Synthesis and Characterization of Novel Renewable Polyesters Based on 2,5-Furandicarboxylic Acid and 2,3-Butanediol

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ABSTRACT: Novel polyesters from 2,5-furandicarboxylic acid or 2,5-dimethyl-furandicarboxylate and 2,3-butanediol have been synthesized via bulk polycondensation catalyzed by titanium (IV) *n*-butoxide, tin (IV) ethylhexanoate, or zirconium (IV) butoxide. The polymers were analyzed by size exclusion chromatography, nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser ionization-desorption time-of-flight mass spectrometry, electrospray ionization quadruple time-of-flight mass spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. Fully bio-based polyesters with number average molecular weights ranging from 2 to 7 kg/mol were obtained which can

INTRODUCTION Polymeric materials synthesized from renewable monomers have already gained an established position among synthetic materials, both in academia and in industry. Owing to a growing concern about the depletion of the fossil fuel stock and the accompanying price fluctuations, a large drive has been created for finding suitable alternatives. Bio-based monomers proved to be very well-suited alternatives for fossil fuel-based building blocks. Materials based on these monomers have been intensively investigated by many research groups.^{1–17}

A particular attractive class of bio-based monomers are the furan-based molecules. These compounds show a high potential in step-growth and chain-growth polymerizations. As reported by Gandini et al.,^{18–20} furanic-based monomers are derived from two compounds, that is furfural (F) and 5hydroxymethylfurfural (HMF).^{18–21} The acid-catalyzed dehydration of fructose to HMF can be performed with high selectivity and yields in high-boiling polar solvents.²² However, owing to expensive purification procedures using highboiling solvents (e.g., dimethyl sulfoxide) for the synthesis of HMF, this is not the most desired route. Recent developments, including the synthesis of HMF performed in be suitable for coating applications. The analysis of their thermal properties proved that these polyesters are thermally stable up to 270–300 °C, whereas their glass transition temperature (T_g) values were found between 70 and 110 °C. Furthermore, a material was prepared with a molecular weight of 13 kg/mol, with a T_g of 113 °C. This high T_g would make this material possibly suitable for hot-fill applications. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 890–898

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supercritical acetone and water or by the addition of phase modifiers, yielded a pure product without the requirement of an extensive purification.²²⁻²⁵ Recently, 2,5-furandicarboxylic acid (FDCA), as a HMF derivative, has gained particular attention as a suitable monomer for step-growth polymerization.^{26,27} Owing to aromatic structure and bio-based origin, FDCA can be considered as an excellent replacement for fossil fuel-based monomers like, for example, terephthalic acid (TPA). Recently, Okkerse and van Bekkum²⁸ and Tavener²⁹ presented strategies toward TPA synthesized from renewable resources such as limonene or FDCA. Nevertheless, the synthesis route of TPA from limonene involved stoichiometric amounts of lithium and chromium trioxide as reactants, which should be rather avoided in a large-scale synthesis. Moreover, there are methods known from the literature in which FDCA or other furans are reacted with a compound with a double bond by a Diels-Alder (DA) reaction.³⁰ However, often these reactions are usually nonselective, yielding a low amount of the desired product.

Monomers based on furanic residues can be successfully used in both chain-growth and step-growth polymerization processes. Furan-based monomers containing double bonds

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or functional groups such as carbonyl or hydroxyl groups have been prepared for these purposes. As mentioned above, some furanic-based monomers can be successfully used to replace fossil fuel-based molecules. Moore and Kelly^{31,32} initially explored the scope and limitations of FDCA in polycondensation reactions. The authors synthesized a series of polyesters based on FDCA and different diols and showed an enormous potential of this furan-based compound. However, owing to the limited availability of high-purity FDCA, the research interest in this field declined in the following years. Nevertheless, owing to the recent developments in the catalytic routes toward high-purity FDCA, it is currently possible to obtain high-purity FDCA in larger amounts. These developments sparked a significant increase in the amount of research carried out toward FDCA-based polycondensates. Gandini et al. have shown that FDCA or related compounds are widely applicable in polymer chemistry. $^{\rm 18-20,33-35}$ Furthermore, recent studies concerning the properties of highmolecular-weight polyesters, that is poly(ethylene-2,5-furandiacrboxylate)^{35,36} revealed that polycondensates based on FDCA or other furanic derivatives could be interesting replacements for fossil fuel-based polymeric materials. It was shown that polyesters based on FDCA reveal higher glass transition temperature (T_g) , heat deflection temperature, and better barrier properties when compared with TPA analogues.³⁷ Furthermore, the strong dienic character of FDCA¹⁹ extends its range of the applications in polymer chemistry and material science. FDCA is very well suited for DA reactions, leading to new possibilities in the reversible curing of FDCA-derived polymers.^{18,20,38,39}

In this article, we present a series of novel, low-molecularweight amorphous polyesters based on FDCA and 2,3-butanediol synthesized by bulk polycondensation. Furthermore, a detailed study of the chemical structure using nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser ionization-desorption time-of-flight mass spectrometry (MALDI-ToF-MS), electrospray ionization time-of-flight mass spectrometry (ESI-ToF-MS), and electrospray ionization quadruple time-of-flight mass spectroscopy (ESI-Q-ToF-MS-MS) an analysis of the thermal properties has been performed. The relatively low-molecular-weight, high $T_{\rm g}$ bio-based polyesters could be successfully applied for (powder) coating applications.

