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Renewable-based poly((ether)ester)s from 2,5-furandicarboxylic acid

Andreia F. Sousa [a, b, *], Jorge F.J. Coelho [b], Armando J.D. Silvestre [a]

[a] CICECO- Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[b] CEMUC, Department of Chemical Engineering, University of Coimbra, 3030-790 Coimbra, Portugal

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ABSTRACT

Polymers based on the renewable monomer 2,5-furandicarboxylic acid (FDCA) have witnessing an incessant growth in recent years, essentially motivated by their unique features and the current concerns about sustainability and environmental issues. However, to date, research has been mainly focused on FDCA-polyesters synthesis, while synthetic routes to afford poly((ether)ester)s remained unexplored until the present study, despite their inherent value. Herein, fully renewable-based poly((ether)ester)s from 2,5-furandicarboxylic acid, poly(ethylene glycol) (PEG) and isosorbide were straightforward synthesised by polycondensation reactions. Interestingly, these materials showed better or comparable thermal properties (e.g. glass transition temperature) than their fossil based counterparts, which can be simply tuned by changing the chain length of PEG segments and also by incorporating (or not) rigid isosorbide moieties. The ensuing products were characterised in detail by means of ATR FTIR, ^{1}H NMR, TGA and DSC.

1. Introduction

Sustainability is at the front line of world agenda, in fact research efforts on the development of sustainable materials, which are preferably based on renewable resources, have grown exponentially in the last years [1–3]. In this context, polymers derived from the renewable-based 2,5-furandicarboxylic acid (FDCA) [4] also have witnessing an incessant growth [1]. The most successful member of this family of polymers is definitely poly(ethylene 2,5-furandicarboxylate) (PEF), announced as the renewable-based substitute of the commercially available poly(ethylene terephthalate) (PET) [1,4–6]. Although several other FDCA-polymers have also emerged [1,7–18], to date, emphasis has essentially been placed on polyesters, nevertheless, synthetic routes to prepare FDCA-based poly((ether)ester)s (PEE) have been broadly neglected, despite their high commercial relevance [19–23]. Indeed, to our knowledge, there is a single work on the topic of synthesis and characterisation of poly(butylene 2,5-furandicarboxylate)-*co*-(poly(tetramethylene glycol) 2,5-furandicarboxylate) [24], although PEE using FDCA and PEG has never been investigated before.

Poly((ether)ester)s (PEE) are an important family of polymers with unique and remarkable properties, like for example thermal properties, among others [19–29]. They are currently mainly composed of hard alkylene terephthalate moieties and soft poly(ethylene glycol) (PEG) sequences of different chain length [21,30]. Their properties can be tailored by the relative content of their soft/hard segments and also by using PEG segments with different average chain lengths [19–26]. In more specific terms their glass transition can span from far below to above room temperature [19,23], and not surprisingly their degradability increases with PEG content [19,24,31].

Some relevant examples of PEEs include poly((ethylene terephthalate)-*co*-(poly(ethylene glycol) terephthalate)) (PET-*co*-PEGT) and especially poly((butylene terephthalate)-*co*-(poly(ethylene glycol) terephthalate)) (PBT-*co*-PEGT) [21,30], commercialized under the trade name PolyActive® [32], for typical applications such as films and microspheres [31,33]. More examples include the poly((butylene terephthalate)-*co*-(poly(tetramethylene glycol) terephthalate)) copolymers [34,35] commercialized under the trade name Hytrel® (DuPont) [36] or Arnitel® (DSM) [37]. In view of the present concerns about sustainability and environmental issues, alternative PEEs entirely based on renewable resources are highly desirable in the long term. Indeed, a judicious selection of monomers that would include FDCA, as alternative to fossil-based terephthalic acid, would enhance even further the value of PEE polymers.

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* Corresponding author. CICECO- Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
E-mail address: andreiafs@ua.pt (A.F. Sousa).

