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Biobased furandicarboxylic acids (FDCA)s: effects of isomeric substitution on polyester synthesis and properties†

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In this study we present the application of different isomers of furandicarboxylic acid, or FDCA, obtained from agro-residues, in polyester synthesis. New polyesters based on 2,4-FDCA and 3,4-FDCA isomers with (linear) diols were thoroughly characterised and compared with their as-synthesised 2,5-FDCA analogues. All polymers were obtained by melt polycondensation of linear diols with FDCA dimethyl esters and exhibit molecular weights in the range $M_w = 34\,000\text{--}65\,000$ and polydispersities close to 2.0. Thermogravimetric analysis (TGA) of the new polyesters shows that they have comparable or even higher thermal stability compared to the 2,5-FDCA polyesters. Interestingly, the glass-transition temperatures (T_g) of 2,4-FDCA derived polyesters are similar to those of the 2,5-FDCA isomers. Both differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) analyses showed that 2,4-PEF is amorphous, while 2,5-PEF and 3,4-PEF are semi-crystalline materials.

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Introduction

Increasing awareness that the still growing use of fossil feedstocks and concomitant emissions of greenhouse gases (GHG) is affecting global climate change¹ is one of the main drivers in the search for sustainable, renewable feedstocks for chemicals and materials. The increasing use of synthetic polymers can contribute to reducing GHG emissions due to the lower weight of those materials compared to *e.g.* steel, aluminum or glass. However, this trend can only become truly positive when these polymeric materials are based on renewable resources. Due to the high oxygen content of the most abundantly available biomass components like polysaccharides and lignin, one can debate whether it is viable to use such feedstock for the production of highly defunctionalised “drop-in” chemical building blocks like olefins. A different approach would be to transform biomass components into “new” chemical building blocks with unique structures and functionalities, following thermodynamically more favorable pathways.

One such “new” biobased building block is furan-2,5-dicarboxylic acid (or 2,5-FDCA) which is widely propagated as an alternative to the ubiquitous terephthalic acid (TA).^{2,3} Recent reports on the application of 2,5-FDCA in a range of polyesters have shown that in comparison with TA, polymer properties are quite often (surprisingly) comparable.^{3–5} Furthermore, preliminary reports on gas barrier properties indicate that PEF synthesized from 2,5-FDCA has superior performance compared to polyethylene terephthalate (PET) derived from TA.³ Nevertheless, before 2,5-FDCA can become a viable alternative to TA, more challenges need to be met, including economic viability. Currently, most synthetic routes to 2,5-FDCA are based on the oxidation of 5-hydroxymethyl-2-furaldehyde (HMF)⁶ which can be obtained by cyclodehydration of C6 sugars like fructose and glucose.⁷ In order to avoid possible competition with the food chain we have investigated several other strategies based on the use of non-digestible agro-residues like sugar beet pulp or bagasse. Pectinic sugars like galacturonic acid can be converted into galactaric acid⁸ and subsequently into 2,5-FDCA. Agro-residues like sugar beet pulp or bagasse are also a source of C5 sugars. In the latter case xylans and arabinans in hemi-cellulose can be cyclodehydrated to furfural, which can be subsequently oxidized to 2-furoic acid.^{9,10} Solid state disproportionation of the latter in a Henkel-type reaction then furnishes 2,5-FDCA together with furan.¹⁰

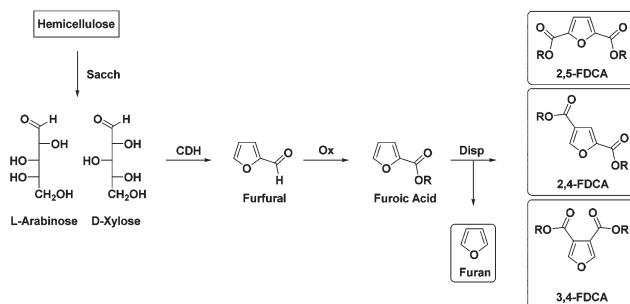
However, as we recently reported, during the Henkel reaction, depending on the reaction conditions, not only the 2,5-

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† Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra, TGA traces, DSC curves and WAXD profiles of all the polyesters. See DOI: 10.1039/c3gc42184h





Scheme 1 Synthesis of FDCAs via disproportionation reaction (Sacch = saccharification, CDH = cyclodehydration, Ox = oxidation, Disp = disproportionation).

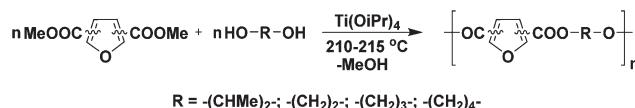
isomer is formed (70%) but also the 2,4- (30%) and to a lesser extent the 3,4-isomer (<5%) (Scheme 1).⁹ Furthermore, we have also shown that separation of the 2,5- and 2,4-isomer is feasible. In order to assess the viability of the Henkel-route it is necessary to gain insight into the value of the separate isomers as polymer building blocks. Whereas there is a limited, yet steadily increasing amount of literature on the synthesis and properties of 2,5-FDCA based polyesters, surprisingly only a very few reports on either 2,4- or 3,4-FDCA polyesters can be found. In 1958, Hachihama *et al.* reported one example of the 2,4-FDCA based polyester with ethylene glycol (2,4-PEF); however, key properties like T_g and molecular weights were not described.¹¹ A few decades later, Gandini *et al.* synthesized poly(butylene-furan-3,4-dicarboxylate) from 3,4-FDCA and 1,4-butanediol. These authors unfortunately only reported a glass-transition temperature.¹²

Hence, here we report a systematic comparison of polyesters containing 2,5-, 2,4- or 3,4-FDCA, and a series of homologous industrially relevant aliphatic diols. The obtained data allow for a structure–property analysis with regard to the furandicarboxylic acid substitution pattern, giving insight into the influence on

- Reactivity of the monomers (molecular weight build-up and isolated yield)
- Stability of the monomers (molecular weight build-up, polydispersity and colour)
- Thermal properties of the polymers (T_g , T_m)
- Thermal stability of the polymers (colour, mass loss)
- Degree of crystallinity and rate of crystallization.

Results and discussion

2,5-FDCA and 2,4-FDCA were prepared and purified (>98%) according to reported procedures.^{5,9,13} All polyesters were prepared according to the same protocol in order to compare the reactivity of the FDCA isomers. Melt polycondensation of the dimethyl esters of 2,5-, 2,4- or 3,4-FDCA with linear (potentially) biobased aliphatic diols (ethylene glycol (EG), 1,3-propanediol (PDO), 1,4-butanediol (1,4-BDO), and 2,3-butanediol (2,3-BDO)) yielded a set of 12 polyesters, of which 6 are novel (Scheme 2).



Scheme 2 Synthesis of dimethyl furandicarboxylate based polyesters.

