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Furan-Based Polyesters from Diethylene Glycol with Facile Chemical Recyclability

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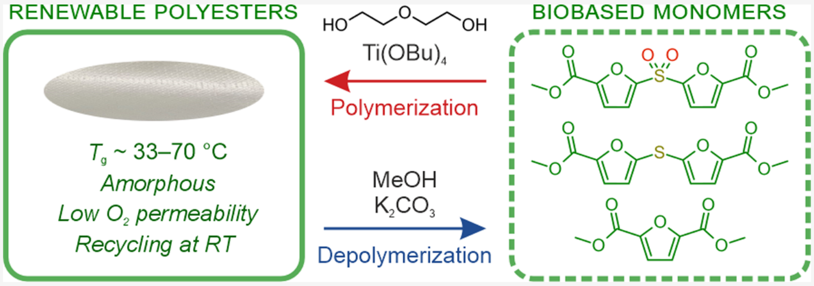

ABSTRACT: Simple renewable furans can be used to derive various monomer structures for use in polymeric materials. The dimethyl esters of 2,5-furandicarboxylic acid (FDCA), 5,5′-thiodi(2-furoic acid), and 5,5′-sulfonyldi(2-furoic acid) were reacted with diethylene glycol, yielding renewable polyesters with excellent O_2 barrier properties and facile chemical recyclability. Glass transition temperatures for the polyesters were 33−70 °C, while thermal decomposition took place at 321 °C or above. Oxygen permeabilities were measured from free-standing films and compared to poly(ethylene terephthalate). The polyesters showed excellent barrier improvement factors (BIFs) of 3.1−6.0 and 5.2−11.0 at 50 and 0% relative humidities, respectively, with the polyester from the sulfide having the highest BIFs, followed by the polyesters of FDCA and the sulfone in an order that depended on humidity. The three polyesters were remarkably easy to chemically recycle under mild conditions. The original dimethyl esters were recovered by filtration after a room temperature reaction with anhydrous methanol and catalytic K_2CO_3. Monomer yields from film recycling reached as high as 96% for the sulfide-based polyester with high purity.

1. INTRODUCTION

Environmental issues caused by the production and release of fossil-based synthetic polymers, which are often very chemically stable, is a recognized issue that could be alleviated by developing polymeric materials that are renewable, less chemically stable in the long term, or more easily recycled for reuse, chemically or otherwise. Supplanting polymers currently in wide use will, of course, require that the new materials are able to provide performance characteristics similar to the current ones. Key polymers in this context are polyesters. They provide inherent chemical reactivity for potential biodegradation or recovery via, e.g., chemical recycling, where the ester groups can be cleaved to yield monomer for the synthesis of virgin polymer.[1−5] Additionally, many polyesters have properties that are desirable, e.g., suitable glass transition temperatures, low gas permeabilities, or the ability to form transparent films, etc. Known biobased polymers that can be seen to fulfill such criteria for wider adoption include poly(ethylene furanoate) (PEF), which in many ways compares very favorably to poly(ethylene terephthalate) (PET), a widely used commodity polyester in packaging.[6−9]

The furan rings present in PEF and its congeners are central moieties here, as the increased polarity and thus altered hydrogen bond network in, e.g., poly(ethylene 2,5-furandicarboxylate) is understood to significantly lower gas permeabilities.[10−16] 2,5-Furandicarboxylic acid (2,5-FDCA) derived from 5-hydroxymethylfurfural (HMF) is therefore becoming a useful renewable alternative to terephthalic acid (TA) (Figure 1). Similar improved gas barrier properties have also been measured for furfural-based polyesters, where furfural served as the starting point for difunctional monomers.[17,18] Additionally, organosulfur moieties can be conducive to good oxygen barrier properties when present in polyesters.[19−22] Some examples that fit both of the previous categories include polyesters derived from 5,5′-thiodi(2-furoic acid) or 5,5′-sulfonyldi(2-furoic acid) (Figure 1).[22,23] Other useful heteroatoms in this

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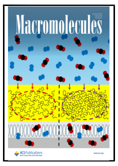

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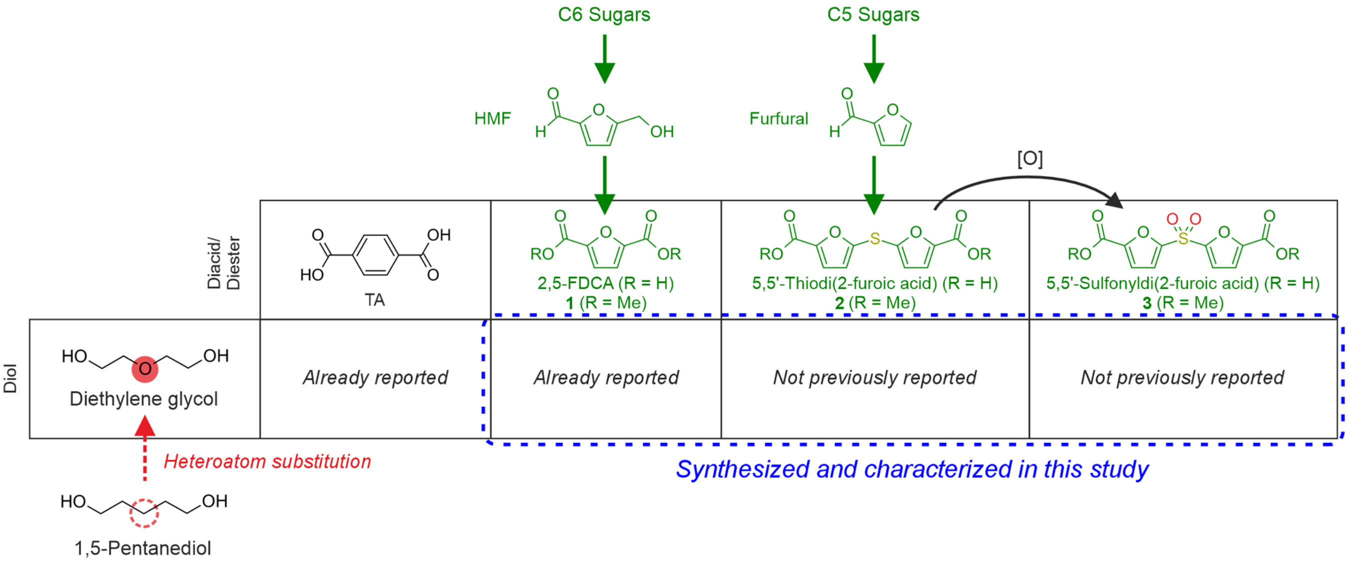


Figure 1. Monomers under study in the current work.

context include oxygen, which when inserted to replace a methylene group appears conducive toward both enhanced gas barrier properties and higher glass transition temperatures.[24−27] An example of this strategy has been the replacement of 1,5-pentanediol with diethylene glycol. Of the two 2,5-FDCA-based homopolyesters, it has also been reported that diethylene glycol as the diol unit leads to a far faster biodegradation than 1,5-pentanediol.[26,28] Diethylene glycol may also lower the stability of materials toward UV irradiation (e.g., outdoors) due to the participation of ether group in various radical reaction pathways.[29]

Considering all of these previous studies, we chose to combine the heteroatom substitution strategy with the sulfur-bridged difuran-based structures (Figure 1). Previously, different aliphatic diols with 5,5′-thiodi(2-furoic acid) yielded polyesters with enhanced oxygen barrier properties, which were expected to combine well with diethylene glycol. We were also interested in the chemical recyclability of these polyesters, since diethylene glycol has been reported to increase the biodegradation rate.[26,28,30] In this work, three polyesters were prepared by combining diethylene glycol and the dimethyl esters of 2,5-FDCA (**1**), 5,5′-thiodi(2-furoic acid) (**2**), or 5,5′-sulfonyldi(2-furoic acid) (**3**) (Figure 1). The polyesters derived from the latter two are described here for the first time. The three polyesters are characterized with techniques, including DSC and oxygen gas permeation under two different relative humidities, which reveal their good performance. Notably, room temperature chemical recycling is demonstrated, enabling high recovery of the initial dimethyl ester monomers in high purity under very mild conditions.

2. EXPERIMENTAL SECTION

Diethylene glycol (>99%) and all solvents were used as received, apart from toluene, which was stored over 4 Å molecular sieves. Methanol used in polymer recycling experiments was anhydrous HPLC grade (>99.9%). Tetrabutyl titanate (TBT, 99%) was used as received. Monomers **1**−**3** were synthesized and purified according to previous reports, with each compound obtained as a white crystalline powder (^{1}H NMR spectra in Figures S1−3).[18,22,23] NMR spectra were obtained at 23 °C (Bruker Avance III 400 MHz spectrometer). Chemical shifts are referenced to internal tetramethyl silane standard (0.00 ppm) or solvent peaks in the case of CF_3COOD (11.50 and 164.20 ppm for ^{1}H and ^{13}C, respectively).

