



## Sulfone-bridged difuran polyesters

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### ABSTRACT

Oxidation of 5,5'-sulfanediyl di(furan-2-carboxylic acid) in acetic acid with aqueous hydrogen peroxide was used to prepare a new dicarboxylic monomer with a central sulfone group flanked by two biomass-derived furan rings. The new sulfone monomer was reacted with ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol to prepare new homopolyesters. Of these diols, 1,5-pentanediol yielded polyester with the most favorable properties in terms of processability and appearance. It could also be recycled back into the starting monomer under mild conditions. Using 1,5-pentanediol, a copolyester containing a 1:1 mixture of sulfone and sulfide difuran units was also prepared for testing alongside the corresponding sulfone difuran homopolyester. From measurements carried out on film samples of these two new materials, it was found that the new sulfone monomer will lead to polyester materials with high glass transition temperatures, high tensile stiffnesses, and low O<sub>2</sub> permeability. The nature of the side reactions related to the difuran sulfone moiety under high temperatures remained unclear, as thermogravimetric analysis indicated relatively good stability characteristics and the monomer appeared relatively stable even at high temperatures.

### 1. Introduction

Furan-derived polymers are an attractive group of materials since they may take advantage of biomass feedstocks rather than non-renewable sources.[1–4] Furfural and 5-(hydroxymethyl)furfural (HMF), obtained from abundant sugars via dehydration, are two possible platform chemicals for such polymers. Furfural, for example, has been applied as a feedstock for furfural and furfuryl alcohol resins. As a much more recent development, an alternative for the wide-spread thermoplastic polyester poly(ethylene terephthalate) (PET, Scheme 1a) called poly(ethylene furanoate) (PEF, Scheme 1b) has been heading towards commercialization.[5–7] PEF has several properties that make it a valid alternative in packaging applications, and its improved barrier characteristics have been considered especially noteworthy.[8,9] Numerous polyesters have been synthesized from 2,5-furandicarboxylic acid (2,5-FDCA) in addition to PEF, and they more often than not show interesting deviations in properties from e.g., their terephthalic acid-based relatives.[10–15] It can therefore be said that novel furan-based polyesters have formed an interesting category of polymers with useful and sometimes surprising properties.

There are very few reports available on polymers where the main chain contains linkages between sulfur atoms and furan rings.[16–18]

Among the different heteroatoms that polymers may be functionalized with, sulfur is interesting owing to its redox properties. Notably, sulfides (thioethers) may be converted into sulfoxides or further into sulfones with oxidants. The oxidation of sulfide into sulfone should entail dramatic changes in polymer properties e.g., increased glass transition and melting temperatures. Such transformations are also relevant in applications involving biological systems.[19–21] Both sulfide and sulfone moieties can be found in high-performance polymers, which typically comprise aryl sulfide or sulfone units, sometimes with other heteroatom-containing groups (e.g., ether or ketone).[22,23] Examples include poly(phenyl sulfide) and poly(phenyl sulfone)s, the latter of which usually contains both ether and sulfone linkages between aryl units. These polymers and their structural congeners are typically characterized by mechanical robustness, high thermal resistance, and good chemical stability.

Recently, we reported a new diacid monomer based on furfural, which contained a sulfide bridge between two furan rings (Scheme 1c). [24] Poly(alkylene sulfanediyl difuranoate)s derived from the monomer had low oxygen gas permeabilities, which is of interest in e.g., packaging applications. In this respect, the novel polyesters proved advantageous over the related 2,2'-bifuran polyesters. As a continuation for that work, we now report results obtained from the corresponding sulfone-based

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system. We were especially interested in seeing how the thermal properties were affected by the sulfone units, since the sulfide-based polyesters were characterized by glass transition temperatures lower relative to PET and PEF, along with pronounced amorphous character. Another aspect we were interested in was the oxygen gas barrier, which in the case of the sulfide-based polyesters was already at an excellent level, matching PEF and surpassing PET.

## 2. Materials and methods

### 2.1. Materials

Ethylene glycol (EG, 99.8%), 1,5-pentanediol (1,5-PeD, 98%), and methanol (99.9%) were used as received. 1,3-Propanediol (1,3-PD) and 1,4-butanediol (1,4-BD) were distilled (under atmospheric and vacuum conditions, respectively) and subsequently stored over 3 Å molecular sieves. 5,5'-Sulfanediylidifuran-2-carboxylic acid (**1**), its dimethyl ester (**1a**), and PPeSF were synthesized as previously reported.<sup>[24]</sup> All syntheses were performed under air unless otherwise noted.