The polycondensation was performed by a conventional two-step melt-polycondensation procedure using titanium(IV) isopropoxide as the catalyst (1.25 mol%). The pre-polymerization was performed at 160 °C for 12 h, followed by further polycondensation at 210–215 °C for 2 h under reduced pressure (0.02 mbar) in the second-step. The polyesters were obtained in excellent isolated yields (80–98%), while after precipitation from methanol all polyesters were obtained as white powders.

While the known polyesters based on 2,5-FDCA merely served as benchmark, all 2,4- and 3,4-FDCA polyesters (except for 2,4-PEF and 3,4-PBF) have not been described before. The structures of all the polyesters were confirmed by NMR (^1H and ^{13}C) (see ESI†) and FTIR spectroscopy. Gel permeation chromatography (GPC) of the furandicarboxylate polyesters showed that all polymers were obtained in medium to high molecular weights, with polydispersity index (PDI) values close to 2 (Table 1).

Table 1 Results of the polyester synthesis of dimethyl furandicarboxylates with various diols (polymerisation conditions are described in the experimental section)

Entry	Code	GPC ^a				
		M_n ^b (g mol ⁻¹)	M_w ^c (g mol ⁻¹)	PDI ^d	Yield ^e (%)	Appearance ^f
Ethylene glycol (EG)						
1	2,5-PEF	19 100	34 200	1.8	91	Opaque
2	2,4-PEF	21 200	39 700	1.9	88	Translucent
3	3,4-PEF	24 200	45 500	1.9	92	Translucent
1,3-Propane diol (PDO)						
4	2,5-PPF	36 300	64 100	1.8	89	Translucent
5	2,4-PPF	21 600	42 100	2.0	92	Translucent
6	3,4-PPF	24 400	44 700	1.8	93	Translucent
1,4-Butane diol (1,4-BDO)						
7	2,5-P14BF	21 400	55 400	2.5	90	Opaque
8	2,4-P14BF	21 800	36 800	1.7	93	Opaque
9	3,4-P14BF	30 700	61 800	2.0	91	Opaque
2,3-Butane diol (2,3-BDO)						
10	2,5-P23BF	8000	12 200	1.5	87	Translucent
11	2,4-P23BF	2700	5200	2.0	83	Translucent
12	3,4-P23BF	9100	18 100	2.0	80	Translucent
Polyethylene terephthalate						
13	PET ^g	11 400	22 500	2.0	98	Opaque
14	PET ^h	34 000	64 200	1.9	—	Opaque

^a Gel permeation chromatography performed on crude samples using HFIP as a solvent. ^b M_n : number-average molecular weight. ^c M_w : weight-average molecular weight. ^d PDI: polydispersity index. ^e Isolated yield (crude). ^f Appearance of the crude polyester in the reactor. ^g As-synthesised PET. ^h Commercial bottle-grade PET sample.



Given the commercial importance of PET, the ethylene glycol (EG) polyesters or PEFs (Table 1, entries 1–3) are the main focus of this study. The reference polymer 2,5-PEF was obtained with an excellent M_n of 19 100 (PDI 1.8), which is comparable to literature values,^{5,14} thereby validating our polycondensation procedure. Polycondensation of either 2,4- or 3,4-FDCA with EG yielded materials with comparable molecular weights, polydispersities and crude isolated yields. This indicates that under comparable polycondensation conditions, the position of the carboxylic acid groups on the furan ring has no significant influence on reactivity. This is all the more striking in the case of 3,4-FDCA, since for the EG polyester of the analogous *ortho*-phthalic acid (PA) it was not possible to obtain high molecular weights by melt polycondensation.¹⁵

Furthermore, contrary to observations on the chemical reactivity of monomeric furans, the absence of high oxidation state substituents on C2 and/or C5 of the furan ring does not seem to have any detrimental effect on chemical selectivity. One major difference in this series is that while 2,5-PEF is opaque after cooling down from the melt, the 2,4- and 3,4 analogues are translucent, indicative of a lower degree of crystallinity, or lower rate of crystallisation. For comparison, two PET examples are included in Table 1; an as-synthesised sample (polycondensation conditions are described in the Experimental section) and a commercial, bottle-grade PET sample. These reference materials will be discussed further in the thermal analysis section.

In the biobased 1,3-propanediol (PDO) series (Table 1, entries 4–6), the significantly higher molecular weight of the 2,5-PPF is striking, while for the other two FDCA isomers there is little difference with the corresponding EG polyesters. In this series all polyesters were obtained as translucent materials. Changing to 1,4-butanediol (1,4-BDO) appears to have more pronounced effects. While the M_n values of 2,5- and 2,4-P14BF are very similar, the former deviates with regard to PDI. In this series the 3,4-FDCA isomer yields the highest molecular weight polyester, while all polyesters were obtained as opaque materials from the melt.

The last diol included in this study is 2,3-butanediol (2,3-BDO). This secondary diol is less reactive than its primary isomer 1,4-BDO, which is obvious from the significantly lower M_w s. While the reference 2,5-P23BF is obtained with a similar M_n as reported in the literature,¹⁶ the 2,4-analogue was obtained as low M_w material only. In contrast, the 3,4-analogue is comparable to the 2,5-isomer. From the data in Table 1 no obvious correlation can be found between the FDCA substitution pattern and reactivity as would follow from systematic differences in molecular weight build-up.

Fig. 1 shows the ^1H -NMR spectra of the three isomeric PEF polymers (^{13}C -NMR spectra are shown in the ESI†). Due to the symmetry of 2,5-FDCA, the ^1H -NMR spectrum of 2,5-PEF shows only 1 furanic proton, and 1 broad singlet for the ethylene glycol residue (Fig. 1a). In the case of 2,4-PEF, 2 furanic singlets at 8.2 (H5) and 7.6 (H3) ppm illustrate the asymmetry of this compound. Furthermore, also the EG residue is split up. While the chemical shift of the EG residue is similar to

that of the 2,5-analogue, H3 has shifted downfield in 2,4-PEF, while H5 resonates even further downfield due to the neighbouring oxygen group (Fig. 1b). The 3,4-isomer is symmetrical, resulting in singlets for the furanic proton and the EG residue respectively. H2/H5 shows a slight upfield shift compared to 2,4-PEF, while this is also observed for the EG signal (Fig. 1c).