EXPERIMENTAL

Materials

FDCA was kindly supplied by Avantium. *Meso*-2,3-Butanediol (99% (2R,3S)-butanediol) (23BD, fractionally distilled prior to use), titanium *n*-butoxide (TiBO), tin (IV) ethylhexanoate (Sn(Oct)₂), zirconium(IV) butoxide (80 wt % solution in 1-butanol) (ZrBO), 37 wt % aqueous solution of hydrochloric acid (HCl), anhydrous magnesium sulfate (MgSO₄), 4-dimethylaminopyridine (DMAP), and 0.1 and 0.5 N methanolic solutions of potassium hydroxide (KOH) were purchased from Sigma Aldrich. Irganox 1330 was obtained from CIBA specialty chemicals. Methanol (MeOH), chloroform (CHCl₃), and tetrahydrofuran (THF) were obtained from Biosolve.

Chloroform-d (CDCl₃, 99.8% atom-d) was obtained from Cambridge Isotope Laboratories. All chemicals were used as received unless stated otherwise.

Synthesis of Dimethyl-2,5-furandicarboxylate (DM-FDCA)

FDCA (10 g, 0.064 mol) was reacted with methanol (118.7 g, 3.4 mol) in the presence of hydrochloric acid (1 mL) as a catalyst. This reaction was allowed to continue for 18 h and subsequently the catalyst was deactivated by adding 30 mL of 0.5 N methanolic KOH solution. The solvent was evaporated and the obtained white solid product was dissolved in CHCl₃. The solution was filtered and washed with demiwater (2 × 200 mL) and brine (1 × 200 mL). Subsequently, this solution was dried over MgSO₄. Then, the solution was filtered and the solvent evaporated using a rotary evaporator. The obtained solids were recrystallized from CHCl₃, affording white crystals.

Yield: 80%. FTIR (ν /cm⁻¹); 3118 (=CH); 2964 (C–H); 1719 (C=O); 1583, 1515 (C=C); 1264 (C–O); 987, 834, 765 (=CH). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 3.94 (s, 6H), 7.23 (d, 2H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 52.36 (OCH₃), 118.44 (furan ring C3 and C4), 146.67 (furan ring C2 and C5), 158.29 (C=O). Melting point = 112 °C, $T_{m,lit}$ = 107-108 °C.⁴⁰ ELEM. ANAL. calc. C₈H₈O₅: C, 52.18; H, 4.38; O, 43.44, found: C, 52.24; H, 4.54; O, 43.18.

Synthesis of Poly(2,3-butylene-2,5-furancarboxylate)

A mixture of FDCA (5 g, 0.032 mol) or dimethyl-2,5-furandicarboxylate (5.9 g, 0.032 mol) and 2,3-butanediol (8.65 g, 0.096 mol) was reacted in a 100-mL three-necked roundbottomed flask equipped with a vigreux column, a Dean-Stark condenser, and a mechanical stirrer. The first step of the polymerization was carried out at 180 °C under argon atmosphere in the presence of Irganox 1330 (1 wt % relative to the amount of furan-based monomer) and the catalyst (0.1 wt % relative to the total amount of the monomers). After the esterification/transesterification process by ¹H-NMR spectroscopy after 24 h, the second portion of catalysts (0.1 wt % relative to the initial total amount of the monomers) was added. The polycondensation was continued under reduced pressure for 4 h at 220 °C. The analyses of the obtained polyesters were performed on crude samples.

METHODS

Size exclusion chromatography (SEC) was performed on a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector at 35 °C, a Waters 2487 dual absorbance detector, and a PSS SDV 5 μ guard column followed by 2 PSS SDV linearXL columns in series of 5 μ (8 × 300) working at 40 °C. THF stabilized with butylated hydroxytoluene and 1 v/v % acetic acid was used as eluent at a flow rate of 1.0 mL/min. The obtained molecular weights were calculated with respect to polystyrene standards (Polymer Laboratories, $M_{\rm p} = 580$ Da up to $M_{\rm p} = 7.1 \times 10^6$ Da).

The acid value (AV) was determined by potentiometric titration. The measurements were carried out using a Metrohm Titrino Plus 848 automatic buret equipped with a Metrohm



801 stirrer and Metrohm metal electrode. A known amount (\sim 0.500 g) of the crude polyester and 7 mL of MeOH were dissolved in THF. Subsequently, the solution was titrated using a 0.1 N methanolic solution of KOH. The AV was calculated using the following formula:

$$AV = \frac{V_{sample} \times C_{KOH} \times 56.1}{W_{sample}}$$
(1)

where V_{sample} , C_{KOH} , and W_{sample} are the volume of the titrant used for the titration of the sample, the concentration of the methanolic KOH solution, and the sample weight, respectively. All samples were measured in duplo.

