalic and 2,5-furandicarboxylic acids: A step forward in the development of biobased polyesters, Polym. 54 (2013) 513–519, https://doi.org/10.1016/j.polymer.2012.11.081.

[37] Z. Terzopoulou, V. Tsanaktsis, M. Nerantzaki, G.Z. Papageorgiou, D.N. Bikiaris, Decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and aliphatic diols with medium and long chain methylene groups, Polym. Degrad. Stab. 132 (2016) 127–136, https://doi.org/10.1016/j.polymdegradstab.2016.03.006.

[38] G.Z. Papageorgiou, D.G. Papageorgiou, Z. Terzopoulou, D.N. Bikiaris, Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties, Eur. Polym. J. 83 (2016) 202–229, https://doi.org/10.1016/j.eurpolymj.2016.08.004.

[39] S. Thiyagarajan, M.A. Meijlink, A. Bourdet, W. Vogelzang, R.J.I. Knoop, A. Esposito, E. Dargent, D.S. van Es, J. van Haveren, Synthesis and thermal properties of bio-based copolyesters from the mixtures of 2,5- and 2,4-furandi-carboxylic acid with different diols, ACS Sustain. Chem. Eng. 7 (2019) 18505–18516, https://doi.org/10.1021/acssuschemeng.9b04463.

[40] C.F. Araujo, M.M. Nolasco, P.J. Ribeiro-Claro, S. Rudić, A.J. Silvestre, P.D. Vaz, A.F. Sousa, Inside PEF: chain conformation and dynamics in crystalline and amorphous domains, Macromolecules 51 (2018) 3515–3526, https://doi.org/10.1021/acs.macromol.8b00192.

[41] H. Kanno, A simple derivation of the empirical rule Tg/Tm = 2/3, J. Non Cryst. Solids 44 (1981) 409–413.

[42] H.R. Kricheldorf, J. Engelhardt, New polymer syntheses. XLII. Thermotropic polyesters of hydroquinone and various aryloxyterephthalic acids, J. Polym. Sci., Part A: Polym. Chem. 28 (1990) 2335–2347, https://doi.org/10.1002/pola.1990.080280909.

[43] Paul Gabbott, Principles and Applications of Thermal Analysis, Blackwell Publishing Ltd, Oxford, UK, 2008. doi: 10.1002/9780470697702.

[44] S. Zaidi, S. Thiyagarajan, A. Bougarech, F. Sbeti, S. Abid, A. Majdi, A. Silvestre, A.F. Sousa, Highly transparent films of new copolyesters derived from terephthalic and 2,4-furandicarboxylic acids, Polym. Chem. (2019) 5324–5332, https://doi.org/10.1039/c9py00844f.