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This study inaugurates, precisely, the development of poly((ether)ester)s based on FDCA and incorporating different number-average molecular weight poly(ethylene glycol) (PEG200, PEG400 or PEG2000). The copolymerisation with renewable-based isosorbide is also an innovation of this study that, to the best of our knowledge, has never been reported before despite the predictable thermal properties enhancement of the ensuing PEEs due to isosorbide stiffness. This unique combination of monomers/oligomers was reacted under conventional solution polycondensation approach, and the ensuing products were characterised in detail by means of ATR FTIR, ^{1}H and ^{13}C NMR, DSC and TGA analyses.

2. Experimental

2.1. Materials

Isosorbide (98%, IS), 1,1,2,2-tetrachloroethane (98%, TCE), anhydrous pyridine (99.8%) and deuterated chloroform (99%, $CDCl_3$) were purchased from Sigma-Aldrich Chemicals Co. Polyethylene glycol with number-average molecular weight equal to 200 (PEG200) and to 400 (PEG400) were purchased from Merck. 2,5-Furandicarboxylic acid (98%, FDCA) was purchased from TCI Europe N.V.. All chemicals were used as received, except for PEGs' and TCE which were dried prior their use (by vacuum or by using molecular sieves, respectively).

2.2. Synthesis of 2,5-furandicarbonyl dichloride (FDCDCl)

Typically, reactions were carried out in solution using FDCA (ca. 5 g) dissolved in dimethylformamide (ca. 50 ml) and an excess of thionyl chloride (ca. 5 ml). The mixture was refluxed at 80 °C for 15 h, with constant stirring. Subsequently, the excess of $SOCl_2$ and DMF was removed under vacuum at room temperature and finally the pure dichloride monomer was isolated by vacuum sublimation, at approximately 80 °C (isolation yield ≈ 50%).

2.3. Synthesis of poly((ether)ester)s

Polycondensation reactions were carried out in solution following an adapted procedure of Gandini et al. [7]. Typically, the dried diol monomer, either approximately 2.6 mmol of PEG (PEG200, PEG400 or PEG2000) or an equimolar mixture of PEG2000 (ca. 1.3 mmol) and IS (ca. 1.3 mmol), dissolved in TCE (1 ml), was dissolved in pyridine (1.7 ml). Then, this mixture was allowed to cool down to about 0 °C using an ice bath, and an equimolar amount of FDCDCl (ca. 2.6 mmol), dissolved in TCE (1 ml), was added dropwise, under nitrogen flux, and with vigorous stirring. The reaction was allowed to proceed until room temperature, while its viscosity increased progressively, during approximately 7 h. The ensuing polymer was precipitated in an excess of cold ethanol; isolated, either by filtration or by decantation depending if it was a solid or a viscous liquid, respectively; and finally dried. Afterwards a film from PEGF2000 was prepared by depositing a polymer solution in chloroform (ca. 0.1 mg ml^{-1}) onto a Teflon surface plate, followed by slow evaporation of solvent until complete dryness, first at room temperature during 1 day and then at 50 °C for 2 days.

2.4. Characterisation

2.4.1. Attenuated total reflectance Fourier transform infrared (ATR FTIR)

Infrared spectra of PEGFs were obtained using a PARAGON 1000 Perkin-Elmer FTIR spectrometer equipped with a single-horizontal Golden Gate ATR cell. The spectra were recorded after 128 scans, at a resolution of 8 cm^{-1}.

2.4.2. Nuclear magnetic resonance (NMR)

^{1}H and ^{13}C NMR spectra of the polymers dissolved in deuterated chloroform ($CDCl_3$) were recorded using a Bruker AMX 300 spectrometer, operating at 300 or 75 MHz, respectively. All chemical shifts are expressed as parts per million downfield from tetramethylsilane, used as internal standard.