2.1. Polyester Synthesis.

Diethylene glycol (2.2 equiv) and ca. 20 mM tetrabutyl titanate solution in dry toluene (0.05 mol % TBT relative to the dimethyl ester) were mixed briefly with a magnetic stirring bar in a round-bottom flask. Furan-based dimethyl ester (**1**−**3**, 6−8 mmol) was then added on top of this mixture. The flask was connected to argon and vacuum lines via a short-path distillation bridge. After 5 argon-vacuum cycles to purge the reaction system of air, the mixture was heated to 180 °C and stirred under an argon balloon for 2 h. Pressure was then gradually decreased to 5 mbar over 2 h to avoid excessive bubbling of the melt. The temperature was ramped to 220 °C during the final 15 min of this step. Pressure was then further lowered to 0.07−0.10 mbar to begin the final polycondensation stage. After 4−6 h of reaction time, the system was allowed to cool to room temperature under argon. For polyesters **5** and **6**, crystalline deposits were then mechanically removed from the top half of the reaction flask, followed by several small rinses with acetone (20 mL in total). From syntheses of **5** and **6**, ca. 150 mg of byproducts **7** and **8**, respectively, could be collected in this way. The polymer left in the flask was dried under vacuum for a short period to remove the remaining acetone before adding 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). In this way, ca. 15% (m/v) polymer solution was obtained after 20 h. Once poured into a 10-fold excess of methanol, the precipitated polymer was collected via filtration and dried under a reduced pressure of 5 mbar at 70 °C until a constant weight was observed. Polymers **4**, **5**, and **6** were finally obtained as white to off-white solids in 89, 75, and 75% yields, respectively.

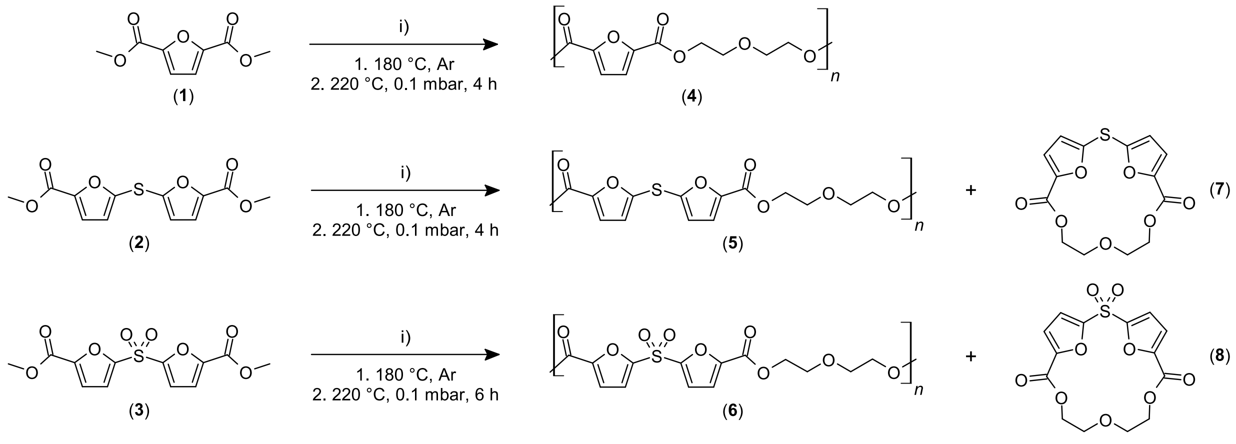
*2.1.1. Poly(oxidiethylene furanoate) (**4**).* ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.20 (s, 2H), 4.50−4.48 (m, 4H), 3.86−3.84 (m, 4H). ^{13}**C NMR** (100 MHz, $CDCl_3$, ppm): δ 157.8, 146.6, 118.7, 68.8, 64.3.

*2.1.2. Poly(oxidiethylene sulfanediyldifuroate) (**5**).* ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.13 (d, J = 3.7 Hz, 2H), 6.69 (d, J = 3.7 Hz, 2H), 4.44−4.42 (m, 4H), 3.82−3.80 (m, 4H). ^{13}**C NMR** (100 MHz, $CDCl_3$, ppm): δ 157.7, 146.7, 146.2, 119.5, 118.5, 68.9, 64.0.

*2.1.3. Poly(oxidiethylene sulfonedifuroate) (**6**).* ^{1}**H NMR** (400 MHz, CF_3COOD, ppm): δ 7.48 (d, J = 3.8 Hz, 2H), 7.36 (d, J = 3.8 Hz, 2H), 4.64−4.63 (m, 4H), 4.11−4.09 (m, 4H). ^{13}**C NMR** (100 MHz, CF_3COOD, ppm): δ 162.1, 152.1, 150.0, 123.5, 121.9, 71.1, 67.4.

*2.1.4. Compound **7**.* ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, J = 3.4 Hz, 2H), 6.62 (d, J = 3.4 Hz, 2H), 4.48−4.46 (m, 4H), 3.89−3.87 (m, 4H). ^{13}**C NMR** (100 MHz, $CDCl_3$, ppm): δ 158.0, 147.7, 144.7, 119.3, 116.6, 68.6, 63.9. **HRMS**: (m/z) calculated for $C_{14}H_{12}O_7SNa$ $[M + Na]^+$: 347.0196, found 347.0174.

Scheme 1. Polyester Syntheses Performed in This Work



i) Diethylene glycol (2.2 equiv), 20 mM tetrabutyl titanate in dry PhMe (0.05 mol% Ti).

*2.1.5. Compound **8**.* ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, J = 3.7 Hz, 2H), 7.24 (d, J = 3.7 Hz, 2H), 4.46–4.44 (m, 4H), 3.92–3.90 (m, 4H). ^{13}**C NMR** (100 MHz, $CDCl_3$, ppm): δ 157.5, 149.9, 148.7, 117.9, 117.8, 68.5, 64.8. **HRMS**: (m/z) calculated for $C_{14}H_{12}O_9SNa$ $[M + Na]^+$: 379.0094, found 379.0102.

2.2. Polymer Recycling. For each polymer, an amount of film pieces corresponding to ca. 0.5 mmol of repeating units was weighed (e.g., **4**: 115.5 mg, **5**: 161.9 mg, **6**: 178.3 mg). The film pieces were cut to ca. 1 cm × 1 cm squares and placed in an oven-dried 5 mL reaction tube with K_2CO_3 (13.8 mg, 0.1 mmol), methanol (2.0 mL, 50 mmol), and a 3 mm × 8 mm stir bar. The tube was sealed with a septum, and its headspace was flushed with argon from a needle for 3 min. The tube was submerged in a 25 °C water bath, and the mixture was stirred magnetically at 1400 rpm for 24 h. In the liquid–liquid extraction workup, deionized water was added (10 mL) to the reaction mixture, which was then extracted with chloroform (3 × 15 mL). The organic layers were filtered through a 1–2 cm layer of silica in a funnel, rinsing with the aid of ethyl acetate. Evaporation to dryness under reduced pressure gave the corresponding dimethyl esters **1**, **2**, or **3**. In the alternate workup, the procedure was started by filtering the methanolic reaction mixture, which had been kept at 4 °C overnight, through filter paper in a small funnel. The tube and funnel were rinsed with deionized water several times (20 mL in total). The resulting filtrate was then extracted as described above to recover any remaining monomer as a separate fraction.

2.3. High-Resolution Mass Spectrometry. The electrospray ionization mass spectrometric measurements were performed using a Thermo Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap high-resolution mass spectrometer. Compound samples (ca. 1 mg/mL in HFIP) were diluted 20-fold with H_2O/acetonitrile 1:3 (v/v) mixture. 30–40 μL of the prepared dilutions was injected into the mass spectrometer. Compounds were detected in the positive mode as sodium adducts. Solvent system: Solvent A: 0.1% formic acid in H_2O, solvent B: 1% formic acid in acetonitrile, A:B 40:60. Flow rate: 0.02 mL/min.