### 2.2. Synthesis of sulfone dimethyl ester **3**

Sulfide **1** (6.35 g) was first ground into a fine powder and suspended in 30 mL of 99% acetic acid. The mixture was heated to 80 °C, and 30% w/w hydrogen peroxide solution (10.2 mL, 4 equiv H<sub>2</sub>O<sub>2</sub>) was then added in dropwise over 30 min under stirring. Two more dropwise additions of 4 and 2 equiv hydrogen peroxide were done after 2 and 10 h, respectively. The reaction was ended after a total reaction time of 22 h. The reaction mixture was cooled to 4 °C and filtered, and the pale-yellow solid was washed with deionized water and dried under suction. A crude product was obtained (6.39 g), which was subjected to NMR analysis (Figs. S1 and S2). Based on <sup>1</sup>H NMR, it contained >96 mol% of the desired sulfone **2a**. The crude product (6.35 g) was then suspended in 250 mL of anhydrous methanol containing 2.4 mL of conc. H<sub>2</sub>SO<sub>4</sub>. The mixture was refluxed overnight under vigorous stirring. The solution was then stored at -18 °C and the precipitated colorless crystals were recovered by filtration from the methanol. The crude product was rinsed using deionized water to wash off any sulfuric acid residue. After

vacuum drying, 6.68 g of crude product was obtained. Final purification consisted of passing the crude product through a small column of silica gel using either chloroform or dichloromethane as an eluent. After collecting the pure sulfone fractions, removal of the solvent by distillation under reduced pressure gave sulfone **3** as a white crystalline powder for a yield of 81% (6.33 g) over two steps. Melting point (DSC): 194 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.42 (d, *J* = 3.7 Hz, 2H), 7.25 (d, *J* = 3.7 Hz, 2H), 3.92 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm): δ 157.7, 149.8, 148.7, 120.4, 118.1, 52.7. HRMS *m/z* calculated for C<sub>12</sub>H<sub>10</sub>O<sub>8</sub>NaS [M + Na]<sup>+</sup>: 336.9989, found 336.9977.

### 2.3. Polyester synthesis (**4a–e**)

All polyesters were synthesized using similar two-step procedures (Table 1). In each case, the titanium catalyst solution, prepared in 1 mL of dry toluene, and the monomer(s) **3** and/or **1a** (4–8 mmol) were added successively into a 50-mL round-bottom flask containing the diol (2.2 equiv). The reaction mixture was initially heated under argon atmosphere starting from 180 °C, with higher temperature applied if necessary to prevent solidification. During the latter half of the transesterification, a gradual vacuum was applied until a pressure of ca. 5 mbar was reached. During this time the excess diol was distilled off. Then, the temperature was increased to the final polycondensation temperature followed by further reduction in pressure to 0.1–0.3 mbar. After the polycondensation, the flask was cooled to room temperature,

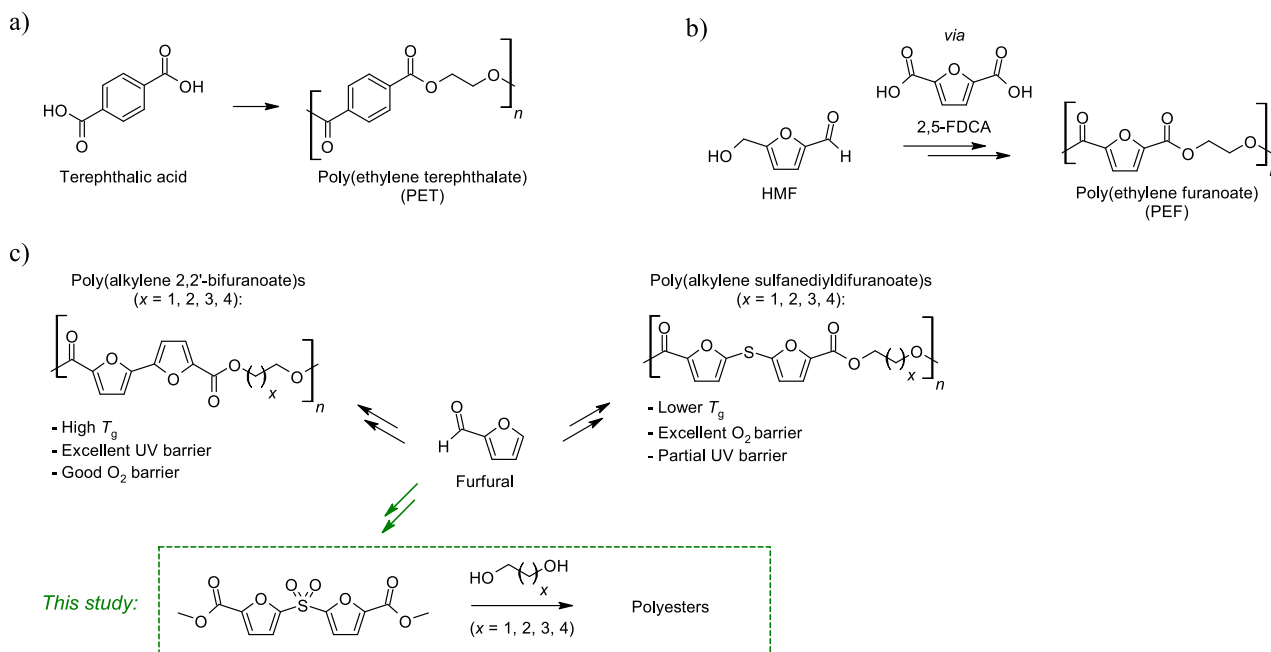
**Table 1**

Reaction conditions applied in the synthesis of polyesters from **3** and different diols.