Detailed analysis of the EG-residue part of the ^1H -NMR spectra of the PEF series shows besides end-groups (M_n values obtained by end-group analysis confirm GPC results) also the presence of signals that can be attributed to diethylene glycol (DEG) (see ESI, Fig. 31†). This is not surprising since the dehydration of ethylene glycol in the presence of acid catalyst leads to the formation of diethylene glycol which was identified as one of the most important side products in PET synthesis.^{17–20} The incorporation of DEG as a co-monomer in PET synthesis results in a decrease in melting temperature of about 5 °C (for each percent increase in DEG concentration). DEG incorporation also affects other properties like mechanical, hydrolytic and light stability as well as the thermal and oxidative degradation behavior of the material.²¹

We estimated the DEG incorporation in the PEF series to be less than 1% (based on ^1H -NMR analysis, see ESI, Fig. 31†), which is lower than typically encountered during PET synthesis.^{22–26} Remarkably, DEG formation and incorporation into PEF has not been reported previously.^{5,27–29}

Sousa *et al.* reported DEG incorporation of up to 5.2% in EG copolymers derived from TA and 2,5-FDCA (80 : 20).³⁰ Furthermore, these authors showed that the DEG content decreases with increasing 2,5-FDCA content (1.7% DEG for 2,5-FDCA-TA, 90 : 10), which is in agreement with our findings for the FDCA-EG homopolyesters. NMR spectra of the other FDCA polyesters are given in the ESI.†

Thermogravimetric analysis (TGA) of the FDCA polyesters shows that all new polyesters have comparable or even higher thermal stability compared to the 2,5-FDCA polyesters (Table 2). The consistently higher thermal stability of the 2,4-FDCA based polyesters is remarkable given the fact that these materials have on average the lowest M_w s according to GPC (see Table 1).

For all polyesters a single stage decomposition mechanism is observed between 350 and 425 °C. Representative TGA traces of poly(ethylene-furandicarboxylates) are shown in Fig. 2 (TGA curves for the other polymers are shown in the ESI†). Fig. 2 also includes the TGA traces of the two PET reference samples. The higher thermal stability of the commercial sample is probably due to the higher M_w and the presence of stabilisers. From Fig. 2 it is clear that the PEF series is intrinsically less thermally stable at temperatures in excess of 350 °C. Nevertheless, all polyfurandicarboxylates are stable up to 300 °C, which still allows for a very broad processing window for these materials.

Whereas TGA analysis showed no dramatic differences between the FDCA polyesters, differential scanning calorimetry (DSC) revealed the remarkable effects of the position of the carboxylic groups in the FDCA isomers (Table 2). In the PEF series the T_g of 2,4-PEF (Table 2, entry 2) is only 6 °C lower



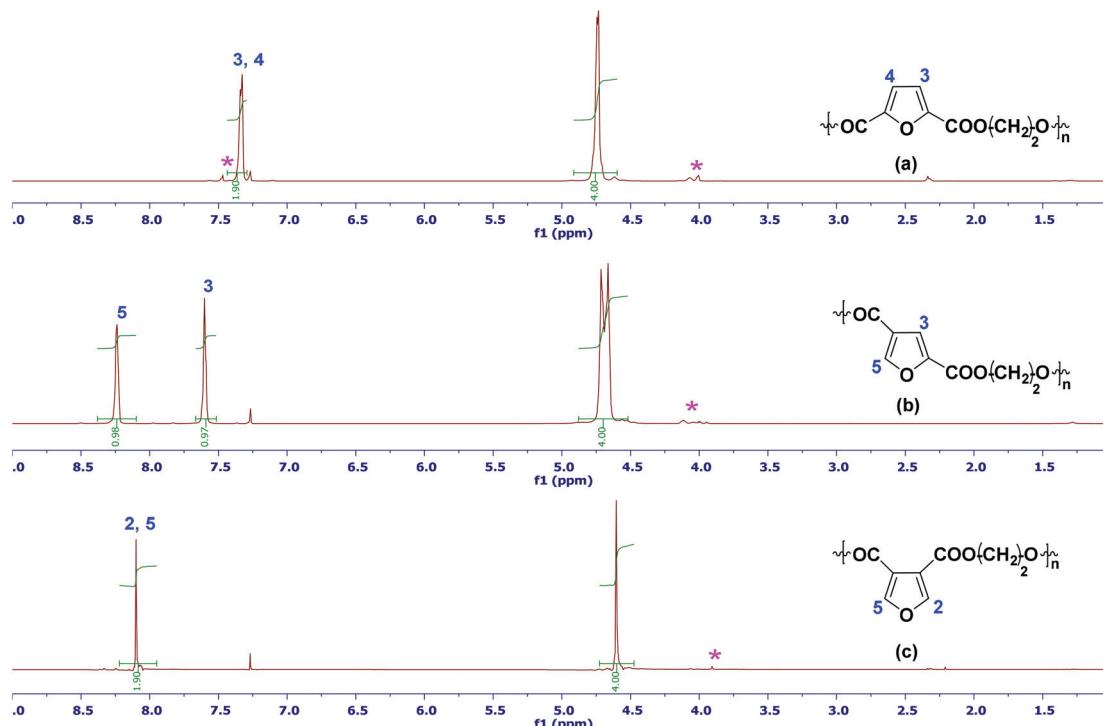


Fig. 1 The representative ^1H -NMR spectra of precipitated (a) 2,5-PEF; (b) 2,4-PEF and (c) 3,4-PEF in CDCl_3 and TFA-d (6 : 1). The asterisk indicates end groups.

Table 2 Thermal properties of the FDCA polyesters obtained by TGA and DSC analyses

Entry	Code	TGA ^a		DSC ^d					
		$T_{5\%}^b$ (°C)	T_{\max}^c (°C)	First heating			Second heating		
				T_g^e (°C)	T_m^f (°C)	ΔH_m (J g ⁻¹)	T_g (°C)	T_m (°C)	ΔH_m (J g ⁻¹)
Polyethylene furandicarboxylate									
1	2,5-PEF	339	411	80	211	55	79	209	55
2	2,4-PEF	345	429	71	n.o. ^h	—	73	n.o. ^h	—
3	3,4-PEF	321	415	36	153	63	35	155 ^g	64
Poly-1,3-propylene furandicarboxylate									
4	2,5-PPF	330	405	54	175	32	51	173	22
5	2,4-PPF	342	415	46	n.o. ^h	—	46	83 ^g	0.5
6	3,4-PPF	328	406	-9	n.o. ^h	—	-6	n.o. ^h	—
Poly-1,4-butylene furandicarboxylate									
7	2,5-P14BF	304	367	51	173	39	38	170	39
8	2,4-P14BF	328	402	29	68/100/116	5/1/10	34	79/103/117 ^g	5/2/8
9	3,4-P14BF	312	395	4	55/70/79	0.7/10/5.5	-6	55/69/80 ^g	1/6.2/1.5
Poly-2,3-butylene furandicarboxylate									
10	2,5-P23BF	279	351	90	— ^h	—	87	—	—
11	2,4-P23BF	279	365	88	— ^h	—	82	—	—
12	3,4-P23BF	285	363	57	— ^h	—	52	—	—
Polyethylene terephthalate									
13	PET ⁱ	355	445	71	243	40	73	243	39
14	PET ^j	371	451	81	242	69	77	245	42

^a TGA was performed on crude materials recorded from 30 to 600 °C at 10 °C min⁻¹ under a N_2 atmosphere. ^b Temperature at 5% weight loss.