2.4.3. Size-exclusion chromatography (SEC)

SEC analyses of polyesters were performed on a chromatographer equipped with a PL-EMD 960 light scattering detector, using a set of two PL HFIP columns (300 mm × 7.5 mm i.d.) and one PL HFIP gel guard column (50 mm × 7.5 mm i.d.), kept at 40 °C and previously calibrated with polystyrene standards in the range of 1800–30,300 g mol^{-1}. A mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol ($CH_2Cl_2/CHCl_3$/HFP) (70/20/10 in V/V/V%) was used as the mobile phase with a flow of 1.0 mL min^{-1}. All polymers (≈3 mg ml^{-1}) were dissolved in $CH_2Cl_2/CHCl_3$/HFP mixture (70/20/10 in V/V/V%) and filtered through PTFE membranes before injection.

2.4.4. Thermogravimetric analyses (TGA)

TGA analyses were carried out with a Shimadzu TGA50 analyser equipped with a platinum cell, using platinum pans to encapsulate the samples. Typically, samples were heated, at a constant rate of 10 °C min^{-1}, from room temperature up to 800 °C, under a nitrogen flow of 20 mL min^{-1}.

2.4.5. Differential scanning calorimetry (DSC)

DSC thermograms were obtained with a TA Instruments Q100 model calorimeter using aluminium pans. Scans were conducted under nitrogen with a heating rate of 10 °C min^{-1} in the temperature range of −80 to 200 °C. Two heating/cooling cycles were repeated. The second heating scans were done after performing a cycle in which the samples were heated from 25 to 200 °C and cooled to −80 °C to eliminate the thermal history. Glass transition temperature was determined using the midpoint approach (second heating trace). Melting temperature was determined as the minimum of the melting endothermic peak during the second heating cycle, respectively.

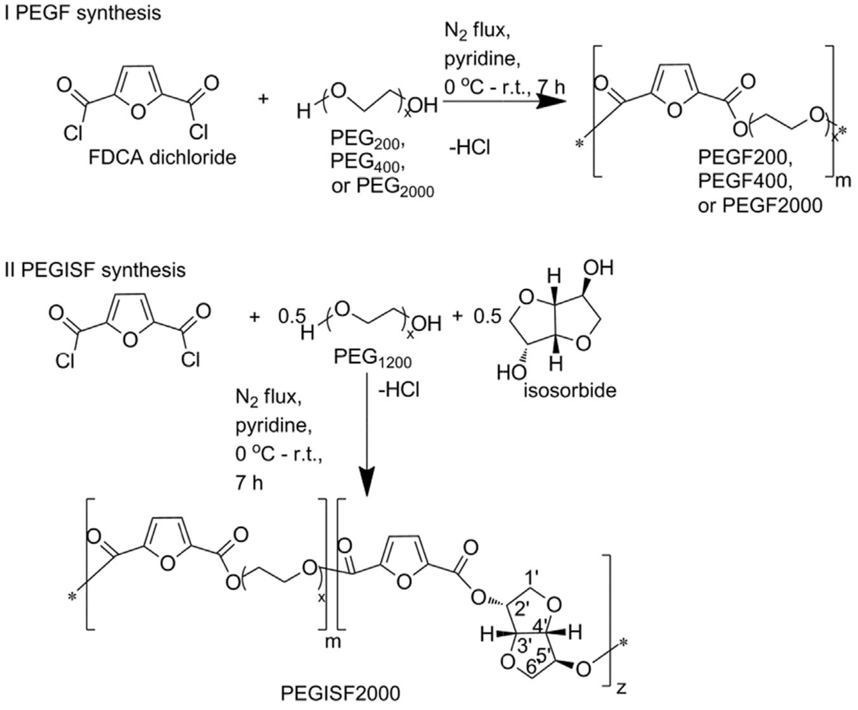
2.4.6. X-ray diffraction (XRD) analyses

XRD diffractograms were acquired using a Philips X'pert MPD instrument operating with Cu K α radiation (λ = 1.5405980 Å) at 40 kV and 50 mA. Samples were scanned in the 2θ range of 3–50°, with a step size of 0.04°, and time per step of 50 s.

3. Results and discussion

One of the most appealing aspect of this study is concerned with the fact that for the first time 100% renewable-based poly((ether)ester)s were straightforward prepared by conventional solution polycondensation reactions [7] (Scheme 1).