Polymer	Diol	Transesterification		Polycondensation	
		Time (h)	Temp (°C)	Time (h)	Temp (°C)
<b>4a<sup>a</sup></b>	Ethylene glycol	3.5	180–260	1	280
<b>4b<sup>a</sup></b>	1,3-Propanediol	3.5	180–280	1	280
<b>4c<sup>b</sup></b>	1,4-Butanediol	3.5	180–210	2	250
<b>4d<sup>b</sup>, 4e<sup>b</sup></b>	1,5-Pentanediol	3.5	180	4	220

<sup>a</sup> 1000 ppm tetrabutyl titanate relative to **3**.

<sup>b</sup> 400 ppm.



**Scheme 1.** Chemical structures of barrier polyesters PET (a) and PEF (b) compared to the structures of furfural derived barrier polyesters from our previous works (c).

and the soluble products (**4c–e**) were dissolved in HFIP (10% w/v). Optionally, the solution was allowed to drain through a fritted glass disc (porosity 1) prior to precipitation in 10-fold excess of methanol (**4d**). The solid products were collected via filtration and dried under vacuum at 60 °C until further mass loss was no longer observed. Polyesters that could not be solubilized in HFIP were instead removed mechanically from the flasks (**4a**, **4b**).

#### 2.4. Polyester recycling experiments

The polyester film of melt-pressed **4d** (thickness 0.1 mm) was first cut into ca. 5 mm × 15 mm sized pieces. An amount corresponding to 0.5 mmol of repeating units was weighed (177.8 mg) and transferred into an oven-dried 5 mL tube along with a PTFE-coated stirring bar, 2 mL of methanol (ca. 100 equiv), and 13.8 mg of K<sub>2</sub>CO<sub>3</sub> (0.2 equiv). The tube was sealed, and the mixture was stirred at 50 °C for 24 h. The mixture was then diluted with ethyl acetate (30 mL) and washed twice with 10 mL deionized water and once with 10 mL brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered through cotton, and evaporated to dryness under reduced pressure, giving pure monomer **3** in 87% average yield (138.7 mg) from duplicate experiments. From of PPeSF films (0.5 mmol of repeating units, 161.2 mg), **1a** was obtained in 90% average yield (125.6 mg) from similar duplicate experiments. In a gram-scale depolymerization experiment, 2.88 g of film pieces from various batches of **4d** were cut into strips and placed in a 100 mL round-bottom flask. Methanol (36 mL) and K<sub>2</sub>CO<sub>3</sub> (0.22 g) were added on top. The mixture was magnetically stirred for 24 h at 50 °C under argon balloon, and then diluted with 250 mL of ethyl acetate. After washing with deionized water (4×50 mL) and brine, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered through a short silica gel plug. Evaporation of the solvent under reduced pressure gave **3** as a white crystalline powder (2.20 g, 86%).

#### 2.5. Characterization

Intrinsic viscosities were calculated via flow time measurements in a 60:40 (w/w) mixture of phenol and 1,1,2,2-tetrachloroethane at 30.0 °C as described in our previous report.<sup>[24]</sup> DSC measurements (Mettler Toledo DSC821e) were carried out under 50 mL/min N<sub>2</sub> flow with samples in 45 µL Al cups sealed with pierced lids. Samples were held for 3 min at the final temperature of the heating scan (at 10 °C/min) to erase thermal history before cooling (at –10 °C/min). Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 or 20 °C/min (for monomers and polymers, respectively) under 20 mL/min N<sub>2</sub> flow (Netzsch STA 409). The polymer samples used for DSC and TGA were either mechanically collected from the reaction flask after the polycondensation (**4a–c**) or after methanol precipitation and drying (**4d** and **4e**). Melt-pressed films were prepared from 1 to 1.5 g of dry polymer, which was melted in a heated press between PTFE-coated glass-fiber sheets (Fiberflon) at 220 °C for 2–3 min. The melt was then compressed under 30–40 kN force, with a frame of glass-fiber sheet controlling the thickness (0.1–0.2 mm), and subsequently cooled to room temperature using the integrated water circulation. For comparison, PET, PEF, PPeSF, and poly(pentamethylene 2,2'-bifuran-5,5'-dicarboxylate) (2,2'-PpEbF) films were prepared according to similar methods.<sup>[25,26]</sup> Dynamic mechanical analysis was performed under air using film tension clamps (TA Instruments DMA Q800) with sample dimensions of ca. 20 mm length, 5 mm width, and 0.1 mm thickness. Tensile tests for the films were conducted at 23 °C and 50% relative humidity. The samples were stored under the same conditions for at least 48 h prior to testing, and at least 5 rectangular specimens (5 mm width, 30 mm gage length) were tested for each material at 5 mm/min strain rate. O<sub>2</sub> permeabilities were measured (Mocon OxTran 2/21, test area 5 cm<sup>2</sup>) in duplicate, with reported value being the measured oxygen permeability after a physical aging time of 3 months at room temperature (21–23 °C). UV–vis transmittances were measured from films ca 0.1 mm thick using a

spectrophotometer (Shimadzu UV-1800). The water contact angle of the melt-pressed films was measured (Krüss DSA100, Germany) with a high-speed camera (1000 frames per second) and drop analyzing software. The droplet size of 2-µm water was used.