2.4. Ultraperformance Liquid Chromatography. Samples for ultraperformance liquid chromatography (UPLC) were prepared by dissolving the compounds of interest into UHPLC grade >99.9% acetonitrile (at ca. 0.4–0.5 mg/mL). Samples were analyzed with Waters I-Class UPLC PLUS system equipped with Atlantis Premier BEH C_{18} AX column (1.7 μm, 2.1 × 100 mm) and AQUITY PDA eλ detector. Column and sample temperatures were 30 and 20 °C, respectively. 1 μL injection volume and 0.3 mL/min flow rate were used. Eluents A (H_2O with 0.1% trifluoroacetic acid) and B (acetonitrile with 0.1% trifluoroacetic acid) with 10 min linear gradient elution from 85:15 (A:B) to 10:90 (A:B) were used. Afterward, the eluent composition was restored to starting conditions within 2 min using a linear gradient and held there for 3.5 min to equilibrate the system for the next injection. Detection was conducted at wavelengths of 210–400 nm.

2.5. Dilute Solution Viscometry. For the viscosity measurement, the precipitated polymer samples were dissolved in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (60/40 w/w) by briefly heating them to 30–40 °C. Intrinsic viscosities were then calculated from flow times of the solutions (c = 0.5 g/dL) and the pure solvent at 30 °C. Flow times were manually timed three times, and the averages were then used to calculate the intrinsic viscosity [η], as reported previously.[22]

2.6. Size-Exclusion Chromatography. A Verotech PL-GPC 50 Plus system equipped with two PLgel 5 μm MIXED-D (300 Å ∼ 7.5 mm^2) columns from Varian and a PL-RI Detector was used to analyze the molecular weights of samples. Chloroform was used as the solvent, and polymer concentration was ca. 3 mg/mL. The solutions were filtered through a PTFE filter (pore size of 45 μm) before the measurement. Polystyrene standards (160–371,000 g/mol) with narrow molecular weight distributions were used for the calibration curve.

2.7. Differential Scanning Calorimetry. The DSC (Mettler DSC821e) was calibrated using In and Zn reference samples. The polymer sample, ca 5 mg, was placed in a 40 μL Al cup that was then closed with a pierced lid. Heating and cooling rates were kept at 10 °C/min with a N_2 flow of 50 mL/min. The temperature ranges for the scans were −20–200 °C (polyesters **4** and **5**), 20–250 °C (polyester **6**), or 20–300 °C (byproducts **7** and **8**). The measurement end points were held for 3 min before reversing. In annealing experiments, **4** and **5** were annealed at 60 °C for 1 h. Annealing at 130 or 160 °C for 1 h was used for **6**. Before annealing, prior thermal history was removed by initial heating and cooling scans, as described above. The annealing temperature was then approached at 10 °C/min. After annealing, the sample was cooled to 20 °C at a rate of 10 °C/min.

2.8. Thermogravimetric Analysis. Thermogravimetry was performed on film pieces (ca. 20 mg) at a heating rate of 10 °C/min under a 40 mL/min N_2 flow (Netzsch STA 409 PC/PG). The temperature range of the measurements was 40–700 °C.

2.9. Film Processing. The methanol-precipitated polymer samples were carefully dried to constant weight under a vacuum prior to processing. For the pressing, the polymer sample was sandwiched between two PTFE-coated glass-fiber mats inside of a heated press. Temperatures for **4** and **6** were 190 °C, while for **5**, 150 °C was used, and after a brief melting period (2–3 min) inside the press, the press was closed for 1 min under 40 kN force. The glass fiber mat frame around the sample limited the thickness to 0.1–0.2 mm. Films were cooled to room temperature (ca. 20 °C) with an integrated water circulation system of the press at ca. 30 °C/min before releasing compression.

2.10. Oxygen Permeability Testing. Oxygen permeability was measured from duplicate film samples using Mocon OxTran 2/21 ML

Table 1. Molecular Weights, Intrinsic Viscosities, and Thermal Properties of Synthesized Polyesters[a]

	SEC		IV	DSC			TGA	
sample code	M_n (kg/mol)	$Đ$	$[\eta]$ (dL/g)	T_g (°C)	T_{cc} (°C)	T_m (°C)	T_{d5} (°C)	T_{d50} (°C)
4	31.8	2.53	0.85	36			350	408
5	34.3	3.54	0.95	33		83	322	380
6			0.49	70	133, 161	150, 178	321	378

[a] M_n, number-average molecular weight; $Đ$, dispersity; $[\eta]$, intrinsic viscosity in phenol/1,1,2,2-tetrachloroethane at 30.0 °C; T_g, glass transition temperature from 2nd cooling; T_{cc}, cold crystallization peak temperature from 1st heating; T_m, peak melting temperature(s) from 1st heating; T_{d5}, 5% mass loss temperature; T_{d50}, 50% mass loss temperature.

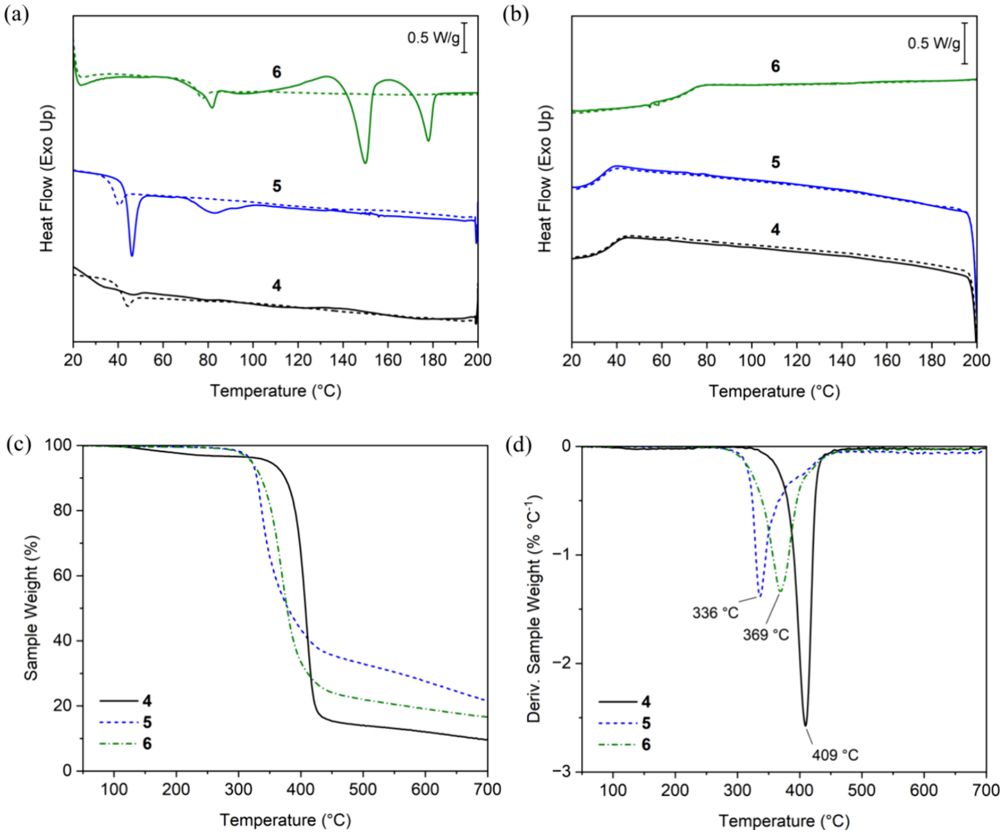


Figure 2. DSC traces for heating (a) and cooling (b) at 10 °C min^{-1} with solid and dashed lines for first and second runs, respectively, and TGA traces (c, d) measured at 10 °C min^{-1} under N_2 flow.

and reported as an average of the two values. The active test area was 5 cm^2, while the temperature was set to 23 °C and the relative humidity (RH) to 50 or 0%. The samples of polyesters PPeSF and PPeSFO$_2$ were those characterized previously under 0% RH.[23] The amorphous PET used for the reference film was synthesized and processed into film, as reported previously.[31]

2.11. Dynamic Mechanical Analysis. TA Instruments DMA Q800 was used in tensile mode (0.08% strain, 1 Hz) to test film specimens (length × width × thickness ca. 20 × 5 × 0.1 mm^3) at a heating rate of 3 °C/min. The test was run under an atmosphere of dry nitrogen generated by the gas cooling accessory.

2.12. Tensile Testing. Tensile tests were carried out under controlled conditions of 23 °C and 50% relative humidity. The film specimens were cut into strips 5 mm wide and then stored for at least 48 h under 23 °C and 50% relative humidity prior to testing. The tensile tester (ZwickRoell 2.5 kN universal testing machine, Xforce P 1 kN load cell) was set to use a 30 mm gage length and a crosshead speed of 5 mm/min (polyesters **5** and **6**) or 15 mm/min (polyester **4**). For each material, 5 specimens were tested.