Hydroxyl value (OHV) measurements were carried out using a potentiometric titration of acetylated hydroxyl end-groups of the polyesters. The measurements were carried out using a Metrohm Titrino Plus 848 automatic buret equipped with a Metrohm 801 stirrer and Metrohm metal electrode. A known amount (~0.500 g) of the crude polyester was dissolved in THF and subsequently reacted with an excess acetic anhydride in the presence of DMAP. Afterward, the unreacted acetic anhydride was hydrolyzed using a mixture of THF and water (3:1 v/v). Subsequently, the samples were titrated with a 0.5 N methanolic solution of KOH. The OHV was calculated using the following formula:

$$OHV = \frac{(V_{ref} - V_{sample}) \times C_{KOH} \times 56.1}{W_{sample}} + AV$$
(2)

where V_{ref} , V_{sample} , C_{KOH} , W_{sample} , and AV are the titrant volume used for the titration of the references, the titrant volume used for the titration of a sample, the concentration of the methanolic KOH solution, the weight of the sample, and the AV, respectively. All samples and references were measured in duplo.

MALDI-ToF-MS was performed on a PerSeptive Biosystem Voyager-DE STR Biospectrometry-Workstation. An acceleration voltage of 20 kV, a grid of 63.2%, a delay time of 320 ns, and 1000 shots per spectrum were applied. For MALDI-ToF-MS analysis, the samples were dissolved in THF with a concentration of 1 mg/mL. Trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-propenylinden]-malononitril was used as the matrix. The matrix, potassium trifluoroacetate, and the polymer solution were premixed in a weight ratio of 4:1:4. The spectra were recorded in the reflector mode at positive polarity.

Proton nuclear magnetic resonance spectroscopy (¹H-NMR) was performed on a Brucker spectrometer at a resonance frequency of 400.167 MHz. For ¹H-NMR experiments, the spectral width was 6402 Hz, the acquisition time was 1.998 s, delay time was 3 s, and the number of scans was equal to 16. Samples were prepared by dissolving 15–20 mg of crude polyester in 0.8 mL CDCl₃. Chemical shifts were reported in parts per million relative to the signal of trimethylsilane used as the internal reference, present in the CDCl₃. Data analysis was performed using Mestrec 4 software.

Correlation 2D-NMR spectroscopy (COSY) was performed on a Varian spectrometer at a resonance frequency of 400.167 MHz. For COSY experiments, the spectral width was 6402 Hz, the acquisition time was 0.15 s, and delay time was 1 s with 200 t1 increments using four scans per increment. Data analysis was performed using Mestrec 4 software.

Carbon nuclear magnetic resonance spectroscopy (¹³C-NMR) was performed on a Varian spectrometer at a resonance frequency of 100.343 MHz. For ¹³C-NMR experiments, the spectral width was 25,510 Hz, the acquisition time was 1.285 s, the delay time was 1 s, and the number of recorded scans was equal to 2000. Samples were prepared by dissolving 20-30 mg of crude polyester in 0.8 mL CDCl₃. Chemical shifts are reported in parts per million relative to the residual solvent peak of CDCl₃ ($\delta = 77.0$ ppm). Data analysis was performed using Mestrec 4 software.

Gradient heteronuclear single-quantum coherence spectroscopy (gHSQC) was performed on a Varian spectrometer at a frequency of 100.343 MHz. For gHSQC experiments, the spectral width was 6377 Hz for the ¹H-NMR and 19,065 Hz for the ¹³C-NMR, the acquisition time was 0.5 s, and delay time was 3 s. The experiments were carried out with 400 *t*1 increments with eight scans per increment. Data analysis was performed using Mestrec 4 software.

FTIR was performed on a Varian FT-IR3100 spectrophotometer using a golden gate setup. The spectra were recorded in the transmission mode at room temperature with a resolution of 2 cm⁻¹. The spectra were obtained applying 100 scans per spectrum and were analyzed in the frequency range of 4000– 700 cm⁻¹. Data acquisition and processing was performed using Varian Resolutions 4 software.

ESI-ToF-MS and ESI-Q-ToF-MS-MS were performed on a Synapt G1 HDMS mass spectrometer. The system was used in a positive ionization electrospray mode. The m/z was calibrated using sodium iodide. The most relevant parameters used for recording of the spectra were as follows: capillary voltage, 2.5 kV; sampling voltage, 40 V; extraction voltage, 4 V; source temperature, 100 °C; desolvation temperature, 280 °C; desolvation gas flow, 400 L/h; cone gas, flow 30 L/h; ion mobility separation (IMS) gas flow, 30 mL/min; IMS wave velocity, 300 m/s; IMS wave height, 0.5 V; trap collision energy, 6 V; and trap gas flow, 1 mL/min. Nitrogen was used as a carrier buffer gas. Data were analyzed using MassLynx 4.1.

Differential scanning calorimetry (DSC) was performed using a DSC Q100 from TA-instruments. The measurements were carried out from -50 to 180 °C with a heating and cooling rate of 10 °C/min under a nitrogen flow of 50 mL/min. The $T_{\rm g}$ s were obtained from the inflection point in the curve recorded during the second heating run.