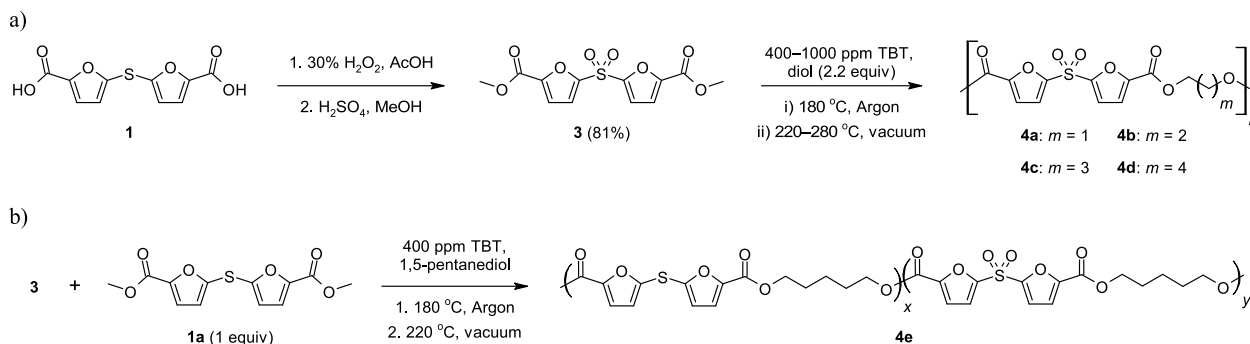
### 3. Results and discussion

#### 3.1. Monomer and polymer synthesis

Oxidation of sulfide diacid **1** into sulfone diacid **2a** was carried out using a classic method (Scheme 2a) where the sulfide is treated with a mixture of aqueous hydrogen peroxide and glacial acetic acid. Upon <sup>1</sup>H NMR analysis, it was concluded that 4 equiv of hydrogen peroxide was enough to convert the sulfide diacid almost fully (ca. 1% remaining), though about 9% of the difuran remained as the sulfoxide diacid, with the rest being the desired sulfone diacid. Increasing the hydrogen peroxide excess substantially (from 4 to 10 equiv) reduced the apparent sulfide and sulfoxide contents to ca. 0.5 and 3 mol%, respectively (see Fig. S1). The oxidation might be partially hindered by the inclusion of the sulfide or the sulfoxide within the poorly soluble sulfone precipitate, a situation that is probably not improved when water is introduced to the mixture with the peroxide solution. Esterifying this crude sulfone diacid with acidified methanol gave a corresponding mixture of the three dimethyl esters. Upon cooling the reaction mixture, the undesired sulfide and sulfoxide mainly remain dissolved in the methanol, and simply filtering the solution mostly removed the byproducts. The crude product was finally subjected to chromatographic purification to separate any remaining sulfide and sulfoxide, yielding sulfone **3** as a bright white crystalline powder.

Polymerization was attempted between dimethyl ester **3** and four common diols to prepare the four homopolyesters **4a–d** shown in Scheme 2a. Tetrabutyl titanate (TBT) was employed as the transesterification catalyst. The reactions had mixed results: With ethylene glycol the polycondensation generally proceeded poorly when 400 ppm of TBT was used. An oligomeric and incompletely transesterified product was obtained despite a lengthy 4 h transesterification time prior to polycondensation. Higher catalyst loading of 1000 ppm improved the reaction, but gradual solidification throughout the reaction necessitated a drastic increase in temperature as well (up to 280 °C). This product was very dark in color. It swelled considerably in HFIP with slight dissolution, which indicated chain branching or cross-linking. Under the same reaction conditions, similar results were obtained with 1,3-propanediol, except that the product (**4b**) was even less affected by solvents such as HFIP or trifluoroacetic acid. In complete contrast to the previous, the reaction between 1,4-butanediol and sulfone monomer **3** was markedly vigorous: Foaming and bubbling could be observed once a homogeneous melt began forming at 180 °C, accompanied by rapid distillation of the released methanol (in as little time as 15 min). The final product **4c**, however, was again very dark in color and brittle after polycondensation despite the slightly lower final temperature of 250 °C. It was, however, more soluble in HFIP than **4a** or **4b**. 1,5-Pentanediol resulted in a similarly vigorous reaction with almost immediate distillation of methanol but, notably, the product (**4d**) could be maintained as a melt at a considerably lower temperature than the others. Therefore, the temperature of the melt polycondensation was lowered to 220 °C in an attempt to avoid the side-reactions and darkening encountered with **4a–c**. The product obtained at this lower temperature was light-yellow to yellow in color instead of brown (Fig. S6). It dissolved easily in HFIP, although some very small gel-like clumps could be removed from the solution via filtration. The intrinsic viscosity was measured to be reasonably high at 0.70 dL/g despite the low polycondensation temperature.

The conclusion drawn from these experiments is that the synthesis of homopolyesters **4a–d** is less straightforward than their sulfide counterparts. Some form of cross-linking or branching process appears to initiate at temperatures higher than 220–240 °C. Since temperatures



**Scheme 2.** Synthesis route to sulfone-based homopolymers **4a–d** (a) and copolyester **4e** (b).

exceeding this range are required to maintain a melt state for **4a–c**, their syntheses were met with limited success. Similarly, melt-processing could not be used to yield useful specimens for further testing from these samples. With **4d**, the same issues were avoided and a homopolymer of reasonable quality was obtained, giving free-standing melt-pressed films. To further compare the sulfone versus sulfide effect, a corresponding sulfone-sulfide copolymer **4e** was also synthesized using 1,5-pentanediol (Scheme 2b). Its intrinsic viscosity at 0.67 dL/g was comparable to **4d**.