^c Temperature at maximum rate of decomposition. ^d DSC was performed from -60 °C to 230 °C with two heating and cooling runs at 10 °C min⁻¹. ^e Glass-transition temperature. ^f Melting temperature. ^g Melting temperature was determined after annealing. ^h No melting endotherm was observed up to the maximum temperature (230 °C). ⁱ As-synthesised PET. ^j Commercial bottle-grade PET.



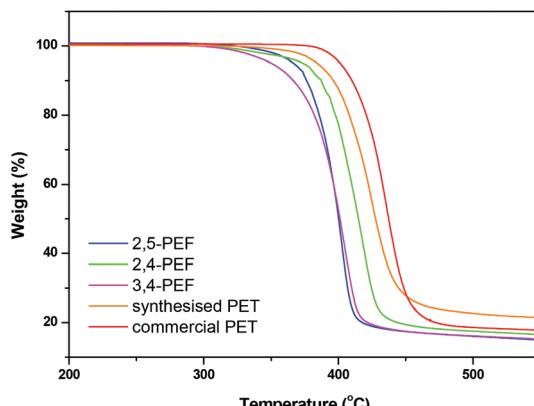


Fig. 2 TGA traces of (crude) polyethylene furandicarboxylates and polyethylene terephthalates recorded from 30 to 600 °C at 10 °C min⁻¹ under a N₂ atmosphere.

than that of 2,5-PEF, while the T_g of 3,4-PEF is significantly lower (Table 2, entry 3). In the PPF series a similar trend can be observed. Again the difference in T_g between 2,5-PPF and the 2,4 isomer is small (5 °C). For 3,4-PPF the T_g is decreased significantly to -6 °C (Table 2, entry 6). Nevertheless, the observed drop in T_g (approx. 40 °C) is only slightly larger compared to the ones observed for the 2,5- and 2,4-isomers (approx. 30 °C). The 1,4-BDO series again displays a comparable trend; while the T_g decreases further, the difference between the 2,5- and 2,4-PBFs remains small, while no further decrease for the 3,4-isomer is observed. The observed values for 2,5-P14BF and 3,4-P14BF are in good agreement with those reported previously.^{5,12,39}

All polyesters based on 2,3-BDO were, as expected, fully amorphous. 2,3-BDO is known to increase the T_g due to hindered rotation about the C2-C3 axis (compared to EG). The T_g value of 87 °C (Table 2, entry 10) found for the 2,5-P23BF corresponds to the one reported recently by Gubbels *et al.*¹⁶ Again, the T_g values of the 2,5 and 2,4 isomers are within a 5 °C range, while the 3,4-isomer shows a considerable increase in T_g . As the M_{ws} of the 2,3-BDO series are significantly lower compared to EG series, the T_g increasing effect of 2,3-BDO is quite dramatic.

The effect of the position of the carboxylic acid groups on the T_g of the polyesters is graphically represented in Fig. 3, which makes it even more clear that the 2,4-analogue is highly comparable to the 2,5-isomer. With regard to melting transitions the position of the carboxylic acid groups in FDCA has a dramatic impact. The observed melting points for the 2,5-FDCA based polyesters are all in good agreement with those reported in the literature.^{5,14,39} Whereas 2,5-PEF already has a substantially lower T_m than PET (209 °C vs. 245 °C), no melting point was observed in the case of 2,4-PEF even after annealing at 90 °C for 5 h. In contrast, for 3,4-PEF a melting point of 155 °C was recorded after annealing at 100 °C for 5 h. The surprising absence of melting point of 2,4-PEF is in sharp contrast to its high T_g of 73 °C. The T_g/T_m ratio (in K) of 2,5- and 3,4-PEF are 0.72 (in line with those reported for other

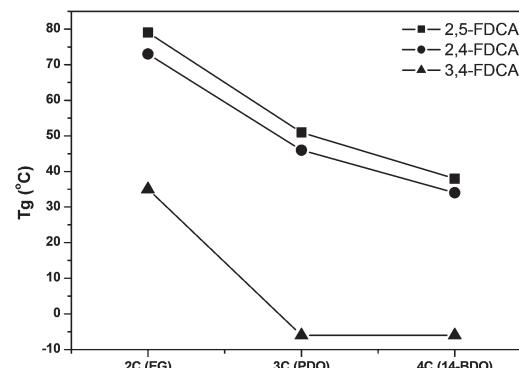


Fig. 3 Plot of T_g s of FDCA polyesters against carbon chain length of linear $\alpha\omega$ -diols.

semi-aromatic EG polyesters).⁴⁰ In the PPF series the T_m of the 2,4-FDCA polyester is approx. 90 °C lower than that of the 2,5-analogue. Again, only after annealing a clear melting endotherm could be observed. Despite several attempts, no melting transitions could be recorded for the 3,4-PPF. In contrast, all polyesters based on P14BF are semi-crystalline. The 2,4-FDCA based polyester showed multimodal melting behavior after annealing at 60 °C for 5 h, with the lowest melting point again approx. 90 °C lower than for the 2,5-analogue. Comparable multimodal melting behavior was observed for 3,4-P14BF after annealing at 40 °C for 5 h.

Fig. 4(a and b) shows the DSC heating and cooling curves of all three PEF isomers. The absence of cold crystallization in the case of 2,4- and 3,4-PEF (as compared to the 2,5-analogue) further indicates that these polymers have very low rates of crystallization.

In order to find an explanation for the observed differences between the FDCA polyesters, we compared the structural characteristics of the FDCA isomers in relation to their phthalic acid analogues, as well as the thermal properties of the ensuing EG polyesters in Table 3. The data are arranged in descending order with respect to the interatomic distance (D) between the carboxylic acid groups in the respective diacids.

With regard to symmetry, 2,4-FDCA is the least symmetrical diacid in the series under investigation. Comparison of the D and the projected angle between the C1-C2 bond and the C5-C6 bond (α) leads to the conclusion that contrary to common opinion in the literature the 2,5-FDCA isomer is not similar to TA, but rather to IPA. While the 2,4-isomer is closer to TA, the 3,4-isomer has characteristics comparable to PA (Fig. 5). A plot of D vs. α , as expected, shows a nearly linear relationship (Fig. 6a). In contrast, no unambiguous correlation can be found between α and T_g or T_m of the EG polyesters (Fig. 6b). Nevertheless, the 2,4-isomer clearly induces anomalous effects in the crystallinity. The main difference between 2,4-FDCA and the other diacids is the lower symmetry of the former. Other factors that could influence crystallinity are *e.g.* dipole moments and π -stacking. Further research is required here, but falls outside of the scope of the present study.