These reactions were carried out by using stoichiometric amounts of FDCA dichloride and diols (either PEG or an equimolar mixture of PEG and isosorbide). The ensuing PEGF polymers were obtained in ca. 65% isolation yield, their number-average molecular weight ranged from 3300 to 17,300 g mol^{-1} and the polydispersity's were close to 1.4 as determined by SEC in $CH_2Cl_2/CHCl_3$/HFP (Table 1). In addition, here, we demonstrate that these renewable-based PEEs, in similarity to the fossil-PEE [31], can also form a film by directly casting a diluted chloroform solution of PEGISF2000 onto the surface of a Teflon plate.



Scheme 1. Syntheses of two series of FDCA-based poly((ether)ester)s by polycondensation reaction: I poly((poly(ethylene glycol)) 2,5-furandicarboxylate) (PEGF) and II poly((poly(ethylene glycol)) 2,5-furandicarboxylate)-co-poly(isosorbide 2,5-furandicarboxylate) (PEGISF2000).

Table 1
Results related to the polycondensations carried out in this study.

Polymer	diol(s) (%)[a]	M_w/g mol^{-1} [b]	$Đ$[c]	Isolation yield (%)[d]
PEGF200	0.5 PEG200	3300	1.8	57.6
PEGF400	0.5 PEG400	7400	1.4	56.8
PEGF2000	0.5 PEG2000	17 300	1.3	76.0
PEGISF2000	0.25 PEG2000 + 0.25 IS	13,200	1.2	68.7

[a] Molar percentage of diol added. PEG200, PEG400 and PEG2000 stands for PEG with number-average molecular weight equal to 200, 400 and 1,200, respectively; and IS for isosorbide.

[b] Weight-average molecular weight of PEEs determined by SEC in $CH_2Cl_2/CHCl_3/$HFP.

[c] Polydispersity index of PEEs determined by SEC in $CH_2Cl_2/CHCl_3/$HFP.

[d] Weight isolation yields of precipitated polymers in ethanol.

3.1. Structural characterisation

These novel PEEs were extensively characterised by means of ATR FTIR spectroscopy, as illustrated in Fig. 1 for PEGF2000 and PEGISF2000 polymers, and their PEG2000 counterpart precursor.

Their main characteristic FTIR spectroscopic features were (Fig. 1): two new bands, one near 1720 cm^{-1}, attributed to the C═O stretching mode ($\upsilon_{C═O}$) of an ester moiety and the other band at 1273 cm^{-1} attributed to C–O–C stretching mode ($\upsilon_{C–O–C}$), also from an ester group. Additionally the absence of a detectable band of O–H stretching mode (υ_{OH}) near 3415 cm^{-1} corroborated, thus, that these polymers reached a reasonable molecular weight.

Additionally, both the characteristic bands of furan moieties were detected. Indeed, their spectra show near 3160 and 3113 cm^{-1}, two weak bands arising from = C–H stretching mode ($\upsilon_{=C–H}$) associated with furan moiety; and several bands at 1580, 959, 840 and 766 cm^{-1} typical of 2,5-disubstituted furan heterocycle.

The signals associated with PEG moiety at 2879 cm^{-1}, arising from the antisymmetric and symmetric stretching of C–H bond of CH_2 groups ($\upsilon_{C–H\ asym,\ sym}$) and the C–H bending vibration near 1465 cm^{-1} were also detected. In the case of PEGISF2000 these peaks were overlapped with the typical isosorbide bands. These attributions were in accordance with literature values for similar polymers [12,38–40].