### 3.2. NMR characterization

<sup>1</sup>H NMR analysis of the homopolymers did not offer much insight into the nature of the side-processes that had occurred with **4a–c**: The spectra mostly matched the expected structures of the homopolymers but with some unexpected features (Figs. S7–9). Product **4a** was found to contain an unusually high amount of end groups and diethylene glycol units, though it was not possible to surmise their ratio because of peak overlap. Since the sample could not be dissolved completely, shorter, more soluble chains also may have contributed more to the spectrum. Homopolymer **4b** in turn had the most conspicuously low solubility in CF<sub>3</sub>COOD and its mixtures with CDCl<sub>3</sub>. As a result, low-quality spectrum was obtained, though the peaks and their integrals did appear to match with the repeating structure of **4b**. Similarly, the spectral features of **4c** seemed to match the expected structure, except for the splitting of the furan ring proton signals. A deviation from the expected integral ratios can be seen as well, which suggests an excess of furan units relative to the butylene unit. In contrast, **4d** gave less ambiguous results, but small additional doublet peaks were seen between the furan doublets (Fig. S10). These additional signals belonged to a compound that was observed to condense on the neck of the reaction flask from where it could be collected for analysis in its pure state (Fig. S13). Its appearance in <sup>1</sup>H NMR is consistent with a cyclic oligomer, and it is clearly responsible for the extra peaks that were seen in polymer **4d**, where it slightly affected the integrals of the two alkyl region peaks. As for copolymer **4e**, the <sup>1</sup>H NMR revealed that the feed ratio (50:50) for the sulfide and sulfone units was faithfully repeated with a calculated sulfide-sulfone ratio of 49.4:50.6 (Fig. S14). Further analysis using <sup>13</sup>C NMR pointed to an almost ideal random distribution of sulfide and sulfide difuran moieties along the chains (Fig. S15). As with **4d**, a small amount of white sublimate collected on the neck of the flask during the synthesis of the copolymer. <sup>1</sup>H NMR showed that this byproduct contained the previously isolated sulfone compound and what appeared to be its sulfide counterpart. The composition of this mixture was slightly skewed towards the presumably more volatile sulfide species (Fig. S17). Considering the structural similarities between the sulfide and sulfone monomers, it is perhaps not surprising that similar byproducts were formed and volatilized to a similar degree. The fact these compounds were only isolated in reactions with 1,5-pentanediol suggests that with the other diols small and volatile byproducts were not formed to the

same extent.

### 3.3. Thermal characterization

Thermal analysis was carried out with the caveat that the final temperatures might induce further decomposition in some of the samples. As expected, signs of crystallinity were observed in all of the samples. Polyesters **4a–c** had high melting temperatures close to or greater than 240 °C (Table 2). The only exceptions were homopolymer **4d** and copolymer **4e**. One shared feature between the sulfone and sulfide difuran series of polyesters is that the 1,3-propanediol homopolymers appear to favor noticeably higher crystallinity or melting temperatures over the others. The only semi-crystalline polyester in the sulfide series was, in fact, the homopolymer of 1,3-propanediol and **1a** [24]. This similarity might be explained by the difuran units of both the sulfide and the sulfone likely adopting similar conformations due to the bent structure caused by the sulfur moiety. [27,28] The bent structure might be hindering crystallization, and indeed, the sulfide series of polyesters was characterized by low crystallinities and melting temperatures. Increased interactions between polar moieties seems to mitigate these difficulties in the sulfone polyester series as evidenced by their prominent melting endotherms and higher melting temperatures.

It is noteworthy that the cold crystallization exotherms and melting endotherms could only be observed during the initial heating scan in the sulfone series: No crystallization was observed from the melt in any of the polyesters, and in each case, the second heating scan only revealed a glass transition step (Figs. S19–21). This behavior appears to be further proof of branching or cross-linking (due to possible partial decomposition of the difuran sulfone unit), suppressing further crystallization in these polyesters. The glass transition temperatures between the first and second cooling scans were very close to each other, meaning the expected polymer structures had only partially degraded. When compared to the corresponding sulfide-bridged polyesters i.e., poly(alkylene sulfanediyldifuranoate)s, the glass transition temperatures were enhanced according to a fairly consistent trend (Fig. 1). When comparing the two series, the difference in *T<sub>g</sub>* was most pronounced between the 1,5-pentanediol homopolymers. We interpret this to be the result of limited polymerization and thus low molecular weight of samples **4a–c** i.e., we

**Table 2**  
Thermal properties of homopolymers **4a–d** and copolymer **4e**.

Polymer	Diol unit	<i>T<sub>g</sub></i> (°C)	<i>T<sub>cc</sub></i> (°C)	<i>T<sub>m</sub></i> (°C)
<b>4a</b>	EG	96	202	225, 241
<b>4b</b>	1,3-PD	81	141	246, 260
<b>4c</b>	1,4-BD	68	119	239
<b>4d</b>	1,5-PeD	63	–	206
<b>4e<sup>a</sup></b>	1,5-PeD	41	–	82, 110, 132

<sup>a</sup> Copolymer containing 1:1 M ratio of sulfone and sulfide difuran units. *T<sub>g</sub>*: glass transition temperature from the 1st cooling scan. *T<sub>cc</sub>*: cold crystallization temperature from the 1st heating scan. *T<sub>m</sub>*: melting temperature(s) from the 1st heating scan.