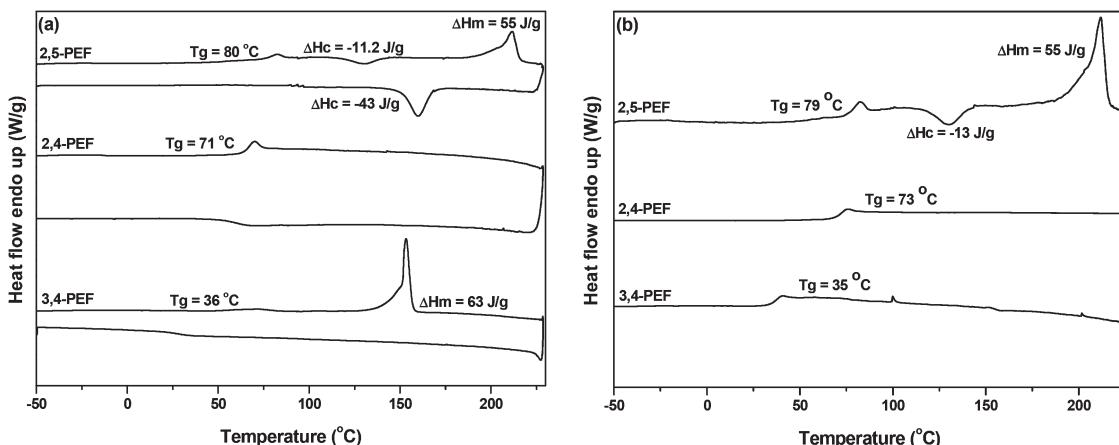


Fig. 4 (a) First heating/cooling and (b) second heating DSC curves of poly(ethylene-furandicarboxylate)s derived from FDCA analogues. The heating and cooling rates are 10°C per minute.

Table 3 Comparison of structural data for monomeric FDCA and phthalates, and thermal properties of corresponding EG polyesters

Diacid	Symmetry	D^a (Å)	α^b (°)	EG polyester T_g (°C)	EG polyester T_m (°C)
TA ³¹	C_i	5.73	180	73	243
2,4-FDCA-Me ⁹	$C_{2/c}$	5.08	150	73	—
2,5-FDCA ³²	C_s	4.83	129	79	209
IPA ³³	C_{2v}	4.40	120	55 ^{34,35}	235
3,4-FDCA-Me ^{36,37}	P_{21}/a	3.37	83	35	155
PA ³⁸	$C_{2/c}$ or C_c	2.67	60	38 ¹⁵	—

^a Interatomic distance between C1 and C6 (carboxylic acid groups).

^b Projected angle between the C1-C2 bond and the C5-C6 bond.

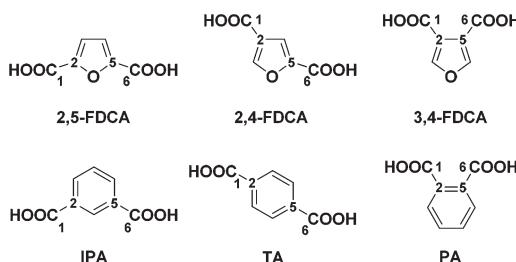


Fig. 5 Atom labelling scheme for FDCA and phthalates.

Fig. 7 shows the wide angle X-ray diffraction (WAXD) patterns of the isomeric PEFs which were used to calculate the degree of crystallinity of these polymers after precipitation from methanol (see also Table 4). The 2,5-isomer showed only a surprisingly low degree of crystallinity of 14% (after subtraction of the amorphous halo, see ESI†). Dividing the melting enthalpy of the first DSC heating run (corrected for cold crystallization) by the degree of crystallinity of the sample allows for estimating the heat of fusion of the 100% crystalline material. When this is done for the precipitated 2,5-PEF an unrealistically high value of 314 J g^{-1} is obtained (compared to reference values for *e.g.* PET and PBT, Table 4). This prompted us to anneal the sample (for 15 h at 175°C), resulting in a

significantly higher degree of crystallinity of 56%, and a heat of fusion of 109 J g^{-1} (DSC traces for annealed 2,5-PEF are shown in the ESI†). In the case of 2,4-PEF, no melting was observed in the DSC of the precipitated material, which was supported by the absence of crystalline reflections in the WAXD diffractogram (Fig. 7). Attempts to induce crystallinity in 2,4-PEF by annealing for up to 5.0 h at 90°C were unsuccessful. In contrast, precipitated 3,4-PEF proved to be highly crystalline from the WAXD analysis (55%), giving an estimated 116 J g^{-1} for the heat of fusion at 100% crystallinity.

Systematic comparison with literature values of analogous phthalate based polyesters is hampered by the surprisingly scarce data on these polymers. Nevertheless, the estimated heat of fusion of 2,5-PEF and 3,4-PEF are comparable to those reported for PET and PBT. Unfortunately, since poly(ethylene phthalate) or PEP is reported to be amorphous,¹⁵ no comparison can be made with this structural analogue. While no literature value is known for the heat of fusion of poly(ethylene isophthalate) (PEI), reported values for poly(butylene isophthalate) or PBI differ strongly, ranging from 115 to 192 J g^{-1} ,^{42,43} which makes it nearly impossible to compare.

Conclusions

We have successfully prepared and characterised a broad set of furandicarboxylic acid based polyesters by melt polycondensation, yielding medium to high molecular weight polymers. Three different FDCA isomers, products obtained by Henkel-type disproportionation of agro-residue based furoic acid, have been investigated. Contrary to expectations, the position of the carboxylic acid groups on the furan ring showed no clear correlation with regard to reactivity (yield, M_n) or selectivity (PDI, colour). TGA analysis showed that all FDCA polyesters had sufficient thermal stability, especially in relation to their respective melting points. Thermal analysis by DSC however revealed dramatic effects of the isomeric substitution. Whereas the T_g s of the 2,4-FDCA polyesters are very similar to



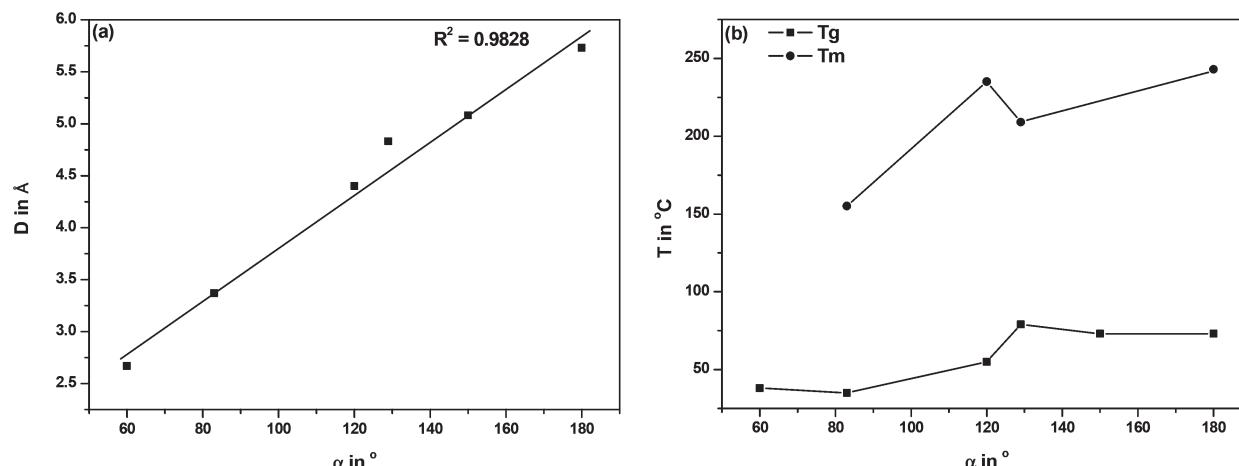


Fig. 6 (a) Plot of angle between the C1–C2 bond and the C5–C6 bonds against interatomic distance between C1 and C6 (carboxylic acid groups); (b) plot of angle between the C1–C2 bond and the C5–C6 bonds against T_g and T_m of EG based polyesters.