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 TGA in a nitrogen atmosphere. Samples were heated from 25 to 600 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

RESULTS AND DISCUSSION

Poly(2,3-butylene-2,5-furandicarboxylate) (P23BF) samples were successfully synthesized from either FDCA or DM-FDCA and 23BD via solvent-free bulk polymerization. The polymerizations were catalyzed by TiBO, $Sn(Oct)_2$, or ZrBO. An overview of the results obtained from the polycondensations is presented in Table 1.

TABLE 1 Molecular Weight, Polydispersity Index, and Acid and Hydroxyl Values of the Poly(2,3-butylene-2,5-furandicarboxylate)s Synthesized by Bulk Polycondensation Catalyzed by Titanium (IV) *n*-butoxide (TiBO), Tin (IV) ethylhexanoate (Sn(Oct)₂), and Zirconium (IV) butoxide (ZrBO)

			Mn	M _w		AV	OHV (mg	$M_{n,NMR}$
Entry	Monomer	Catalyst	(kg/mol)	(kg/mol)	PDI	(mg KOH/g)	KOH/g)	(kg/mol)
1	FDCA	ТВО	2.5	4.6	1.8	2.7	59.3	1.8
2	FDCA	Sn(Oct) ₂	3.7	8.5	2.1	2.9	27.7	4.2
3	FDCA	ZrBO	2.0	2.9	1.5	6.7	70.2	2.0
4	DM-FDCA	ТВО	2.2	3.6	1.6	0.3	70.2	2.0
5	DM-FDCA	Sn(Oct)2	7.0	18	2.6	0.0	3.70	n.d. ^a
6	DM-FDCA	ZrBO	2.4	4.0	1.7	11.3	25.6	1.9
7	DM-FDCA	Sn(Oct) ₂	13	26	2	0.2	0.4	n.d. ^a

^a n.d. indicates not determined owing to a low signal intensity of the signals from the end-groups in the ¹H-NMR spectrum.

Clearly, one can observe an influence of the catalyst and type of furan monomer on the molecular weight and endgroup content of the synthesized polyesters. As reported earlier, TiBO and Sn(Oct)₂ are active catalysts in the synthesis of polyesters. Nevertheless, the polycondensation of FDCA and 23BD catalyzed by Sn(Oct)₂ afforded higher molecular weights and thus proved a better activity of the catalyst. The lower activity of TiBO in the synthesis of FDCAbased polyester has been observed by Khrouf et al.³⁴ It was shown that this lower activity was caused by coordination of the furan-ring with the titanium, yielding a lower efficiency of the catalyst in the polycondensation reaction between diols and FDCA-based monomers. On the other hand, a high activity of $Sn(Oct)_2$ was noticed for the synthesis of DM-FDCA-based polyesters, yielding products with the $M_{\rm n}$ value around 7000 g/mol (Table 1, entry 5). Although the obtained molecular weight of these materials was higher than for the systems catalyzed by TiBO or ZrBO, their polydispersity index increased as well. This is most likely caused by transesterification side reactions, leading to cyclic products.⁴¹⁻⁴³ No indications, that branching or gelation was taking place, have been noted. On the contrary, when TiBO was used as the catalyst, no significant increase in molecular weight or PDI was observed when DM-FDCA was used as an alternative for FDCA. Similar activities were observed when ZrBO was used as catalyst, yielding polyesters with a M_n in the range of 2000–3000 g/mol (Table 1). Furthermore, the obtained PDIs for systems catalyzed by TiBO or ZrBO were lower when Sn(Oct)₂ was used, which shows different activities of the different catalysts for the side reactions. Using Sn(Oct)₂, a polyester with higher molecular weight (Table 1, entry 7) was also prepared. This molecular weight was obtained after 8 h of vacuum processing instead of the 4 h used in the other examples. The obtained P23BF samples proved to be brittle polyesters. This is most probably caused by the low molecular weight of the polyesters. Owing to the low amount of entanglements per polymer chain, the stress cannot be properly transferred to the P23BF matrix. We expect that the materials having higher molecular weights can be tougher and more suitable for applications other than powder coatings.

However, no systematic study toward to mechanical properties has been attempted at this moment.

The obtained polyesters were almost exclusively hydroxyl end-capped, which is clear from the OHV and AV data summarized in Table 1, and which was targeted as well as expected in view of the relatively large excess of 23BD used in the polymerization process. This large excess of 23BD basically generates a low-molecular-weight dihydroxy endcapped prepolymer in the first synthesis step from which the excess of diol is eliminated by transesterification under reduced pressure. Differences in the total end-group content are most likely caused by the varying molecular weights of the poly(2,3-butylene-2,5-furandicarboxylate)s. Moreover, in the cases when Sn(Oct)₂ was used as catalyst also larger amounts of cyclics could be present, resulting in a lower end-group content. Furthermore, it is interesting to note that when ZrBO was used as the catalyst the obtained AVs were significantly higher when compared with the polymers obtained via TiBO or Sn(Oct)₂-catalyzed polycondensation.

To elucidate the structures and type of end-groups formed during the reaction, MALDI-ToF-MS was applied. The analysis of the MALDI-ToF-MS spectra showed the presence of P(23BF) distributions with different end-groups, which was also supported by titration data (Table 1). In Figure 1, a representative MALDI-ToF-MS spectrum of the polyesters (Table 1, entry 1) prepared by bulk polycondensation of FDCA and 23BD is shown. The repeating unit of the synthesized polyesters was indicated by the m/z differences between the adjacent MALDI-ToF-MS signals, being equal to 210 g/mol and corresponding to the molar mass of one FDCA and one 23BD unit.