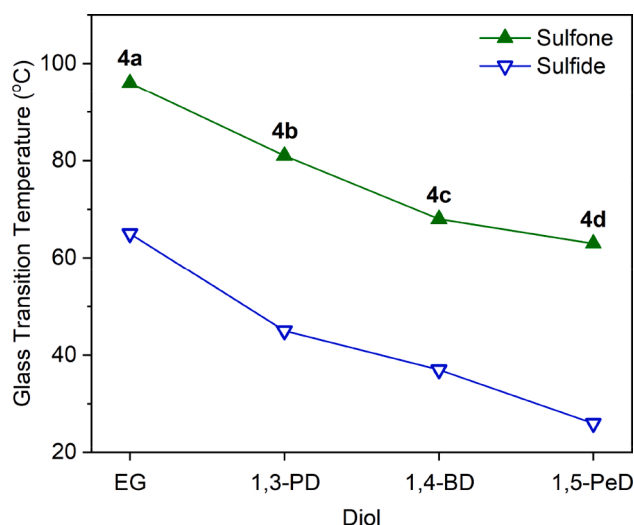


Fig. 1. Comparison between the glass transition temperatures of the synthesized sulfone homopolyesters 4a–d and the corresponding sulfide polyesters [24]. Lines are drawn as a guide to the eye.

expect that the glass transition temperatures of these polymers would be elevated if higher degree of polymerization could be reached. Furthermore, the high  $T_g$  of 4d is worth mentioning as it exceeds that of many other reported homopolyesters derived from 1,5-pentanediol and aromatic dicarboxylate monomers, including terephthalic acid, 2,5-FDCA, 2,2'-bifuran-5,5'-dicarboxylic acid, and 2,6-naphthalenedicarboxylic acid.[29–31].

While the observable glass transition and melting temperatures were certainly elevated in the difuran sulfone series, the problems encountered during the polyester syntheses clearly suggested that they are more thermally labile. Conventional diaryl sulfone polymers, in contrast, are known for being rather heat stable and usually suitable for demanding high-temperature applications. On the other hand, the strength of the carbon–sulfur bonds generally decreases in the order C–S > C–SO<sub>2</sub> > C–SO, although some aryl sulfones may be far more thermally stable than suggested by simple bond energy considerations.[32,33] Here, TGA did not provide clear evidence supporting any major thermal stability difference between the difuran sulfone and the difuran sulfide polyesters. In the case of the dimethyl ester monomers, sulfone 3 had a mass-loss temperature some 40 °C higher than the corresponding sulfide monomer 1a (Fig. S24a). This result may simply be a consequence of the higher melting point (ca. 40-degree difference) and lower volatility of the sulfone. A 200 mg sample of sulfone monomer 3 was also heated in a small, capped glass vial under argon at 250 °C for several hours. A light-red color appeared in the melt, but the <sup>1</sup>H NMR spectrum obtained from this product was identical to that of the pure compound. These results indicate that the difuran sulfone moiety itself should be reasonably stable towards high temperature. It can be speculated that the strong electron-withdrawing character of the sulfone group can promote degradation pathways involving the alkylene ester moiety, e.g., beta scission. Via this pathway, the alkylene segment can be cleaved into volatile alkene(s) while the chain end is left with a carboxylic acid group that is then free to decarboxylate and potentially lead to the formation of reactive monosubstituted furan end groups.[34–36] Such processes could explain the observed cross-linking or branching at higher temperatures. However, the difuran sulfone homopolyesters 4a–d had very similar 5% and 50% mass-loss temperatures, based on TGA, as the previously reported difuran sulfide homopolyesters (Fig. S24b, Table S1). We envision that further studies are needed to clarify what mechanism underlies the seemingly facile darkening and cross-linking of the difuran sulfone unit at high temperatures and to what degree it is impacted by the catalyst. Nevertheless, the challenging thermal

characteristics of homopolyesters 4a–c prevented us from preparing any free-standing film samples for further testing. The following material characterizations for film samples were thus limited to 1,5-pentanediol polyesters 4d and 4e only.

### 3.4. Thermomechanical characterization and water contact angles

First, the melt-pressed films from 4d and 4e were subjected to dynamic mechanical analysis (Fig. 2). For both materials, the peak of loss modulus  $E''$  closely matched the  $T_g$  measured using DSC. It is also notable that despite the slow heating rate (3 °C/min), homopolyester 4d did not cold-crystallize during DMA, providing further proof of its poor crystallizability. Tensile testing carried out on the films revealed that the difuran sulfone units will lead to highly rigid materials: Despite its flexible 1,5-pentanediol moieties, 4d appeared very stiff and brittle (Table 3). The same was true of copolyester 4e, which performed almost identically. The high tensile modulus of 4d (and 4e) appears notably high among various 1,5-pentanediol homopolyesters.[15,29,37,38] The properties of the sulfone-containing polyesters contrast strongly with the sulfide-based PPeSF, which is a soft, ductile material due to its near-room temperature  $T_g$ . However, the water contact angles (WCA) between 4d, 4e, and PPeSF films did not differ dramatically (Table S2). While PPeSF was the least hydrophilic of the three (WCA = ~88°), 4d and 4e yielded practically identical values (WCAs of ~84° and 83°, respectively). In other words, WCAs were not greatly impacted by the sulfone groups in these difuran polyesters. Coincidentally, these contact angles were similar to the values measured for PEF and PET.