Additionally, the success of these polymerisations and the expected structure of the ensuing polymers were also confirmed by ^{1}H and ^{13}C NMR spectroscopies (Table 2, Fig. 2 and Table S1 of Supplementary Information). The ^{1}H NMR spectra of PEEs (Table 2 and Fig. 2) display significant differences compared with their precursors, viz.: two resonances at ca. δ 4.49 and 3.82 ppm, attributed to the methylene protons of OCH_2 and OCH_2CH_2 groups of PEG (*Ha*, *Hb*), owing to the neighbouring carbonyl group of furan moiety, respectively. Additionally, in the particular case of PEGISF2000 the ^{1}H NMR spectra also show several resonances associated with isosorbide moieties at ca. δ 5.46–5.41, 5.06, 4.69 and 4.05–4.11 ppm arising from *H2′* and *H5′*, *H3′*, *H4′* and *H1′* and *H6′* protons, near the carbonyl group of furan moiety, respectively [41–43].

These spectra also display the typical furan resonances associated with *H3* and *H4* protons at $\delta \approx 7.26$ and/or at 7.23 ppm due to the near isosorbide or PEG moieties, respectively; and a singlet at $\delta \approx 3.65$ ppm, arising from *Hc* and *Hd* protons of OCH_2 group of PEG block.

Moreover, a deeper inspection of PEGISF2000 ^{1}H NMR results allowed assessing the real molar ratios of IS and PEG units in the polymer, calculated using the integration areas of *H3* and *H4* furanic proton resonances near IS or PEG moieties at $\delta \approx 7.26$ and at 7.23 ppm ($ratio \approx A_{H3,H4;F-IS}/A_{H3,H4;F-PEG}$), respectively. Results have shown that isosorbide moieties were incorporated in relatively higher quantities rather than PEG ones (around 3 times more), despite the starting feed ratio used (equimolar amounts of IS and PEG) (Table 2). This observation could be due to the lower reactivity of PEG oligomers under the polycondensation reaction conditions used. Nevertheless, the incorporated PEG had an impact on PEGISF2000 properties as discussed below.

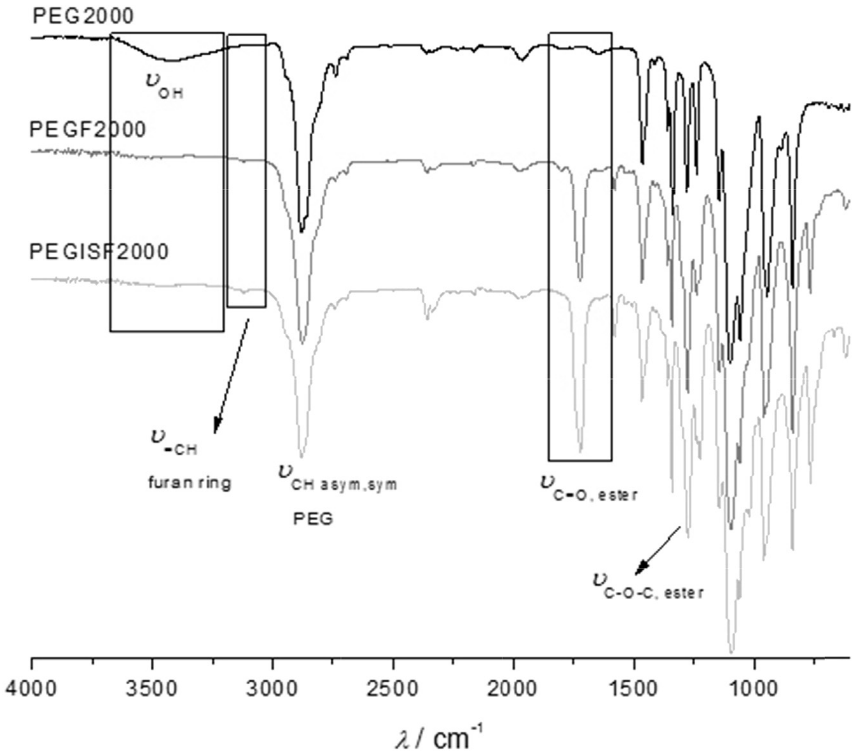


Fig. 1. ATR FTIR spectra of PEG2000 macromonomer and related polyesters PEGF2000 and PEGISF2000.

Table 2
Main ^{1}H NMR resonances of PEGFs.