Figure 1 shows the presence of seven different distributions. The m/z signals described as 1 and 6 can be attributed to α, ω -hydroxy-end-capped polymer chains. These signals originate from hydroxyl-functional polyester chains with different counter ions, that is potassium (1) and sodium (6). Furthermore, the distribution described as (4) corresponds to cyclic structures, whereas (5) proved the presence of linear structures with one hydroxyl- and one carboxylic acid end-group.



FIGURE 1 MALDI-ToF-MS spectrum of the poly(2,3-butylene-2,5-furandicarboxylate) (Table 1, Entry 1) obtained by polycondensation reaction catalyzed by TiBO.

Finally, distributions (2), (3), and (6') correspond to the chains having one ether linkage in the backbone. In the MALDI-ToF-MS spectrum, (2) and (3) are attributed to α,ω hydroxyl-functionalized chains with different counter ions, that is sodium and potassium, respectively, whereas the distribution (6') corresponds to cyclic structures. Although the MALDI-ToF-MS spectra do not show the signals corresponding to polyester chains that are carboxylic acid-functionalized at both chain ends, the presence of this less abundant structure cannot be excluded. One should realize that MALDI-ToF-MS is not a quantitative analytical technique. The synthesis most probably exclusively yielded linear and cyclic species as no indications for branched structures were observed. As discussed by many authors, ^{18,38,39} FDCA can participate in a DA reaction as diene. However, from our recorded MALDI-ToF-MS spectra, one can conclude that under the applied polycondensation conditions no significant amount of DA adducts was obtained.

In Figure 2, the MALDI-ToF-MS spectrum of the polyester synthesized from DM-FDCA and 23BD using TiBO as a catalyst (Table 1, entry 4) is shown. The spectrum shows a similar distribution pattern as recorded for the FDCA-based polyester. The expected signals for α, ω -hydroxyl-end-capped macromolecules (1) and (6), α, ω -hydroxyl-end-capped species with one ether bond linkage in the backbone (2), cyclic structures (3), and cyclic structures with one ether linkage

(6') as well as hydroxyl and methyl ester end-capped molecules (4) were observed. Hence, these polyesters show a close resemblance to FDCA-derived polyesters (Fig. 1). The spectrum of DM-FDCA-based polyesters shows one additional distribution (5). However, we were unable to assign this distribution to any of the expected structures. Moreover, the obtained distribution did not also correspond to macromolecules with vinylic end-groups (possibly formed by decarboxylation) or DA adducts.

The chemical structure of the polyesters was proven by ¹H-NMR and ¹³C-NMR spectroscopy. The ¹H-NMR spectrum of Entry **1** (Table 1) recorded in $CDCl_3$ is shown in Figure 3. The end-group resonances were assigned by analyzing the ¹H-NMR (Supporting Information Fig. S1) and COSY (Supporting Information Fig. S2) spectra of the P23BF oligomers. These materials show intense resonances of the end-groups, and thus are ideal for the peak assignment. The signals from the methylene groups of 23BD (e and f) can be found at 1.4 and 1.2 ppm, respectively. The use of the meso-form (2R,3Sbutanediol) of 23BD resulted in not well-resolved methylene signals in the range of 1.2-1.5 ppm. The chemical shifts of the signals of the 23BD meso-form, that is c, c', d, and d', clearly show the difference in the stereochemistry from the end-groups of the 99% meso-form of 23BD. The ratio between the end-group signals (e.g., d and d') did not change



FIGURE 2 MALDI-ToF-MS spectrum of the poly(2,3-butylene-2,5-furandicarboxylate) (Table 1, Entry **4**) obtained by polycondensation reaction catalyzed by TiBO.



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FIGURE 3 ¹H-NMR spectrum of poly(2,3-butylene-2,5-furandicarboxylate) (Table 1. Entry 1) recorded in CDCl₃.

significantly during the polycondensation reaction. Hence, the stereochemistry of the monomer was retained during the polyester synthesis. Signal d was assigned to the protons from the 23BD units which were within the main chain. Moreover, the furanic signal (signal a) clearly suggests that the furan ring does not participate in DA additions on a significant scale as no signals of the corresponding vinylic protons were observed. The presence of different proton resonances of the end-groups allowed to calculate the molecular weight of the synthesized polyesters (Table 1). As, the $M_{n,NMR}$ values are comparable to those obtained from SEC, it is clear that there is a deviation from the end-group to repeat unit ratio. Cyclics could account for this deviation because these do not have end-groups but are taken into account when calculating the number of repeat units. Furthermore, for the calculation of the $M_{n,NMR}$ values of the polyesters, the possible influence of the concentration of (the undetectable) carboxylic acid end-groups has been omitted. Besides, resonances originating from structures with an ether linkage were not found in the ¹H-NMR spectra, which can result from their too low content to allow detection by NMR experiments.