### 3.5. O<sub>2</sub> permeability and UV–vis transmittance

To appreciate the possible influence of the oxidation state of the sulfur atom on gas barrier, the O<sub>2</sub> permeability of 4d was compared against its sulfide analog, PPeSF. Surprisingly, their O<sub>2</sub> permeabilities were found to be very comparable, with BIF<sub>PET</sub> values of ca. 2 for both (Table 4). Therefore, the difuran sulfide and the difuran sulfone structures appear to be rough equals in terms of endowing a reasonably low oxygen gas permeability. However, the gas permeability of the 50:50 mol% copolyester, 4e, was lower, giving BIF<sub>PET</sub> = 2.9. In previous literature, sulfone moieties have endowed both increases and decreases in gas permeability depending on the polymer system in question. For wholly aromatic polyimides intended towards gas separation membranes, the sulfone moiety can result in generally higher gas permeability than the sulfide moiety.[39,40] On the other hand, polymerization of a sulfonated 1,10-decanediol analog gave polycarbonates, polyurethanes, and polyesters with very low CO<sub>2</sub> permeabilities.[41] Under current conditions, the difuran sulfone seems to endow 4d with a slight edge over PPeSF in terms of barrier performance. On the other hand, the low  $T_g$  of PPeSF (26 °C) [24] probably hinders its performance somewhat, as it is very close to the temperature the tests were carried out at (23 °C). It should also be noted that if the sulfur moiety is absent (whether –S– or –SO<sub>2</sub>–), as in the homopolyester of 2,2'-bifuran-5,5'-dicarboxylic acid and 1,5-pentanediol (Table 4, 2,2'-PPeBf), increased O<sub>2</sub> permeability results. In this sense, the combination of sulfur moieties and furan rings can be seen as a useful strategy towards decreased gas permeability.

Oxidation of the difuran sulfide into a difuran sulfone also affects the transmission of UV light. The ultraviolet cut-off wavelength of a free-standing film of 4d is lower by ca. 25 nm compared to its sulfide analogue PPeSF (Fig. 3). In other words, the strongly electron-withdrawing sulfone moieties in 4d result in UV light cut-off that is more comparable to “monofuran” polyesters, e.g., PEF, than PPeSF. Copolyester 4e performed similar to PPeSF (Fig. S25). Far broader UV-absorbance can be obtained with 2,2'-bifuran-based polyesters, e.g., the previously mentioned 2,2'-PPeBf: 2,2'-Bifuran is a much better UV absorber since the conjugation between the furan rings is not impeded by non-conjugating moieties such as the sulfone unit.[42].

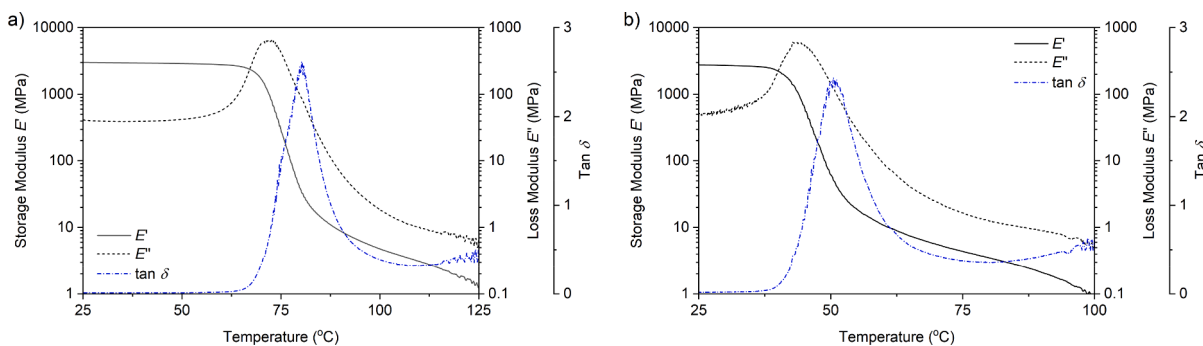


Fig. 2. DMA thermograms obtained from melt-pressed films of **4d** (a) and **4e** (b).

Table 3

Tensile test results for **4d** and **4e**.

Polymer	$E$ (MPa)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Reference
<b>4d</b>	$2096 \pm 51$	$43.3 \pm 3.1$	$2.3 \pm 0.2$	This work
<b>4e</b>	$1969 \pm 50$	$45.4 \pm 15.5$	$3.0 \pm 1.3$	This work
PPeSF	$445 \pm 27$	$6.3 \pm 0.5$	$440 \pm 100$	[24]

$E$ : Tensile modulus.  $\sigma_b$ : Tensile stress at break.  $\varepsilon_b$ : Tensile elongation at break. Measurements from at least 5 separate specimens.

Table 4

Oxygen gas permeability results for **4d** and **4e**.