2.13. UV–Vis. Transmittances were measured from free-standing melt-pressed film specimens with a Shimadzu UV-1800 spectrophotometer from 200 to 800 nm.

2.14. Water Contact Angle. Free-standing film samples were used for water contact angle (WCA) measurements at 20.0 °C (Krüss DSA100, Germany, 2 μm droplet size). A mean value from 6 data points over 1 min time was taken from three separate measurements to calculate an average value for each polyester.

3. RESULTS AND DISCUSSION

3.1. Results of Polyester Synthesis. Polyesters **4**−**6** were synthesized via transesterification of dimethyl ester monomers **1**−**3** with diethylene glycol, followed by melt polycondensation under reduced pressure and increased temperature according to Scheme 1. To limit possible byproduct-forming reactions and discoloration, the polycondensation temperature was kept at 220 °C. Under these conditions, polyester **4** obtained a faint yellow color, whereas **5** and **6** were light brown to brown in appearance. All three were glassy transparent solids. As for the solubility of the polyesters, both **4** and **5** were soluble in chloroform, whereas **6** required the addition of HFIP or trifluoroacetic acid for complete dissolution. For the sake of consistency, all polymers were collected from the reaction

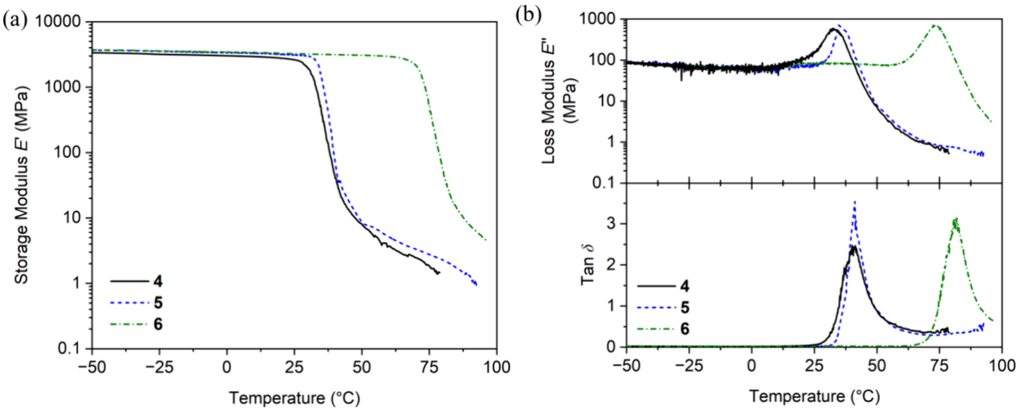


Figure 3. DMA traces for storage modulus E' (a) and loss modulus E'' and tan δ (b).

flasks via dissolution in HFIP, followed by precipitation in methanol. Upon precipitation in methanol, **4** and **5** formed dense clumps, while **6** had a looser, more fibrous appearance. ^{1}H and ^{13}C NMR spectra obtained from the polymers (Figures S4−9) matched the expected signals in all cases.

Molecular weights of the products were evaluated using SEC, with **6** excluded from the analysis due to its insolubility in chloroform. Polyesters **4** and **5** had reached relatively high molecular weights, as average molecular weights (M_n) well above 30 kg/mol were measured (Table 1). The dispersity value ($Đ$) was higher than expected for both polyesters at >2.5, though the distributions were unimodal (Figure S10). The intrinsic viscosities (IVs) of **4**, **5**, and **6**, measured in the typical mixed solvent of phenol and 1,1,2,2-tetrachloroethane, were 0.85, 0.95, and 0.49 dL/g, respectively. Polyester **4** has been prepared in several previous reports, with values roughly comparable to the current M_n and IV values, with some consideration given to the slight variations in methods.[24−26] The intrinsic viscosities reveal that despite the extended 6 h polycondensation, the sulfone polyester struggled to reach half the viscosity value of the other two polyesters. On the other hand, the reactivity of the sulfone monomer during the transesterification appeared to be high, since methanol was collected at a comparable rate to the other two. Our experience with monomer **3** suggests that further increase in polycondensation temperature will slightly increase the intrinsic viscosity value at the cost of significant gelling of the polymer, which stems from cross-linking.[23]

Another synthetic aspect worth a brief discussion is the tendency of byproducts, **7** or **8**, to collect on the necks of the reaction flasks when diethylene glycol was polymerized with **2** or **3**, respectively. Diesters **2** and **3** previously gave similar products with 1,5-pentanediol, a diol structurally analogous to diethylene glycol.[23] Just as previously, ^{1}H and ^{13}C NMR analyses of these solids were consistent with highly pure cyclic compounds formed from the difuran diesters and the diol component (Figures S11−14). Here, using high-resolution mass spectroscopy (Figure S15), we found that **7** and **8** are, surprisingly, monomeric, as illustrated in Scheme 1. DSC revealed relatively high melting points (T_m = 214 °C for **7**, T_m = 234 °C for **8**), with sharp endothermic peaks characteristic of pure compounds (Figure S16). The amount of **7** or **8** isolated from the reactions corresponded to ca. 5−10% yield, and it is remarkable that only one cyclic species was observed to have formed in both cases. The formation of these particular compounds must, therefore, be favorable. Considering that the difuran sulfide and the sulfone moieties must adopt a bent shape due to the central sulfur atom, their structures likely favor cyclization.[32] Second, since a monomeric cycle is possible, a low-molecular-weight ring with higher volatility is formed, which allows for easier evaporation under vacuum compared to larger rings that quickly increase in molecular weight as ring size increases. It must be noted that careful collection of all loose solids from the upper parts of the reaction flasks with the help of acetone yielded polymers that were essentially free from the cyclic compounds, as the ^{1}H and ^{13}C NMR signals associated with them do not appear in the respective NMR spectra of the final polymers (Figures S4−9). The use of **7** and **8** as potential monomers in ring-opening polymerizations may well merit a further, detailed study.

3.2. Thermal Properties of Synthesized Polyesters.

DSC measurements (Table 1 and Figure 2a,b) carried out on the precipitated polymers revealed that **4** and **5** had similar glass transition temperatures of 36 and 33 °C, respectively, whereas **6** had a far higher T_g of 70 °C. The 1,5-pentanediol-derived analogs for **4**−**6** have glass transition temperatures ca. 7−19 degrees lower, i.e., a polar ether group increases T_g noticeably compared to a methylene group.[22,23,25] The FDCA-based polyester **4** appeared to be devoid of any crystallinity during DSC measurement. A broad but small endothermic peak was detected with **5** at around 83 °C (with enthalpy of melting ΔH_m of 4.2 J/g) but with no signs of cold crystallization. The sulfone-based polyester **6**, by comparison, was more semicrystalline in character, showing two cold crystallization exotherms (with cold crystallization enthalpies of 13.9 and 5.8 J/g) and two melting endotherms (ΔH_m of 11.9 and 6.9 J/g) upon the first heating run. However, upon cooling from the melt, neither **5** nor **6** showed crystallization or melting in subsequent scans. The narrow temperature difference between T_g and T_m of these polyesters is indicative of imperfect crystals. Thermal annealing of the polyesters failed to produce noticeable crystallinity in the samples (Figure S17). All three polyesters are thus perhaps better described as being amorphous with a low tendency to crystallize unless solvent processing is involved. The terephthalic analog, poly(oxidiethylene terephthalate), has been reported to behave similarly, as it is reluctant to crystallize unless solvents and long crystallization times are involved.[33]

Thermogravimetric analysis showed that FDCA-derived polyester **4** was the most stable in terms of 5 and 50% mass loss temperatures (Table 1). However, the TGA trace showed a small mass loss (ca. 3%) that occurred over a temperature range of 100−250 °C, whereas **5** and **6** had lost <1% sample weight upon reaching 250 °C (Figure 2c). The TGA of polyester **4** by Guidotti and co-workers showed the same peculiar phenomenon, which leads us to believe that this small, early mass loss is a characteristic of this polyester rather than of our sample only.[26] Otherwise, the mass-loss characteristics of **4** have previously been shown to be comparable to PEF.[25] Comparing the difuran polyesters **5** and **6**, we found that they had remarkably similar mass loss characteristics between them, with 5 and 50% mass loss temperature values differing by only 1−2 degrees (Table 1). The shapes of the TGA traces were very distinct, however, and the derivative curves revealed that the temperatures of the peak decomposition rates differ by 33° (Figure 2d). The diethylene glycol units themselves appear to lower the onset of thermal degradation (T_{d5}) by about 20 degrees when compared against 1,5-pentanediol units in otherwise similar polyesters.[22,23] Nevertheless, the major decomposition steps in all three cases are clearly above reasonable processing temperatures. The residual weights, or char yields, at 700 °C decreased according to **5** > **6** > **4**, with values of 21.6, 16.7, and 9.7%, respectively.