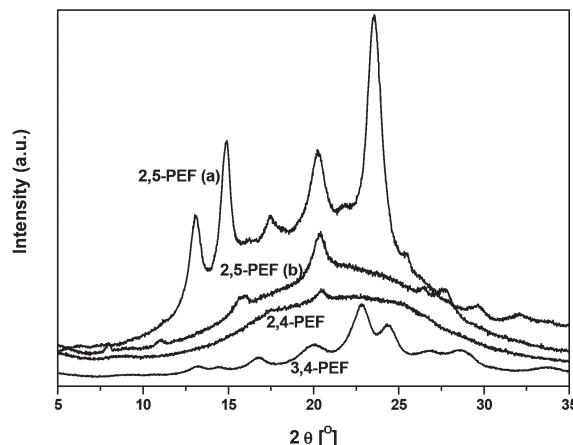


Fig. 7 WAXD diffractograms of 2,5-PEF ((a) annealed at 175 $^{\circ}\text{C}$ for 15 h, (b) precipitated from MeOH) and precipitated 2,4-PEF and 3,4-PEF.

Table 4 Degree of crystallinity and estimated heat of fusion of 100% crystalline polyesters based on FDCAs and phthalates

Polyester	D^a (%)	ΔH_m^b (J g^{-1})	ΔH_m^0 (J g^{-1})
2,5-PEF	14	44	314
2,5-PEF	56	61	109
2,4-PEF	— ^c	—	—
3,4-PEF	55	64	116
PET	—	—	140 ⁴¹
PBT	—	—	145 ⁴¹
PBI	—	—	115/192 ^{42,43}

^a Degree of crystallinity from WAXD. ^b From first DSC heating runs, corrected for cold crystallisation. ^c Amorphous material.

those based on the 2,5-isomer or even TA, no melting point of the former was observed. Furthermore, DSC analysis indicates a very low rate of crystallisation, which is apparent from the need for extensive annealing in order to induce crystallinity. Preliminary attempts to identify the parameters responsible for the observed differences in polymer properties by means of

a structure–property analysis did not reveal any clear correlations. WAXD analysis confirmed the semi-crystalline nature of the 2,5- and 3,4-PEF isomers, and allowed us to estimate their respective heat of fusion for the first time. Overall we have shown that 2,4- and 3,4-FDCA polyesters can be made in sufficient M_w s by industrially applicable methods, and that these materials have (commercially) interesting, and sometimes outrightly intriguing properties. More in-depth analysis of these new materials, as well as application in specific product areas is part of ongoing investigations.

Experimental section

Materials

The synthesis of dimethyl furan-2,5-dicarboxylate and furan-2,4-dicarboxylate was described in recent publications.^{5,9} Dimethyl furan-3,4-dicarboxylate (98%, Sigma-Aldrich), ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich), 1,3-propane diol ($\geq 99.6\%$, Sigma-Aldrich), 1,4-butane diol ($\geq 99\%$, Sigma-Aldrich), 2,3-butane diol ($\geq 99\%$, Sigma-Aldrich), titanium(IV) isopropoxide ($\geq 97\%$, Sigma-Aldrich), toluene (anhydrous, 99.8%, Sigma-Aldrich), *o*-xylene (anhydrous, 97%, Sigma-Aldrich) trifluoroacetic acid (99%, Sigma-Aldrich), chloroform (Merck, p.a.), Methanol (Merck, p.a.) and chloroform-d (99.8 atom% D, Sigma-Aldrich). All the chemicals were used as received, unless denoted otherwise.

Methods

Fourier transform infrared (FT-IR) spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer equipped with a Pike MIRacle ATR Diamond/ZnSe single reflection plate and a DTSG-detector. The measurement resolution was set at 4 cm^{-1} , and the spectra were collected in the range 4000–650 cm^{-1} with 32 co-added scans. NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.17 MHz (^1H) and 100.62 MHz (^{13}C). Differential Scanning



Calorimetry (DSC) measurements were conducted on a Perkin Elmer Diamond series DSC. The temperature range used was -60 °C up to 230 °C at a heating rate and cooling rate of 10 °C min $^{-1}$. The thermal stabilities of the polyesters were determined by thermogravimetric analysis (TGA) with a STA 6000 (Simultaneous Thermal Analyser) from PerkinElmer Instrument. The samples were heated from 30 to 600 °C at a heating rate of 10 °C min $^{-1}$ under a nitrogen flow of 40 mL min $^{-1}$. The absolute molecular weights of the polyesters were determined by Gel Permeation Chromatography (GPC) on a Viscotek HP-SEC system, VE-2001 GPC max (pump and auto sampler) equipped with TDA305 Triple Detector Array (Right Angle Light Scattering (RALS) + Low Angle Light Scattering (LALS), Refractive Index (RI) Detector and Viscometer). 2X GPC column PSS PFG analytical linear M and guard column, molecular range ~ 250 – 2.5×10^6 D (PMMA in HFIP). Data were calculated with OmniSECTM, Version 4.6 software. Hexafluoroisopropanol (HFIP) containing 0.02 M potassium trifluoroacetate was used as an eluent with a flow-rate of 0.7 mL min $^{-1}$. Control measurements were performed with Easy vial PMMA standards from Agilent. Wide angle X-ray scattering (WAXS) powder diffractograms were recorded on a Philips PC-APD diffractometer in the reflection geometry in the angular range 4 – 40 °(2 θ), with a step size of 0.02 °(2 θ) and an acquisition time of 1.0 s per step. The Cu K $\alpha 1$ radiation from the anode, generated at 40 kV and 30 mA, was monochromatized using a 15 μ m Ni foil ($\lambda = 0.1542$ nm). The diffractometer was equipped with a 1 ° divergence slit, a 0.2 mm receiving slit, and a 1 ° scatter slit.