Polymer	OP	BIF <sub>PET</sub>	Reference
<b>4d</b>	2211	2.1	This work
<b>4e</b>	1589	2.9	This work
PPeSF	2397	1.9	This work
PET	4638	1	[25]
2,2'-PPeBf	3080	1.5	[25]

OP: Oxygen permeability ( $\text{mL } \mu\text{m m}^{-2} \text{d}^{-1} \text{atm}^{-1}$ ) at 23 °C and 0% relative humidity. BIF<sub>PET</sub>: Barrier improvement factor versus amorphous PET.

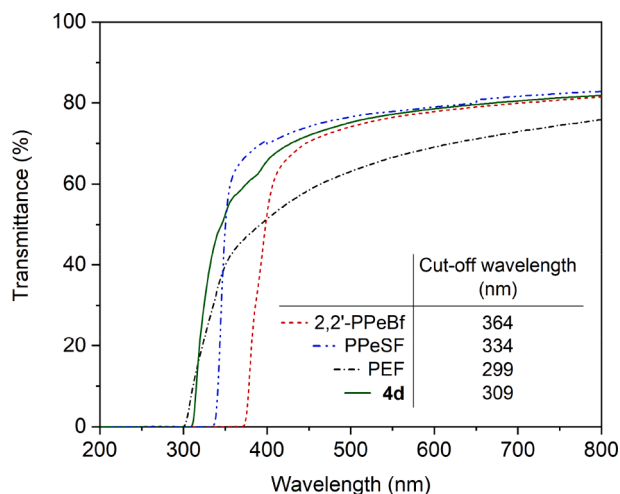


Fig. 3. UV-vis transmittance of **4d** compared to furan and 2,2'-bifuran derived polyesters.

### 3.6. Chemical recycling

Lastly, a chemical recycling experiment was run, where film pieces were reacted with methanol in order to break the polyester back down to the starting monomer **3**. A mild method for methanolysis of PET was previously reported by Pham et al., where catalytic amount of  $\text{K}_2\text{CO}_3$  in dichloromethane and methanol was used to obtain dimethyl

terephthalate in high yield at room temperature.[43] Here, we found that for the difuran sulfone polyester **4d**, dichloromethane as cosolvent can be readily excluded. An average yield of 87% for the recovered monomer was still obtained within 24 h if a slightly elevated temperature (50 °C) was used (Scheme 3). An experiment in 3 g scale yielded a similar result. We expect that further optimizations in reaction time and temperature along with meticulous drying of the polyester, methanol, and  $\text{K}_2\text{CO}_3$  would increase the high yield even further. Importantly,  $^1\text{H}$  NMR analysis showed that only minor impurities, such as 1,5-pentanediol and solvent traces, were present in the recycled monomer **3** (Fig. S18). To provide a direct comparison, the same recycling experiment was carried out on PPeSF to obtain dimethyl ester **1a**. A virtually identical result was obtained (90% yield of sulfide **1a**), suggesting that both of the difuran structures will lead to similarly recyclable polyesters.

## 4. Conclusions

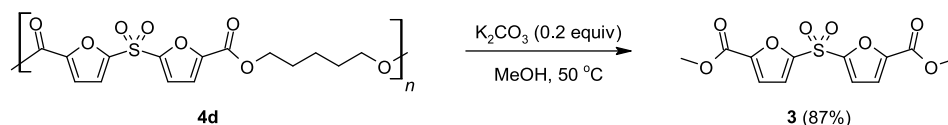
The synthesized biobased difuran sulfone diacid monomer is interesting as its structural features suggest uses in high-performance polymers. The preparation of well-defined homopolyesters using short-chain diols such as ethylene glycol under commonly applied reaction conditions was nevertheless found to be challenging. Many of the simple homopolyesters appeared semi-crystalline with high measured melting temperatures, which required relatively high polycondensation temperatures. The resulting side-reactions and darkening issues were avoidable when lower temperatures were sufficient, which was the case in the polycondensation between the difuran sulfone monomer and 1,5-pentanediol. Compared to other simple dicarboxylic monomers such as the corresponding sulfide (and e.g., terephthalic acid, 2,5-furandicarboxylic acid, and 2,2'-bifuran-5,5'-dicarboxylic acid), the difuran sulfone monomer can offer higher glass transition temperatures. As for the barrier properties, the difuran sulfone provides performance close to the sulfide analog, which was previously shown to yield high barrier polyesters with various different diols. Polyesters derived from the novel difuran sulfone monomer could be used as materials with high glass transition temperatures, high mechanical stiffnesses, and low gas permeability characteristics. One potential limitation is the need to keep the polycondensation temperatures relatively low (e.g., 220 °C) to limit side-reactions, unless appropriate stabilizing agents were to be used.

### CRedit authorship contribution statement

**Tuomo P. Kainulainen**: Conceptualization, Formal analysis, Investigation, Visualization, Writing – original draft. **Asmaa M. Ahmed**: Investigation, Writing – review & editing. **Juha Antti Sirviö**: Investigation, Resources, Writing – review & editing. **Juha P. Heiskanen**: Resources, Writing – review & editing, Supervision.

### Declaration of Competing Interest

The authors declare that they have no known competing financial



Scheme 3. Methanolysis of 4d back into monomer 3.

interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2023.112540>.

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