Continuing with thermomechanical analysis, film specimens subjected to DMA showed behavior consistent with DSC analysis, confirming the glass transition temperatures and the absence of cold crystallization (Figure 3). In slight deviation from the DSC measurements, the storage and loss modulus traces suggest that **4** enters the rubbery state before **5**. However, the high overlap of the tan δ peaks (Figure 3b) for **4** and **5** indicates that the glass transitions occur at virtually the same temperature (41 °C). It is also notable that the sulfide and sulfone polyesters **5** and **6** have similar storage moduli that lie above that of **4** (3.2, 3.3, and 2.8 GPa, respectively, at 20 °C), pointing to a stiffening effect by the difuran sulfur moieties regardless of the oxidation state.

3.3. UV−Vis Properties of Films. Melt-pressed film specimens were transparent to the naked eye as expected from amorphous polymers (Figure S18). Polyester **4** showed a very flat transmission curve at visible wavelengths (Figure 4), a result that was in accord with a film that was colorless to the naked eye. Polyesters **5** and **6** are differentiated from **4** by their lower transmission of visible light at shorter wavelengths. The cutoff wavelengths, situated in the UV area, follow previously observed trends for the three different furan monomers, increasing according to **5** > **6** > **4**. That is, the sulfide difuran unit has broader UV absorption than the sulfone, as expected.

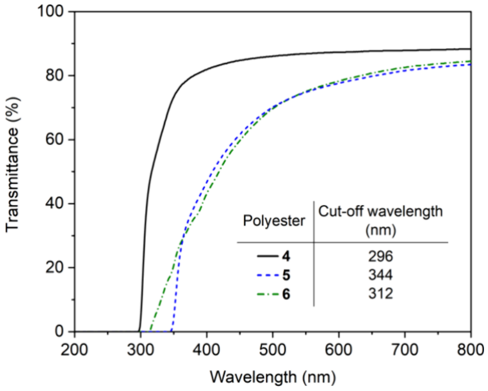


Figure 4. UV−vis transmittance curves from melt-pressed films of polyesters **4**−**6**.

3.4. Oxygen Barrier Properties. Oxygen barrier measurements were carried out on various film specimens under relative humidities of 0 and 50%, with comparisons also drawn to some previously reported data (Table 2). Under both 0 and 50% RH, polyesters **4**−**6** showed much improved O_2 barrier performance relative to amorphous PET. The best performing of the three prepared polyesters, the sulfide-based polyester **5**, had oxygen permeability significantly lower than PET and, remarkably, even lower than PEF. The result further supports the improved oxygen barrier properties that can be derived from sulfur-containing furan monomers, including the current combination with a heteroatom containing diol monomer.[22,34] Humidity is a relevant factor affecting the gas barrier, as illustrated by the improved oxygen barrier of PET under increased humidity.[35] For other polyesters tested here, the effect of the humidity was variable. Notably, the FDCA polyester **4** and the difuran sulfide polyester **5** both showed increased oxygen permeability when RH was increased from 0 to 50%. The sulfone-derived polyester **6** appeared largely unaffected, with no significant difference arising from a change in humidity. The FDCA-derived polyester **4** is a particularly interesting material, as large deviations are found in the literature regarding its oxygen gas permeability, and some of this difference appears linked to humidity. Our measurements at 50% RH seem to fall in line with the results reported by Meng et al., where a BIF_{PET} value of just above 3 was observed under 50% RH.[24] Their measurements indicate that **4** has a barrier performance inferior to that of PEF, particularly against humidity. As for 0% RH, the result here for **4** was comparable to that which was reported by Tian et al. (BIF_{PET} = 9.06).[25] It is noteworthy that polyester **4** has been reported to behave similarly to poly(pentylene furanoate) (PPeF), in that under some processing conditions, it can yield films with gas permeabilities many orders of magnitude lower than PET.[24,26,36,37]

Table 2. Oxygen Permeabilities Measured under 0 and 50% Relative Humidities at 23 °C[a]

	0% relative humidity		50% relative humidity	
polyester sample	OP	BIF_{PET}	OP	BIF_{PET}
4	472	7.9	920	3.1
5	342	11.0	480	6.0
6	725	5.2	693	4.2
PET[b]	3750	1.0	2877	1.0
PEF	487[c]	9.7[c]		5.9[d]
PPeF	16[e]	0.58[f]		0.26[g]
PPeSF	2397[h]	1.9[h]	2805	1.0
$PPeSFO_2$	2211[h]	2.1[h]	1 759	1.6

[a] OP, oxygen permeability in mL μm m^{-2} atm^{-1} day^{-1}; BIF_{PET}, barrier improvement factor relative to amorphous PET; PPeF, Poly(pentylene furanoate); PPeSF, Poly(pentylene sulfanediyldifuroate); $PPeSFO_2$, Poly(pentylene sulfonedifuroate). [b] Melt-pressed amorphous PET.[31] [c] Ref 34. [d] Ref 24. [e] Ref 26. [f] Ref 25. [g] Ref 36. [h] Ref 23.

Overall, the O_2 barrier properties of the diethylene glycol-based polyesters **4**, **5**, and **6** were significantly improved compared to their 1,5-pentanediol analogs (abbreviated PPeF, PPeSF, and $PPeSFO_2$, respectively, see Table 2). The barrier enhancing effect of the ether oxygen versus methylene group is interesting, in that it seems to extend to other monomers as well, and for instance, diglycolic acid yields polyester with improved oxygen barrier when it replaces glutaric acid as the diacid component.[27] It is also apparent that while the polar sulfone group increases T_g considerably and induces a degree of semicrystallinity under some processing conditions, the barrier properties become less affected by humidity. This result is somewhat surprising and could be a sign that polyester **6** is not easily plasticized due to the rigidity of the difuran sulfone unit. In fact, **6** (and PPeSFO$_2$) showed a slight decrease in the permeability of the O$_2$ at 50% RH.

3.5. Tensile Properties. The FDCA-based polyester (**4**) had the lowest values of tensile modulus and tensile strength of the three polyesters tested (Table 3). Conversely, it showed the highest ductility, with elongation at break reaching on average 300%. Elongations of up to 500% were reported previously for **4**, indicating very high ductility.[26] However, Meng et al. did report drastically different values, with yield strength of 49 MPa and elongation at break of less than 60%.[24] They also measured the tensile modulus of **4** to have a very high value of 2.82 GPa. Of the three tested polyesters here, the mechanical properties of the difuran sulfide derived polyester **5** were most balanced and closest to those of amorphous PET or PEF, with a tensile modulus of ca. 2 GPa and tensile strength of 37 MPa, which was more than double that of **4**. Ductility was relatively high at an average elongation at break of 130%. The sulfone counterpart (**6**) was found to have the highest tensile modulus of the three, at 2.6 GPa, but the film samples proved to be quite brittle, resulting in lower tensile strength and minimal elongation. Yielding was therefore not observed for **6**, in contrast to **4** and **5** (Figure S19). The intrinsic viscosity of **6**, which was the lowest of the three polyesters, was most likely too low for ductile and strong films, limiting its tensile strength. However, comparisons of **4**−**6** with PPeF, PPeSF, and PPeSFO$_2$ show that substituting 1,5-pentanediol with diethylene glycol results in enhancements in the form of a higher tensile modulus or strength (Table 3). Conversely, elongation at break is decreased. The substitution of FDCA units for difuran sulfur units, on the other hand, gives significant increases in tensile strength and stiffness with either diol among respective polyesters.

Table 3. Tensile Test Results for Polyesters 4−6 and Comparable Polyesters[a]

polymer	E (GPa)	σ_M (MPa)	ε_b (%)	reference
4	1.4 ± 0.1	16 ± 1	300 ± 110	This work
5	2.0 ± 0.2	37 ± 3	130 ± 90	
6	2.6 ± 0.1	32 ± 3	1.3 ± 0.1	
PEF	2.0 ± 0.1	93.2 ± 2.3	7.2 ± 0.2	38
PET	1.522 ± 0.070	58 ± 10	600 ± 40	31
PPeF	0.009 ± 0.001	6 ± 1	1050 ± 200	26
PPeSF	0.445 ± 0.027	6.3 ± 0.5	440 ± 100	22
PPeSFO$_2$	2.096 ± 0.051	43.3 ± 3.1	2.3 ± 0.2	23

[a] E, tensile modulus; σ_M, maximum tensile stress; ε_b, elongation at break; PPeF, Poly(pentylene furanoate); PPeSF, Poly(pentylene sulfanediyldifuroate); PPeSFO$_2$, Poly(pentylene sulfonedifuroate).