In Figure 4, a representative ¹³C-NMR spectrum of Entry 1 (Table 1) is shown. To assign ¹³C resonances properly, the ¹³C-NMR and gHSQC spectra of the oligomer were recorded and analyzed (Supporting Information Figs. S3 and S4). The first group of signals originates from the FDCA residues and is visible at lower field (higher ppm values than 100 ppm). Signals from the FDCA residues described as (a), (g), and (h) were found at 118.7, 146.7, and 157.1 ppm, respectively. The chemical shift of these signals proves that the original chemical structure of FDCA is retained during the polymerization. An examination of the aliphatic region of the carbon spectrum allowed the assignment from the signals of 23BD. Signals from the 23BD backbone (b), (e), and (f) were found at 72.7, 16.2, and 15.2 ppm, respectively. Furthermore, owing to the different conformations of the protons in 23BD also the ¹³C-NMR signals (d), (d'), (c), and (c') are visible as wellresolved resonances at 69.1, 69.5, 76.1, and 76.5 ppm, respectively. Signal (x) shown in Figure 4 originates from unreacted 23BD residuals, which is also reflected by the proton resonances (e) and (f) shown in Figure 3. Moreover, the presence of ether linkages, present in the macromolecules and visible in MALDI-ToF-MS spectra, was not proven by NMR. This might result from the relatively low content of ether bonds, undetectable by NMR techniques.

To elucidate further, the type of functional groups present and to obtain complementary insight regarding the chemical structure of FDCA/DM-FDCA-based polyesters FTIR was employed. FTIR spectra of FDCA (1) and DM-FDCA (5) (Fig. 5) show a close resemblance, proving that the chemical structure of FDCA and DM-FDCA-based polyesters is similar. In both spectra, a signal at 3361 cm^{-1} can be observed, this being the stretch vibration of hydroxyl groups and implying the presence of both free and hydrogen-bonded hydroxyl groups. Simultaneously, the formation of ester bonds was proven by the bands at 1714 \mbox{cm}^{-1} characteristic for the C=0 stretching vibrations. The pronounced signals at 1448 and 1380 cm^{-1} were assigned to the CH₃ bending vibrations from 23BD residues in the polyester backbone. The signals at 1579 and 1500–1510 $\rm cm^{-1}$ correspond to the vibrations of the furan ring. Furthermore, the signals below 1300 cm^{-1} belong to various bending vibrations of the disubstituted furan rings. Careful analysis of the FTIR spectra once again did not show the presence of DA products formed during polycondensation process. Furthermore, the signals originating from ether groups, present in the polyester backbone according to the MALDI-ToF-MS analysis, were not detected. This result from their relatively low content and/or overlapping with the signals attributed to the ester groups.



FIGURE 4 ¹³C-NMR spectrum of poly(2,3-butylene-2,5-furandicarboxylate) (Table 1, Entry 1) recorded in CDCl₃.



FIGURE 5 FTIR spectrum of poly(2,3-butylene-2,5-furandicarboxylate)s, Entries **1** (solid line) and **5** (dashed line) in Table 1. The spectra were recorded at room temperature and show frequency ranges between 4000 and 700 cm⁻¹.

ESI-ToF-MS and ESI-Q-ToF-MS-MS were used to study the presence of ether-linkages in the synthesized polyester, the presence of which was shown by MALDI-ToF-MS (Fig. 1). Figure 6(a) shows an ESI-ToF-MS spectrum. The advantage of ESI-ToF-MS over MALDI-ToF-MS is the possibility to select one distribution, by IMS, and fragment the chosen distributions further. The results of the chain fragmentation of the polyester with m/z 605 g/mol are shown in Figure 6(b). The analysis of the isotope patterns revealed the presence of signals corresponding to chain fragments containing an ether bond with an m/z of 129 g/mol ([Fig. 6(b)], inset). The other signals were analyzed and proved the expected structure of poly(2,3-butylene-2,5-furandicarboxylate).

The thermal properties of poly(2,3-butylene-2,5-furandicarboxylate) were studied using DSC and TGA. An overview of the thermal properties of the synthesized polyesters is presented in Table 2. The TGA of the synthesized polyesters was performed under nitrogen atmosphere and revealed that, by using proper synthesis routes and suitable catalysts, polyesters with tunable thermal properties could be obtained. The first step in the decomposition of the polyesters was noted above 280 °C, whereas the maximum rate of their degradation was observed above 300 °C (Table 2). A slight dependency of the molecular weight of the polyesters on their decomposition temperature was observed as with an increasing molecular weight of the polymers their thermal stability increased.