General polycondensation procedure for FDCAs analogues

In a typical experiment, polycondensations were conducted in 100 mL three-neck round-bottom flasks equipped with a mechanical overhead stirrer, nitrogen inlet and water-condenser. Furandicarboxylic acid (1.5 g, 8.14 mmol) and diol (16.2 mmol) were charged into the reaction flask. The set-up was placed under vacuum and purged with nitrogen gas, and this cycle was repeated three times. The polycondensation method involves two stages. During the first stage, the reaction was carried out under nitrogen gas to form oligomers. The reaction mixture was heated in the silicone-oil bath at 115 °C for 15 min with constant stirring. After observing the complete melt of the mixture, the catalyst Ti(O*i*Pr) $_4$ (1.25 mol%) in 1 mL of toluene was added into the flask under a continuous flow of nitrogen gas. The temperature was now increased to 160 °C and stirred for 12 h, and finally to 200 – 215 °C for 1.5 h to complete the first stage of the pre-polymerization reaction. The methanol and toluene were collected in the cooling flask. During the second stage of the polycondensation to obtain high molecular weight polyesters, a high vacuum of 0.02 mbar was applied gradually to the polycondensation set-up at 210 – 215 °C for 2 h. After completion of the reaction, the reaction mixture was cooled down to room temperature under a nitrogen atmosphere. The polymer was purified by dissolving in 10 mL of chloroform-TFA mixture (6 : 1) and precipitated in 100 mL of methanol, filtered and dried *in vacuo* at 40 °C for 12 h to yield a white fibrous material.

100 mL of methanol, filtered and dried *in vacuo* at 40 °C for 12 h to yield a white powder.

Polycondensation procedure for PET synthesis

In a typical experiment, polycondensations were conducted in 100 mL three-neck round-bottom flasks equipped with a magnetic stirrer, nitrogen inlet and water-condenser. DMT (10.6 g, 54.6 mmol) and diol (4.5 g, 72.5 mmol) were charged into the reaction flask. The set-up was placed under vacuum and purged with nitrogen gas, and this cycle was repeated three times. The polycondensation method involves two stages. During the first stage, the reaction was carried out under nitrogen gas to form oligomers. The reaction mixture was heated in a salt bath (a mixture of KNO₃ (53 wt%), NaNO₂ (40 wt%), and NaNO₃ (7 wt%)) at 165 °C for 15 min with constant stirring. After observing the complete melt of the mixture, the catalyst Ti(O*i*Pr) $_4$ (0.02 mol%) in 2 mL of *o*-xylene was added into the flask under the continuous flow of nitrogen gas. The temperature was now increased to 165 °C and stirred for 12 h, and finally to 265 °C for 4 h to complete the first stage of the pre-polymerization reaction. The methanol and *o*-xylene were collected in the cooling flask. During the second stage of the polycondensation to obtain high molecular weight polyesters, a high vacuum of 0.1 mbar was applied gradually to the polycondensation set-up at 265 °C for 3 h. After completion of the reaction, the reaction mixture was cooled down to room temperature under a nitrogen atmosphere. The polymer was purified by dissolving in 10 mL of chloroform-TFA mixture (6 : 1) and precipitated in 100 mL of methanol, filtered and dried *in vacuo* at 40 °C for 12 h to yield a white fibrous material.

Poly(ethylene-2,5-furandicarboxylate) (2,5-PEF)

FT-IR (neat): $\nu = 3126, 2966, 1722, 1582, 1269, 1021, 969, 829, 763$ cm $^{-1}$; 1 H NMR (400 MHz, CDCl₃ + CF₃COOD): $\delta = 7.3$ (s, 2 H), 4.7 (s, 4 H) ppm; 13 C NMR (100 MHz, CDCl₃ + CF₃COOD): $\delta = 159.5, 146.1, 121.1, 63.7$ ppm.

Poly(ethylene-2,4-furandicarboxylate) (2,4-PEF)

FT-IR (neat): $\nu = 3142, 2960, 1726, 1591, 1264, 1080, 978, 868, 760$ cm $^{-1}$; 1 H NMR (400 MHz, CDCl₃ + CF₃COOD): $\delta = 8.2$ (s, 1 H), 7.6 (s, 1 H), 4.7 (d, 4 H) ppm; 13 C NMR (100 MHz, CDCl₃ + CF₃COOD): $\delta = 163.8, 160.0, 152.7, 144.8, 120.4, 118.8, 63.9, 63.6$ ppm.

Poly(ethylene-3,4-furandicarboxylate) (3,4-PEF)

FT-IR (neat): $\nu = 3144, 2948, 1726, 1545, 1268, 1064, 878, 835, 761$ cm $^{-1}$; 1 H NMR (400 MHz, CDCl₃ + CF₃COOD): $\delta = 8.1$ (s, 2 H), 4.6 (s, 4 H) ppm; 13 C NMR (100 MHz, CDCl₃ + CF₃COOD): $\delta = 163.0, 150.8, 116.7, 63.2$ ppm.

Poly(propylene-2,5-furandicarboxylate) (2,5-PPF)

FT-IR (neat): $\nu = 3121, 2950, 1723, 1581, 1272, 1035, 967, 828, 765$ cm $^{-1}$; 1 H NMR (400 MHz, CDCl₃ + CF₃COOD): $\delta = 7.5$ (s, 2 H), 4.7 (t, 4 H), 2.4 (q, 2 H) ppm; 13 C NMR (100 MHz, CDCl₃ + CF₃COOD): $\delta = 154.6, 141.0, 114.6, 57.8, 22.0$ ppm.



Poly(propylene-2,4-furandicarboxylate) (2,4-PPF)

FT-IR (neat): ν = 3143, 2958, 1718, 1590, 1260, 1076, 978, 827, 760 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.2 (s, 1H), 7.5 (s, 1H), 4.5 (m, 4H), 2.2 (m, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 163.7, 159.8, 151.9, 144.7, 120.4, 118.4, 62.9, 62.4, 27.4 ppm.

Poly(propylene-3,4-furandicarboxylate) (3,4-PPF)

FT-IR (neat): ν = 3148, 2964, 1719, 1540, 1270, 1055, 932, 884, 754 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.0 (s, 2H), 4.4 (t, 4H), 2.2 (m, 2H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 163.8, 150.6, 116.9, 62.7, 27.2 ppm.

Poly(1,4-butylene-2,5-furandicarboxylate) (2,5-P14BF)

FT-IR (neat): ν = 3120, 2965, 1730, 1579, 1274, 1023, 968, 824, 768 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 7.3 (s, 2H), 4.4 (m, 4H), 1.9 (m, 4H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 159.1, 145.3, 118.6, 65.3, 23.6 ppm.

Poly(1,4-butylene-2,4-furandicarboxylate) (2,4-P14BF)

FT-IR (neat): ν = 3139, 2964, 1720, 1588, 1262, 1078, 979, 864, 761 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.2 (s, 1H), 7.5 (s, 1H), 4.4 (d, 4H), 1.9 (s, 4H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 163.8, 162.4, 150.1, 143.1, 118.7, 116.3, 64.4, 64.0, 23.0 ppm.

Poly(1,4-butylene-3,4-furandicarboxylate) (3,4-P14BF)

FT-IR (neat): ν = 3146, 2954, 1730, 1538, 1273, 1063, 937, 886, 761 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.0 (s, 2H), 4.4 (s, 4H), 1.9 (s, 4H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 164.2, 150.5, 116.9, 65.9, 24.6 ppm.