3.6. Chemical Recycling of Films. As briefly discussed in the introduction, the potential ease of chemical recycling from polymer to monomer is a benefit of polyesters. It allows the recovery and reuse of carbon into new materials more directly when compared to waste polymer incineration or biodegradation. Ideally, depolymerization would take place when a simple stimulus is applied to the material, e.g., heat or perhaps UV light.[39,40] Alternatively, catalysts can be added to drive depolymerization, as shown with certain polyesters derived from cyclic monomers.[41,42] Labile groups, e.g., acetal, present in the backbone can be used to assist in breaking down the polymer once under specific conditions.[43] Methanolysis is another mild way of chemically breaking down ester-based polymers such as PET and others like it, though potentially harmful cosolvents such as dichloromethane may be required.[44−47] For PEF, chemical recycling has been mostly studied under relatively vigorous conditions involving temperatures of 120−180 °C or higher.[48−53] Depending on the reaction conditions, various end products have been obtained, such as dimethyl ester **1**, cyclic PEF oligomers, or the bis(2-hydroxyethyl) ester of FDCA. The latter can be polymerized by itself to form PEF in a closed loop manner. Room temperature depolymerization of PEF into FDCA using potassium hydroxide in methanol has also been demonstrated.[54] The process was significantly more efficient when the methyl ether of sesamol, a biobased solvent, was present.

Polyesters **4**−**6** were found to be ideal candidates for chemical recycling via methanolysis, as all three disintegrated and reacted with neat methanol at room temperature (25 °C) in the presence of catalytic K$_2$CO$_3$ (20 mol % relative to polymer repeating unit). For example, ca. 0.1 mm thick film pieces cut from **6** were largely degraded in anhydrous methanol within a few hours under vigorous stirring. This result contrasts with our previous work on the related 1,5-pentanediol polyester, where some film pieces were left intact at 25 °C, necessitating higher temperatures to achieve proper chemical degradation.[23] Yields of the dimethyl esters were also slightly higher than previously; e.g., dimethyl ester **3** was obtained in 89% yield after liquid−liquid extraction (Table 4).

Table 4. Chemical Recycling Results for 4, 5, and 6

$$\text{Polyesters } \mathbf{4–6} \xrightarrow[\text{MeOH, rt, 24 h}]{K_2CO_3\ (20\ \text{mol\%})} \text{Monomers } \mathbf{1–3}$$

	monomer yield (%)	
polyester	via extraction	via filtration
4	82	55 (84[a])
5	94	96 (96[a])
6	89	89 (89[a])

[a] Combined yield for filtration with successive extraction of the filtrate.

The sulfide polyester (**5**) afforded an even higher, near-quantitative monomer recovery (94%), whereas the FDCA-based polyester (**4**) gave the lowest monomer yield (82%) of the three. It is expected that the main byproducts will be potassium mono- or dicarboxylates formed due to the presence of water traces in the polyesters or the methanol.[47] Polyester **4** having the highest affinity toward water and other highly polar solvents appears reasonable on the basis that simple submersion in methanol at room temperature turned the film pieces hazy and distorted their shape quite quickly (Figure 5, top left corner). This notion was supported by water contact angle (WCA) measurements, which showed a decrease in WCA according to **5** > **6** > **4** (Table S1). Additionally, the WCAs make it clear that the diethylene glycol unit increases hydrophilicity noticeably when compared against the 1,5-pentanediol unit, potentially facilitating methanolysis.[23,26] It was also noted that despite polyesters **5** and **6** yielding films with distinct colors, the corresponding monomers were obtained with little color after chemical recycling.

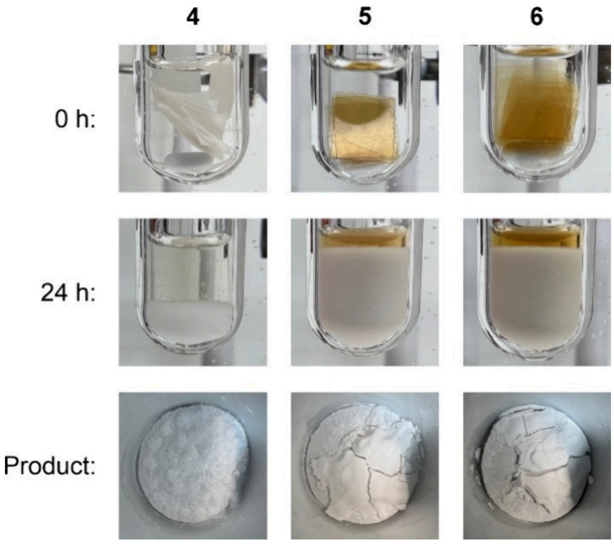


Figure 5. Digital images showing the appearance of samples before and after room-temperature methanolysis (top and middle row) and of the final products after filtration (bottom row).

Though the liquid−liquid extraction with organic solvent facilitated complete recovery, it is a less attractive method compared to simple filtration from the reaction mixture. We thus examined an alternative workup, where filtration of the reaction mixture is followed by a water rinse, avoiding the use of organic solvents. The difuran monomers **2** and **3** especially have low solubility in methanol, which helps to essentially achieve quantitative recovery by filtration alone (Table 4). The dimethyl ester of 2,5-FDCA is substantially more soluble in methanol under the same conditions, as ca. one-third remained dissolved in the reaction mixture even after being stored at 4 °C. Further extraction of the filtrate was required to reach yield parity with the extraction method (Table 4). By comparison, negligible amounts of **2** and **3** remained in solution after filtration, and yields could not be increased with liquid−liquid extractions of filtrates. The separation method, surprisingly, did not appear to impact purity, and in all cases, the separated monomer fractions did not contain any impurities detectable by ^{1}H NMR (Figures S20−22). Only trace peaks from solvents used during workup were present in some samples. UPLC measurement was further used to confirm that identical chromatograms were obtained from the filtered monomers with respect to the original, purified monomers (Figure S23). The degree of color retained on the monomers after filtration was also minimal, with colored impurities remaining in the methanol solution or being washed away with water (Figure 5, bottom row). Any unreacted polymer or oligomer is expected to be retained on the filter cake during filtration, and thus, the absence of these expected impurities points to full chemical degradation of these polyesters at room temperature. It is the complete conversion that ultimately allows this unusually facile recovery of the diesters in purity that is comparable to that of the initial pure monomers.

4. CONCLUSIONS

Three polyesters derived from diethylene glycol and three different dimethyl ester monomers were synthesized and processed into free-standing films. All three materials were amorphous, with the furan and difuran sulfide monomers leading to very similar glass transition temperatures. By comparison, the difuran sulfone monomer resulted in a much higher T_g. In terms of barrier performance, all polyesters perform well, having lower oxygen permeability than PET. The oxygen permeability decreased according to the order FDCA ∼ difuran sulfone > difuran sulfide, showing that the sulfur-bridged difuran moieties were beneficial for low permeability, with performance comparable to, or better than PEF. The ether group of the diol was also beneficial for lowering oxygen permeability relative to 1,5-pentanediol. Good mechanical properties with relatively high ductility were observed for films of polyesters **4** and **5**, which stood in contrast with **6** and, for instance, PEF. Importantly, polyesters **4**−**6** could be recycled back to their respective dimethyl ester monomers by simply stirring the film pieces and a catalytic amount of potassium carbonate in anhydrous methanol at room temperature, which is milder than typical processes used to recycle PEF. The difuran sulfur monomers **2** and **3** were recovered in high yields of 89−96%, while the FDCA monomer (**1**) was recovered in a slightly lower 82% yield. A larger difference was observed when the workup was simplified to a filtration procedure, where the low solubility of **2** and **3** in methanol allows for practically quantitative recovery of the formed monomer, whereas **1** remained partially dissolved. The results therefore showed that the sulfur-bridged difuran monomers offered even better recyclability than did the FDCA monomer. Overall, diethylene glycol seems to confer many advantages over 1,5-pentanediol in furan-based polyesters, in terms of key material properties and chemical recyclability. Particularly, good balance of mechanical properties, high oxygen barrier, and facile chemical recyclability was obtained with the furfural-derived monomer **2** and diethylene glycol.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02050.