The DSC analysis shows that these polyesters are fully amorphous and only exhibit $T_{\rm g}$ values between 71 and 113 °C. Based on the results summarized in Table 2, it follows that, within the studied $M_{\rm n}$ range, the molecular weight of the polyester macromolecules strongly influences their $T_{\rm g}$ values. Along with increasing the number average molecular weight of the polyesters from 2200 to 7000 g/mol, their $T_{\rm g}$



Mass (m/z)

FIGURE 6 Mass spectra of poly(2,3-butylene-2,5-furandicarboxylate) (1) (a) ESI-ToF-MS and (b) ESI-Q-Tof-MS-MS.

increased from 71 to 109 °C. This behavior was studied using the Fox–Flory equation (eq 3). 44

$$T_{\rm g} = T_{\rm g,\infty} - \frac{\rm K}{M_{\rm n}} \tag{3}$$

In this equation, T_{g} , $T_{g,\infty}$, K, and M_n are the glass transition temperature of the material, the glass temperature of the polymer at infinite molecular weight, the Fox–Flory constant,

TABLE 2 Thermal Properties of Poly(2,3-butylene-2,5-furandicarboxylate)s Obtained by DSC and TGA

Entry	<i>T</i> _g (°C)	<i>T</i> _{deg,5%} (°C)	$T_{deg,max}$ (°C)
1	80 ^a	299	342
2	96	296	342
3	74	276	343
4	71	280	334
5	109	301	335
6	81	277	304
7	113	n.d. ^b	n.d.

 $^{\rm a}$ $T_{\rm g}$ obtained from the first heating curve; no clear $T_{\rm g}$ could be determined from the second heating run.

^b n.d., not determined.



FIGURE 7 T_{gs} as obtained from DSC versus the molecular weight fitted to a Fox-Flory equation.

and the number molecular weight of the polymer, respectively. The resulting trend is shown in Figure 7, which also includes low-molecular-weight polyesters not reported in Table 1. The data were fitted with eq 3 and $T_{\rm g,\infty}$ equals to 125 °C together with a K-value of 96,000 was found. The K-value shows a strong dependence of the $T_{\rm g}$ on the molecular weight of the polyester. A polyester with a similar structure to the FDCA-based polyesters is poly(ethylene terephthalate) (PET) and shows a K-value of 56,000.45 Therefore, PET reveals a less significant molecular weight dependence on the $T_{\rm g}$ value. As P23BF has a stiffer backbone compared with PET, the end-groups would have a greater relative effect on increasing molecular mobility. As the type of end-groups of the prepared polyesters was not dependent on the used monomers, this relationship can be applied for both methods of the polyester synthesis.

The high $T_{\rm gs}$ for number average molecular weights in the range of 2000–3000 g/mol make these poly(2,3-butylene-2,5-furandicarboxylate)s very interesting candidates for powder-coating applications. Moreover, the material with a molecular weight of 13 kg/mol showed a $T_{\rm g}$ value of 113 °C, which is high for such a material. For example, P23BF shows a 30 °C increase in $T_{\rm g}$ when compared with poly(ethylene-2,5-furandicarboxylate).³⁷ This could make this material also suitable for hot-fill applications (e.g., drink bottles). Nowadays, the semi-crystalline PET is used for this purpose. This material is usually annealed before filling. By using P23BF, having a higher $T_{\rm gr}$ such a problem can be easily overcome.

CONCLUSIONS

Poly(2,3-butylene-2,5-furancarboxylate)s were successfully synthesized by bulk polycondensation using titanium (IV) *n*-butoxide (TiBO), tin (IV) ethylhexanoate $(Sn(Oct)_2)$, or zirconium (IV) butoxide (ZrBO) as the catalyst. The analysis of the molecular weights of the polyesters proved a significant activity of $Sn(Oct)_2$, yielding products with molecular weights above 7.0 kg/mol. Simultaneously, $Sn(Oct)_2$ was



found to be a very efficient transesterification catalyst for these polycondensations, leading to the formation of cyclic structures. MALDI-ToF-MS spectra showed several distributions, representing α, ω -hydroxyl-end-capped polymer chain fragments, cyclic structures, and polyester chains having both one hydroxyl and one carboxylic acid end-groups. The formation of ether linkages in the backbone was proven using a combination of MALDI-ToF-MS, ESI-ToF-MS, and ESI-Q-ToF-MS-MS techniques. Furthermore, NMR and FTIR analysis confirmed the expected chemical structure and the presence of predominantly hydroxyl end-groups in the P(23BF). Besides, the meso structure of the 23BD was clearly reflected by the presence of well-resolved ¹H and ¹³C-NMR signals at 5.1, 4.1, 69, and 76 ppm, respectively. However, no indications were found for a DA reaction under applied reaction conditions although the furan rings have been reported to be very prone to these DA additions.

The analysis of the thermal properties of the polyesters confirmed their suitability for practical applications. $T_{\rm g}$ values of the synthesized poly(2,3-butylene-2,5-furandicarboxylate)s, with number average molecular weights in the range of 2000–7000 g/mol, were found between 71 and 113 °C, strongly depending on their molecular weights. This dependence was studied using a Fox–Flory relationship and the Fox–Flory parameters for this polyester were determined. All obtained polyesters are fully amorphous and thermally stable up to 270–300 °C. The thermal stability also proved to be slightly affected by the molecular weight of the P(23BF)s.

The analysis of the chemical structure of the P(23BF)s and their thermal properties proved that these fully bio-based materials can be suitable for (powder) coating applications. A possible way of curing these systems might occur either via DA addition to the FDCA unsaturated bonds or by crosslinking reactions involving the hydroxyl end-groups upon exposure to polyfunctional isocyanates.