δ/ppm	Mult[a]	Assignment	Integration area			
			PEGF200	PEGF400	PEGF2000	PEGISF2000
7.26	s	*H3*, *H4*, *F*-IS	–	–	–	1.0
7.23	s	*H3*, *H4*, *F*-PEG	1.0	1.0	1.0	0.3
5.46–5.41	s, q	*H2′*, *H5′*, F-*IS*	–	–	–	1.0
5.06	t	*H3′*, F-*IS*	–	–	–	0.5
4.69	d	*H4′*, F-*IS*	–	–	–	0.5
4.49	t	*Ha*, F-*PEG*	2.1	2.0	2.1	1.5
4.05–4.11	m	*H1′*, *H6′*, F-*IS*	–	–	–	2.1
3.82	t	*Hb*, F-*PEG*	2.1	2.1	2.3	1.7
3.65	s	*Hc*, *Hd*, *PEG-PEG*	4.9	13.8	83.9	64.8

[a] Mult stands for multiplicity

The ^{1}H NMR spectrum of PEGISF2000 provided another important piece of information related with how F, IS, and PEG were preferentially linked, viz., F-IS or F-PEG. Hence, the related molar ratios $A_{H3,H4;F-\mathrm{IS}}/(A_{H3,H4;F-\mathrm{PEG}}+A_{H3,H4;F-IS})$ and $A_{H3,H4;F-\mathrm{PEG}}/(A_{H3,H4;F-\mathrm{PEG}}+A_{H3,H4;F-IS})$ were calculated and estimated to be approximately equal to 0.76 and 0.23, respectively. F-IS linkage, thus, prevailed, which is consistent with the formation of a copolymer with isosorbide-furandicarboxylate blocks and incorporating PEG segments.

3.2. Thermal and XRD properties

An important aspect of these furan-based poly((ether)ester)s are their tailor-made properties, especially in terms of thermal behaviour, simply achieved by using different number-average molecular weight PEGs (i.e. 200, 400 and 2000 g mol^{-1}) or by incorporating rigid isosorbide units (Scheme 1) providing thus, to the ensuing polymers, soft hydrophilic moieties of different length (PEGFs' series) or rigid structures (PEISF2000), respectively. The TGA values (Table 3 and Fig. S2 of Supplementary Information) of these polymers confirmed, precisely, that the thermal stability can be tailored by changing the monomers used. Indeed, they were typically thermally stable up to ≈248–352 °C, in the following increasing temperature order: PEGF200 ≈ PEGF400 < PEGF2000 ≪ PEGISF2000. The highest thermal stability temperature (ca. 352 °C) was achieved for the polymer incorporating isosorbide, i.e. PEGISF2000, in accordance with reported studies about isosorbide-based polyesters [7,42,44]. Thereafter, these polymers decomposed with a major decomposition step at ca. 371–423 °C; followed by a broader second step at approximately 500 °C (only for PEGF200 and PEGF400), which left ca. 5% residue at this temperature.

The DSC thermograms of the PEGF series of polymers (Table 3 and Fig. 3) display a single glass transition (T_g), below room temperature, ascribed to the soft PEG segments. The T_g values decreased with the increasing chain length of these segments, associated with a decreasing polymer backbone stiffness. Therefore, PEGF200 has the highest T_g, followed by PEGF400, and PEGF2000 ($T_g \approx -6.5, -29.0, -35.1$ °C, respectively). As expected, these T_g values are substantially higher than those of their PEG precursors (with similar molecular-weights) [45], due to the