^{1}H and ^{13}C NMR spectra of compounds and polymers and additional figures (PDF)

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Notes

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■ REFERENCES

(1) Wang, Y.; van Putten, R.-J.; Tietema, A.; Parsons, J. R.; Gruter, G.-J. M. Polyester Biodegradability: Importance and Potential for Optimisation. *Green Chem.* **2024**, *26* (7), 3698−3716.

(2) Shi, C.; Quinn, E. C.; Diment, W. T.; Chen, E. Y.-X. Recyclable and (Bio)Degradable Polyesters in a Circular Plastics Economy. *Chem. Rev.* **2024**, *124* (7), 4393−4478.

(3) Kim, M. S.; Chang, H.; Zheng, L.; Yan, Q.; Pfleger, B. F.; Klier, J.; Nelson, K.; Majumder, E. L.-W.; Huber, G. W. A Review of Biodegradable Plastics: Chemistry, Applications, Properties, and Future Research Needs. *Chem. Rev.* **2023**, *123* (16), 9915−9939.

(4) Clark, R. A.; Shaver, M. P. Depolymerization within a Circular Plastics System. *Chem. Rev.* **2024**, *124* (5), 2617−2650.

(5) Aarsen, C. V.; Liguori, A.; Mattsson, R.; Sipponen, M. H.; Hakkarainen, M. Designed to Degrade: Tailoring Polyesters for Circularity. *Chem. Rev.* **2024**, *124* (13), 8473−8515.

(6) de Jong, E.; Visser, H. R. A.; Dias, A. S.; Harvey, C.; Gruter, G.-J. M. The Road to Bring FDCA and PEF to the Market. *Polymers (Basel)* **2022**, *14* (5), 943.

(7) Eerhart, A. J. J. E.; Faaij, A. P. C.; Patel, M. K. Replacing Fossil Based PET with Biobased PEF; Process Analysis, Energy and GHG Balance. *Energy Environ. Sci.* **2012**, *5* (4), 6407.

(8) Sanders, J. H.; Cunniffe, J.; Carrejo, E.; Burke, C.; Reynolds, A. M.; Dey, S. C.; Islam, Md. N.; Wagner, O.; Argyropoulos, D. Biobased Polyethylene Furanoate: Production Processes, Sustainability, and Techno-Economics. *Adv. Sustain. Syst.* **2024**, *8* (11), No. 2400074.

(9) Stegmann, P.; Gerritse, T.; Shen, L.; Londo, M.; Puente, Á.; Junginger, M. The Global Warming Potential and the Material Utility of PET and Bio-Based PEF Bottles over Multiple Recycling Trips. *J. Clean Prod* **2023**, *395*, No. 136426.

(10) Ye, B.; Shao, Q.; Long, L.; Wu, B.; Liu, Z.; Li, Y.; Wang, Z. Intermolecular ═C−H···O═C Hydrogen Bonding and Conformational Preference in Crystalline Poly(Butylene 2,5-Furandicarboxylate). *Macromolecules* **2023**, *56* (10), 3595−3606.

(11) Lightfoot, J. C.; Buchard, A.; Castro-Dominguez, B.; Parker, S. C. Comparative Study of Oxygen Diffusion in Polyethylene Terephthalate and Polyethylene Furanoate Using Molecular Modeling: Computational Insights into the Mechanism for Gas Transport in Bulk Polymer Systems. *Macromolecules* **2022**, *55* (2), 498−510.

(12) Toledano, O.; Gálvez, O.; Sanz, M.; Garcia Arcos, C.; Rebollar, E.; Nogales, A.; García-Gutiérrez, M. C.; Santoro, G.; Irska, I.; Paszkiewicz, S.; Szymczyk, A.; Ezquerra, T. A. Study of the Crystal Structure and Hydrogen Bonding during Cold Crystallization of Poly(Trimethylene 2,5-Furandicarboxylate). *Macromolecules* **2024**, *57* (5), 2218−2229.

(13) Papamokos, G.; Dimitriadis, T.; Bikiaris, D. N.; Papageorgiou, G. Z.; Floudas, G. Chain Conformation, Molecular Dynamics, and Thermal Properties of Poly(*n* -Methylene 2,5-Furanoates) as a Function of Methylene Unit Sequence Length. *Macromolecules* **2019**, *52* (17), 6533−6546.

(14) Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon Dioxide Sorption and Transport in Amorphous Poly(Ethylene Furanoate). *Macromolecules* **2015**, *48* (7), 2184−2193.

(15) Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudić, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Inside PEF: Chain Conformation and Dynamics in Crystalline and Amorphous Domains. *Macromolecules* **2018**, *51* (9), 3515−3526.

(16) Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J. Chain Mobility, Thermal, and Mechanical Properties of Poly(Ethylene Furanoate) Compared to Poly(Ethylene Terephthalate). *Macromolecules* **2014**, *47* (4), 1383−1391.

(17) Edling, H. E.; Sun, H.; Paschke, E.; Schiraldi, D. A.; Tanko, J. M.; Paradzinsky, M.; Turner, S. R. High Barrier Biosourced Polyester from Dimethyl [2,2′-Bifuran]-5,5′-Dicarboxylate. *Polymer (Guildf)* **2020**, *191*, No. 122258.

(18) Kainulainen, T. P.; Hukka, T. I.; Özeren, H. D.; Sirviö, J. A.; Hedenqvist, M. S.; Heiskanen, J. P. Utilizing Furfural-Based Bifuran Diester as Monomer and Comonomer for High-Performance Bioplastics: Properties of Poly(Butylene Furanoate), Poly(Butylene Bifuranoate), and Their Copolyesters. *Biomacromolecules* **2020**, *21* (2), 743−752.

(19) Guidotti, G.; Soccio, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Munari, A. Poly(Propylene 2,5-Thiophenedicarboxylate) vs. Poly(Propylene 2,5-Furandicarboxylate): Two Examples of High Gas Barrier Bio-Based Polyesters. *Polymers (Basel)* **2018**, *10* (7), 785.

(20) Wang, J.-G.; Zhang, X.-Q.; Shen, A.; Zhu, J.; Song, P.-A.; Wang, H.; Liu, X.-Q. Synthesis and Properties Investigation of Thiophene-Aromatic Polyesters: Potential Alternatives for the 2,5-Furandicarboxylic Acid-Based Ones. *Chin. J. Polym. Sci.* **2020**, *38* (10), 1082−1091.

(21) Guidotti, G.; Soccio, M.; Gazzano, M.; Siracusa, V.; Lotti, N. Poly(Alkylene 2,5-Thiophenedicarboxylate) Polyesters: A New Class of Bio-Based High-Performance Polymers for Sustainable Packaging. *Polymers (Basel)* **2021**, *13* (15), 2460.

(22) Ahmed, A. M.; Kainulainen, T. P.; Sirviö, J. A.; Heiskanen, J. P. Renewable Furfural-Based Polyesters Bearing Sulfur-Bridged Difuran Moieties with High Oxygen Barrier Properties. *Biomacromolecules* **2022**, *23* (4), 1803−1811.

(23) Kainulainen, T. P.; Ahmed, A. M.; Antti Sirviö, J.; Heiskanen, J. P. Sulfone-Bridged Difuran Polyesters. *Eur. Polym. J.* **2023**, *200*, No. 112540.

(24) Meng, H.; Li, Z.; Wu, L.; Li, B.; Hu, Y.; Wang, K. Synthesis and Properties of Poly(Ethylene-co-diethylene Glycol 2,5-furandicarboxylate) Copolymers. *J. Appl. Polym. Sci.* **2022**, *139* (15), No. 51921.

(25) Tian, S.; Cao, X.; Luo, K.; Lin, Y.; Wang, W.; Xu, J.; Guo, B. Effects of Nonhydroxyl Oxygen Heteroatoms in Diethylene Glycols on the Properties of 2,5-Furandicarboxylic Acid-Based Polyesters. *Biomacromolecules* **2021**, *22* (11), 4823−4832.

(26) Quattrosoldi, S.; Guidotti, G.; Soccio, M.; Siracusa, V.; Lotti, N. Bio-Based and One-Day Compostable Poly(Diethylene 2,5-Furanoate) for Sustainable Flexible Food Packaging: Effect of Ether-Oxygen Atom Insertion on the Final Properties. *Chemosphere* **2022**, *291*, No. 132996.

(27) Weinland, D. H.; van der Maas, K.; Wang, Y.; Bottega Pergher, B.; van Putten, R.-J.; Wang, B.; Gruter, G.-J. M. Overcoming the Low Reactivity of Biobased, Secondary Diols in Polyester Synthesis. *Nat. Commun.* **2022**, *13* (1), 7370.