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REFERENCES AND NOTES

1 I. O. Bakare, C. Pavithran, F. E. Okieimen, C. K. S. Pillai, *J. Appl. Polym. Sci.* **2006**, *100*, 3748–3755.

2 I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky, A. Springer, Chem. Eng. Technol. 2008, 31, 647–654.

- 3 D. Braun, M. Bergmann, J. Prak. Chem. 1992, 334, 298-310.
- 4 S. Dhamaniya, J. Jacob, Polymer 2011, 51, 5392-5399.

5 J. A. Galbis, M. G. García-Martín, B. Mohamed Naceur, G. Alessandro, Monomers, Polymers and Composites from Renewable Resources; Elsevier: Amsterdam, **2008**; pp 89–114.

- 6 A. Gandini, Green Chem. 2011, 13, 1061-1083.
- 7 A. Gandini, Macromolecules 2008, 41, 9491–9504.

8 J. P. Jain, M. Sokolsky, N. Kumar, A. J. Domb, *Polym. Rev.* 2008, *48*, 156–191.

9 L. Jasinska, M. Villani, J. Wu, D. van Es, E. Klop, S. Rastogi, C. E. Koning, *Macromolecules* **2011**, *44*, 3458–3466.

10 H. R. Kricheldorf, J. Macromol. Sci. Part C: Polym. Rev. 1997, 37, 599–631.

11 M. Lindblad, Y. Liu, A.-C. Albertsson, E. Ranucci, S. Karlsson, Advances in Polymer Science; Springer: Berlin/Heidelberg, **2002; Vol.** *157*, pp 139–161.

12 S. Mecking, Angew. Chem. 2004, 116, 1096-1104.

13 S. Mecking, Angew. Chem. Int. Ed. 2004, 43, 1078-1085.

14 M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* 2007, *36*, 1788–1802.

15 D. S. Ogunniyi, Biores. Technol. 2006, 97, 1086–1091.

16 F. Seniha Güner, Y. Yağcı, A. Tuncer Erciyes, *Prog. Polym. Sci.* **2006**, *31*, 633–670.

17 J. B. Van Beilen, Y. Poirier, *Plant J.* 2008, 54, 684–701.

18 A. Gandini, Polym. Chem. 2010, 1, 245-251.

19 A. Gandini, M. N. Belgacem, *Prog. Polym. Sci.* **1997**, *22*, 1203–1379.

20 A. Gandini, D. Coelho, M. Gomes, B. Reis, A. Silvestre, *J. Mater. Chem.* **2009**, *19*, 8656–8664.

21 J. C. Serrano-Ruiz, R. Luque, A. Sepúlveda-Escribano, *Chem. Soc. Rev.* 2011, *40*, 5266–5281.

22 C. Moreau, M. N. Belgacem, A. Gandini, *Topic. Catal.* 2004, 27, 11–30.

23 Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* 2006, *312*, 1933–1937.

24 H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* 2007, *316*, 1597–1600.

25 M. Bicker, J. Hirth, H. Vogel, Green Chem. 2003, 5, 280-284.

26 Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen, A. Riisager, *ChemSusChem* 2009, *2*, 672–675.

27 N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, *Green Chem.* **2011**, *13*, 824–827.

28 C. Okkerse, H. van Bekkum, Green Chem. 1999, 1, 107-114.

29 S. Tavener, Green Chem. 2003, 5, G46-G48.

30 Y. T. Cheng, G. W. Huber, Green Chem. 2012, 14, 3114-3125.

31 J. A. Moore, J. E. Kelly, *Polymer* 1979, 20, 627–628.

32 J. A. Moore, J. E. Kelly, Macromolecules 1978, 11, 568-573.

33 A. Khrouf, S. Boufi, R. E. Gharbi, N. M. Belgacem, A. Gandini, *Polym. Bull.* **1996**, *37*, 589–596.

34 A. Khrouf, S. Boufi, E. R. Gharbi, A. Gandini, *Polymer Int.* **1999**, *48*, 649–659.

35 M. Gomes, A. Gandini, A. J. D. Silvestre, B. Reis, *J. Polym. Sci. Part A: Poly. Chem.* **2010**, *49*, 3759–3768.

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

37 M. A. Dam, G. M. Gruter, L. Sipos, E. de Jong, D. Den Ouden, Society of Plastics Engineers—EUROTEC 2011 Conference Proceedings, Barcelona, Spain, November 14–15, **2011**.

38 A. Gandini, A. J. D. Silvestre, D. Coelho, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2053–2056.

39 K. Ishida, N. Yoshie, *Macromol. Biosci.* 2008, 8, 916–922.

40 A. A. Morton, G. H. Patterson, *J. Am. Chem. Soc.* **1943**, *65*, 1346–1348.

41 H. R. Kricheldorf, G. Behnken, G. Schwarz, *Polymer* **2005**, *46*, 11219–11224.

42 N. Jacquel, F. Freyermouth, F. Fenouillot, A. Rousseau, J. P. Pascault, P. Fuertes, R. Saint-Loup, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 5301–5312.

43 H. Jacobson, W. H. Stockmayer, *J. Chem. Phys.* **1950**, *18*, 1600–1606.

44 T. G. Fox Jr., P. J. Flory, J. Appl. Phys. 1950, 21, 581-591.

45 S. Montserrat, P. Colomer, Polym. Bull. 1984, 12, 173-180.