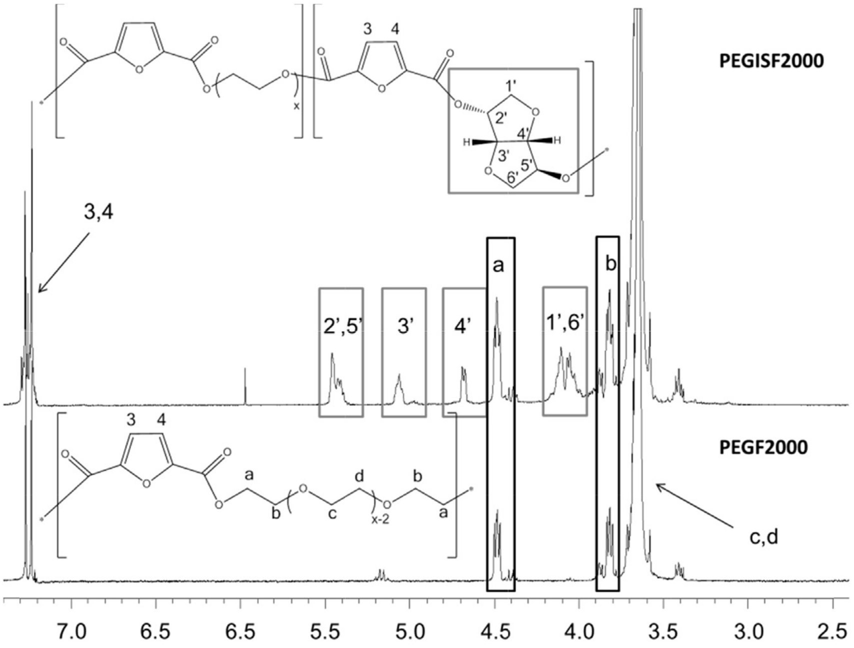


Fig. 2. ^{1}H NMR spectra of PEGF2000 and PEGISF2000.

Table 3
Characteristic glass transition (T_g), melting (T_m), decomposition at 5% weight loss ($T_{d,5\%}$) and at maximum decomposition ($T_{d,max}$) temperatures of all PEGFs studied.

Polymer	T_g/°C	T_m/°C	$T_{d,5\%}$/°C	$T_{d,max}$/°C
PEGF200	−6.5	–	253.5	371.4, 493.9
PEGF400	−29.0	–	248.2	372.9, 523.6
PEGF2000	−35.1	49.1	318.3	377.3
PEGISF2000	−26.4; 168.1[a]	40.9	352.2	422.6

[a] T_g values obtained from the second heating scan at 20 °C min^{-1}, after quenching.

presence of the stiff furan moieties, but are in accordance with their fossil counterparts [19,46,47]. Also, in the case of PEGF2000 a T_m around 49 °C was detected, probably due to the fact that only the longest soft PEG segments has enough chain mobility to form crystalline domains [46]. However, comparing the T_m of PEGF2000 with that of its PEG2000 precursor a depression of about 5 °C is noted.

In the particular case of PEGISF2000, the corresponding thermogram displays three different thermal events: one T_g below room temperature (ca. −26 °C), associated with PEG soft segments amorphous domains; one T_m around 40 °C also associated with PEG2000; and an additional T_g, at 168 °C, ascribed to a second amorphous phase enriched in the stiff isosorbide-furandicarboxylate segments. Noteworthy, the T_g value of poly(-isosorbide 2,5-furandicarboxylate) homopolyester reported in the literature (*ca.* 180 °C [7]) is in accordance with this quite high value (*ca.* 168 °C), although slightly higher. Another aspect is that a substantial increase in this T_g value was achieved compared with those reported in the literature for their fossil counterpart (which typically vary between ca. 26–58 °C) [19], enlarging thus the service temperature range of typical PEEs.

The existence of several distinct thermal events is indicative of microphase separation promoted by the existence of two different blocks, one corresponding to the hydrophilic soft segments of PEG2000 and the other typical of hard isosorbide-furandicarboxylate segments as also pointed out by ^{1}H NMR analysis.