(28) Haernvall, K.; Zitzenbacher, S.; Amer, H.; Zumstein, M. T.; Sander, M.; McNeill, K.; Yamamoto, M.; Schick, M. B.; Ribitsch, D.; Guebitz, G. M. Polyol Structure Influences Enzymatic Hydrolysis of Bio-Based 2,5-Furandicarboxylic Acid (FDCA) Polyesters. *Biotechnol. J.* **2017**, *12* (9), No. 1600741.

(29) Horne, F. J.; Liggat, J. J. Photo-oxidation of Poly(Diethylene Glycol Terephthalate). *J. Appl. Polym. Sci.* **2023**, *140* (16), No. e53760.

(30) Gigli, M.; Negroni, A.; Soccio, M.; Zanaroli, G.; Lotti, N.; Fava, F.; Munari, A. Influence of Chemical and Architectural Modifications on the Enzymatic Hydrolysis of Poly(Butylene Succinate). *Green Chem.* **2012**, *14* (10), 2885.

(31) Ahmed, A. M.; Kainulainen, T. P.; Heiskanen, J. P. Furfural-Based Modification of PET for UV-Blocking Copolymers with Decreased Oxygen Permeability. *Ind. Eng. Chem. Res.* **2021**, *60* (19), 7495−7504.

(32) Lian, F.-Y.; Yuan, D.-Q.; Jiang, F.-L.; Hong, M.-C. 4,4′-Sulfonyldibenzoic Acid. *Acta Crystallogr. Sect E Struct Rep. Online* **2007**, *63* (6), o2870−o2870.

(33) Guzmán, J.; Fatou, J. G. Crystallization of Poly(Diethylene Glycol Terephthalate). *Eur. Polym. J.* **1978**, *14* (11), 943−949.

(34) Ahmed, A. M.; Kainulainen, T. P.; Sirviö, J. A.; Heiskanen, J. P. Flexible Furfural-Based Barrier Polyester from a Self-Condensable Monomer. *Macromolecules* **2023**, *56* (18), 7561−7570.

(35) Müller, K.; Scheuerer, Z.; Florian, V.; Skutschik, T.; Sängerlaub, S. Comparison of Test Methods for Oxygen Permeability: Optical Method versus Carrier Gas Method. *Polym. Test* **2017**, *63*, 126−132.

(36) Xie, H.; Wu, L.; Li, B.-G.; Dubois, P. Modification of Poly(Ethylene 2,5-Furandicarboxylate) with Biobased 1,5-Pentanediol: Significantly Toughened Copolyesters Retaining High Tensile Strength and O_2 Barrier Property. *Biomacromolecules* **2019**, *20* (1), 353−364.

(37) Martínez-Tong, D. E.; Soccio, M.; Robles-Hernández, B.; Guidotti, G.; Gazzano, M.; Lotti, N.; Alegria, A. Evidence of Nanostructure Development from the Molecular Dynamics of Poly(Pentamethylene 2,5-Furanoate). *Macromolecules* **2020**, *53* (23), 10526−10537.

(38) Wang, B.; Tu, Z.; Zhang, X.; Sang, L.; Chan, W.; Wang, L.; Pu, X.; Ling, F.; Qi, M.; Wei, Z. New Advance in Biorenewable FDCA-Based Polyesters: Multiple Scale-up from Lab Bench to Pilot Plant. *Chemical Engineering Journal* **2023**, *474*, No. 145911.

(39) Lloyd, E. M.; Lopez Hernandez, H.; Feinberg, E. C.; Yourdkhani, M.; Zen, E. K.; Mejia, E. B.; Sottos, N. R.; Moore, J. S.; White, S. R. Fully Recyclable Metastable Polymers and Composites. *Chem. Mater.* **2019**, *31* (2), 398−406.

(40) Liang, X.; Gillies, E. R. Self-Immolative Amphiphilic Diblock Copolymers with Individually Triggerable Blocks. *ACS Polymers Au* **2022**, *2* (5), 313−323.

(41) Tu, Y.-M.; Wang, X.-M.; Yang, X.; Fan, H.-Z.; Gong, F.-L.; Cai, Z.; Zhu, J.-B. Biobased High-Performance Aromatic−Aliphatic Polyesters with Complete Recyclability. *J. Am. Chem. Soc.* **2021**, *143* (49), 20591−20597.

(42) Wang, Y.; Zhu, Y.; Lv, W.; Wang, X.; Tao, Y. Tough While Recyclable Plastics Enabled by Monothiodilactone Monomers. *J. Am. Chem. Soc.* **2023**, *145* (3), 1877−1885.

(43) Valsange, N. G.; Warlin, N.; Mankar, S. V.; Rehnberg, N.; Zhang, B.; Jannasch, P. Improved Chemical Recyclability of 2,5-Furandicarboxylate Polyesters Enabled by Acid-Sensitive Spirocyclic Ketal Units. *Green Chem.* **2024**, *26* (5), 2858−2873.

(44) Wu, X.; Hartmann, P.; Berne, D.; De Bruyn, M.; Cuminet, F.; Wang, Z.; Zechner, J. M.; Boese, A. D.; Placet, V.; Caillol, S.; Barta, K. Closed-Loop Recyclability of a Biomass-Derived Epoxy-Amine Thermoset by Methanolysis. *Science* **2024**, *384* (6692), No. eadj9989.

(45) Musgrave, G. M.; Bishop, K. M.; Kim, J. S.; Heiner, A. C.; Wang, C. Polyester Networks from Structurally Similar Monomers: Recyclable-by-Design and Upcyclable to Photopolymers. *Polym. Chem.* **2023**, *14* (25), 2964−2970.

(46) Tanaka, S.; Koga, M.; Kuragano, T.; Ogawa, A.; Ogiwara, H.; Sato, K.; Nakajima, Y. Depolymerization of Polyester Fibers with Dimethyl Carbonate-Aided Methanolysis. *ACS Materials Au* **2024**, *4* (3), 335−345.

(47) Pham, D. D.; Cho, J. Low-Energy Catalytic Methanolysis of Poly(Ethyleneterephthalate). *Green Chem.* **2021**, *23* (1), 511−525.

(48) Wu, S.; Li, L.; Song, L.; Zhou, G.; Liu, L.; Kang, H.; Zhou, G.; Wang, R. A Simple, Efficient and Selective Catalyst for Closed-Loop Recycling of PEF *in Situ* towards a Circular Materials Economy Approach. *Green Chem.* **2024**, *27*, 179.

(49) Li, J.; Wang, S.; Lu, H.-J.; Lan, Y.-J.; Li, X.-H.; Tu, Y.-F. Chemical Recycling of Poly(Ethylene Furanoate) into Value-Added Poly(Ethylene-Co)-Isosorbide Furanoate). *Chin. J. Polym. Sci.* **2023**, *41* (10), 1533−1542.

(50) Gabirondo, E.; Melendez-Rodriguez, B.; Arnal, C.; Lagaron, J. M.; Martínez de Ilarduya, A.; Sardon, H.; Torres-Giner, S. Organocatalyzed Closed-Loop Chemical Recycling of Thermo-Compressed Films of Poly(Ethylene Furanoate). *Polym. Chem.* **2021**, *12* (10), 1571−1580.

(51) Razinkov, D.; Agostinho, B.; Suman, S. G.; Sousa, A. F. Leveraging Molybdenum Sulfur Compounds as Catalysts for the Synthesis of Biobased Poly(Ethylene 2,5-Furandicarboxylate) and Recycling. *RSC Sustainability* **2025**, *3*, 323.

(52) Qu, X.; Zhou, G.; Wang, R.; Yuan, B.; Jiang, M.; Tang, J. Synergistic Catalysis of Imidazole Acetate Ionic Liquids for the Methanolysis of Spiral Poly(Ethylene 2,5-Furandicarboxylate) under a Mild Condition. *Green Chem.* **2021**, *23* (4), 1871−1882.

(53) Alberti, C.; Matthiesen, K.; Wehrmeister, M.; Bycinskij, S.; Enthaler, S. Zinc-Catalyzed Depolymerization of the End-of-Life Poly(Ethylene 2,5-furandicarboxylate). *ChemistrySelect* **2021**, *6* (31), 7972−7975.

(54) Dargó, G.; Kis, D.; Ráduly, A.; Farkas, V.; Kupai, J. Furandicarboxylic Acid (FDCA): Electrosynthesis and Its Facile Recovery From Polyethylene Furanoate (PEF) via Depolymerization. *ChemSusChem* **2025**.