Poly(2,3-butylene-2,5-furandicarboxylate) (2,5-P23BF)

FT-IR (neat): ν = 3127, 2987, 1719, 1580, 1268, 1079, 964, 826, 764 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 7.42–7.08 (m, 2H), 5.60–5.20 (m, 2H), 1.60–1.19 (m, 6H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 156.44, 143.86, 117.25, 71.62, 13.04, 11.92 ppm.

Poly(2,3-butylene-2,4-furandicarboxylate) (2,4-P23BF)

FT-IR (neat): ν = 3145, 2988, 1717, 1589, 1255, 1191, 976, 864, 758 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.31–8.00 (m, 1H), 7.53 (t, J = 4.0 Hz, 1H), 5.36 (ddqd, J = 19.0, 12.7, 6.8, 6.4, 3.0 Hz, 2H), 1.42 (p, J = 5.4, 4.7 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 162.12, 158.30, 151.09, 144.05, 119.73, 119.62, 117.36, 73.07, 72.63, 14.72, 14.72, 13.66 ppm.

Poly(2,3-butylene-3,4-furandicarboxylate) (3,4-P23BF)

FT-IR (neat): ν = 3431, 2987, 1723, 1539, 1267, 1050, 1000, 843, 755 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 8.15–7.93 (m, 2H), 5.28 (hept, J = 5.3, 4.0 Hz, 2H), 1.37 (t, J = 5.7 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$): δ = 161.02, 149.07, 115.85, 71.91, 14.16, 13.00 ppm.

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Notes and references

- 1 Climate Change 2013: The Physical Science Basis.
- 2 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539–554.
- 3 E. d. Jong, M. A. Dam, L. Sipos and G. J. M. Gruter, in *Bio-based Monomers, Polymers, and Materials*, American Chemical Society, 2012, pp. 1–13.
- 4 D. S. van Es, *J. Renew. Mater.*, 2013, **1**, 61–72.
- 5 R. J. I. Knoop, W. Vogelzang, J. van Haveren and D. S. van Es, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4191–4199.
- 6 J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
- 7 R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499–1597.
- 8 F. van der Klis, A. E. Frissen, J. van Haveren and D. S. van Es, *ChemSusChem*, 2013, **6**, 1640–1645.
- 9 S. Thiagarajan, A. Pukin, J. van Haveren, M. Lutz and D. S. van Es, *RSC Adv.*, 2013, **3**, 15678–15686.
- 10 T. Pan, J. Deng, Q. Xu, Y. Zuo, Q.-X. Guo and Y. Fu, *ChemSusChem*, 2013, **6**, 47–50.
- 11 Y. Hachihama, T. Shono and K. Hyono, *Technol. Rep. Osaka Univ.*, 1958, **8**, 475–480.
- 12 A. Chaabouni, S. Gharbi, M. Abid, S. Boufi, R. E. Gharbi and A. Gandini, *J. Soci T Chimique Tunisie*, 1999, **4**, 547–558.
- 13 I. W. Ashworth, M. C. Bowden, B. Dembofsky, D. Levin, W. Moss, E. Robinson, N. Szczer and J. Virica, *Org. Process Res. Dev.*, 2002, **7**, 74–81.
- 14 M. Gomes, A. Gandini, A. J. D. Silvestre and B. Reis, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 3759–3768.
- 15 B. Lee, J. W. Lee, S. W. Lee, J. Yoon and M. Ree, *Polym. Eng. Sci.*, 2004, **44**, 1682–1691.
- 16 E. Gubbels, L. Jasinska-Walc and C. E. Koning, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 890–898.
- 17 L. H. Buxbaum, *Angew. Chem., Int. Ed.*, 1968, **7**, 182–190.
- 18 L. H. Buxbaum, *Angew. Chem., Ger. Ed.*, 1968, **80**, 225–233.
- 19 R. Janssen, H. Ruysschaert and R. Vroom, *Makromol. Chem.*, 1964, **77**, 153–158.
- 20 H. Zimmerman and N. T. Kim, *Polym. Eng. Sci.*, 1980, **20**, 680–683.
- 21 J. M. Besnoin and K. Y. Choi, *J. Macromol. Sci., C*, 1989, **29**, 55–81.
- 22 S. G. Hovenkamp and J. P. Munting, *J. Polym. Sci., Part A: Polym. Chem.*, 1970, **8**, 679–682.
- 23 J.-W. Chen and L.-W. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 3073–3080.



24 J.-W. Chen and L.-W. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1797–1803.

25 L.-W. Chen and J.-W. Chen, *J. Appl. Polym. Sci.*, 2000, **75**, 1229–1234.

26 L.-W. Chen and J.-W. Chen, *J. Appl. Polym. Sci.*, 2000, **75**, 1221–1228.

27 A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa and M. Gomes, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 295–298.

28 J. Ma, Y. Pang, M. Wang, J. Xu, H. Ma and X. Nie, *J. Mater. Chem.*, 2012, **22**, 3457–3461.

29 M. Jiang, Q. Liu, Q. Zhang, C. Ye and G. Zhou, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 1026–1036.

30 A. F. Sousa, M. Matos, C. S. R. Freire, A. J. D. Silvestre and J. F. J. Coelho, *Polymer*, 2013, **54**, 513–519.

31 M. Bailey and C. J. Brown, *Acta Crystallogr.*, 1967, **22**, 387–391.

32 E. Martuscelli and C. Pedone, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 175–179.

33 R. Alcala and S. Martinez-Carrera, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 1671–1677.

34 Y. S. Hu, A. Hiltner and E. Baer, *J. Appl. Polym. Sci.*, 2005, **98**, 1629–1642.

35 S. W. Lee, M. Ree, C. E. Park, Y. K. Jung, C. S. Park, Y. S. Jin and D. C. Bae, *Polymer*, 1999, **40**, 7137–7146.

36 Y. Okada, K. Nakatsu and A. Shimada, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 928–933.

37 D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, 1964, **86**, 1660–1666.

38 T. G. D. Van Schalkwyk, *Acta Crystallogr.*, 1954, **7**, 775–775.

39 J. Zhu, J. Cai, W. Xie, P.-H. Chen, M. Gazzano, M. Scandola and R. A. Gross, *Macromolecules*, 2013, **46**, 796–804.

40 W. A. Lee and G. J. Knight, *Brit. Poly. J.*, 1970, **2**, 73–80.

41 B. Wunderlich, *Thermal Analysis of Polymeric Materials*, Springer, 1990.

42 M. C. Righetti, M. Pizzoli and A. Munari, *Macromol. Chem. Phys.*, 1994, **195**, 2039–2047.

43 H. K. Yip and H. L. Williams, *J. Appl. Polym. Sci.*, 1976, **20**, 1209–1215.