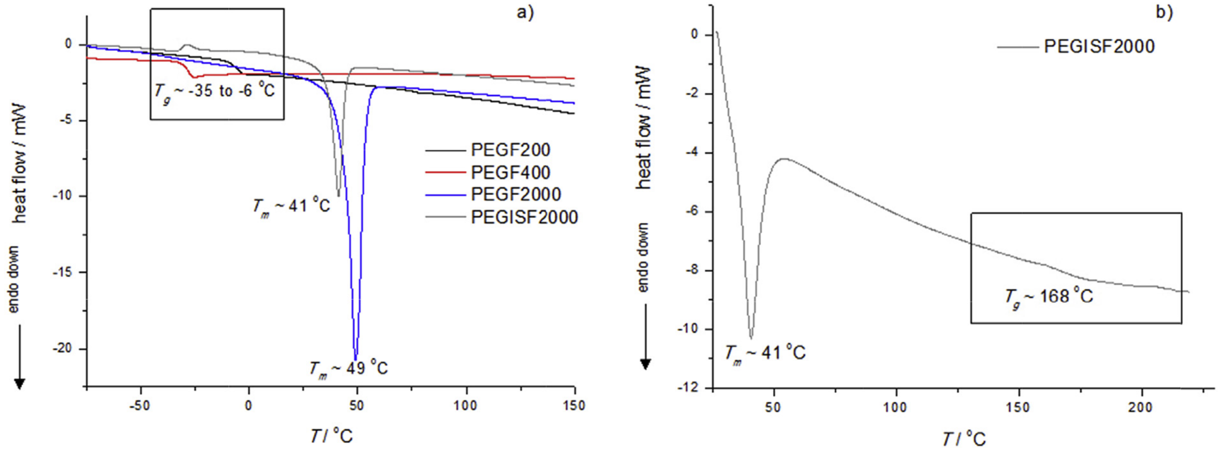


Fig. 3. DSC thermograms of a) all PEGFs and PEGISF2000 (heating rate of 10 °C min^{-1}) and b) of PEGISF2000 displaying the high glass transition (taken at a faster heating rate of 20 °C min^{-1}).

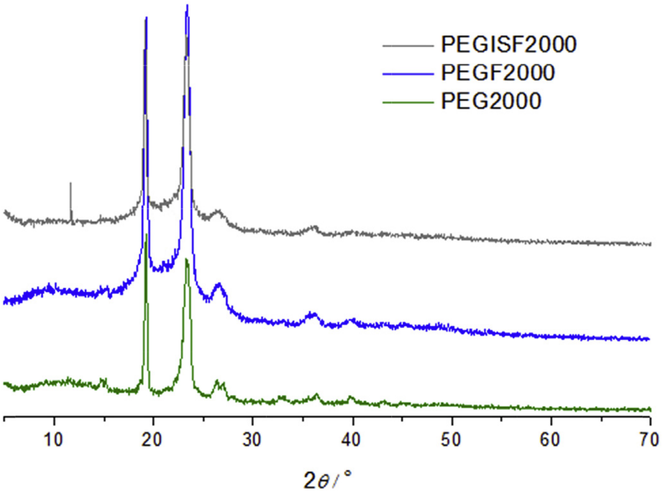


Fig. 4. XRD patterns of PEGF2000, PEGISF2000 and PEG2000 precursor.

The semi-crystalline character of PEGF2000 and PEGISF2000 polymers was corroborated by the presence of two sharp signals in their X-ray diffractograms (Fig. 4), at $2\theta \approx 19$ and 23°, i.e., a pattern similar to that of PEG2000. Additionally, an amorphous halo centred at ca. 20° is also observed in the case of PEGF2000 and PEGISF2000, albeit not present in their more crystalline PEG precursor.

4. Conclusions

In conclusion, novel FDCA-poly((ether)ester)s entirely based on renewable monomers (i.e. FDCA, PEG and isosorbide) were successfully synthesised. Moreover, their general properties can compete with terephthalic acid-based polymers or at least they are comparable, which indicates that FDCA-based poly((ether)ester)s are a viable alternative to their highly successful commercially-available counterparts derived from petrochemicals [32]. Indeed, these new PEEs present film-forming ability and the properties can be fine-tuned, by the simple adjustment of the chain length of PEG segments and also by incorporating (or not) rigid isosorbide moieties. An attractive challenge is the development of FDCA-based PEEs porous specimens (including composite ones) and to assess their properties including the mechanical performance.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.06.015.

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