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Effects of Methyl Branching on the Properties and Performance of Furandioate-Adipate Copolyesters of Bio-Based Secondary Diols

Alastair Little, Alessandro Pellis, James W. Comerford, Edwin Naranjo-Valles, Nema Hafezi, Mark Mascal,* and Thomas J. Farmer*

ABSTRACT: Furandioate-adipate copolyesters are an emerging class of bio-based biodegradable polymers with great potential to replace fossil-derived terephthalic acid-based copolyesters such as poly(butylene adipate-co-terephthalate) (PBAT). Furandioate-adipate copolyesters have almost exclusively been prepared with conventional primary (1°) alcohol diols, while secondary (2°) alcohol diol monomers have largely been overlooked until now, despite preliminary observations that using methyl-branched diols increases the Tg of the resultant copolyesters. Little is known of what impact the use of 2° alcohol diols has on other properties such as material strength, hydrophobicity, and rate of enzymatic hydrolysis—all key parameters for performance and end-of-life. To ascertain the effects of using 2° diols on the properties of furandioate-adipate copolyesters, a series of copolyesters from diethyl adipate (DEA) and 2,5-furandicarboxylic acid diethyl ester (FDEE) using different 1° and 2° alcohol diols was prepared. Longer transesterification times and greater excesses of diol (diol/diester molar ratio of 2:1) were found to be necessary to achieve Ms > 20 kDa using 2° alcohol diols. All copolyesters from 2° diols were entirely amorphous and exhibited higher Tg than their linear equivalents from 1° diols. Compared to linear poly(1,4-butylenedipropionate-co-1,4-butylenefurfurandioate), methyl-branched, poly(2,5-hexanediol adipate-co-2,5-hexanediol furandioate) (0.7:0.3 furandioate/adipate ratio) displayed both higher modulus (67.8 vs 19.1 MPa) and higher extension at break (89.7 vs 44.5 mm). All other methyl-branched copolyesters displayed lower modulus but retained higher extension at break compared with their linear analogues. Enzymatic hydrolysis studies using Humicola insolens cutinase revealed that copolyesters from 2° alcohol diols have significantly decreased rates of biodegradation than their linear equivalents synthesized using 1° alcohol diols, allowing for fine-tuning of polymer stability. Hydrophobicity, as revealed by water contact angles, was also found to generally increase through the introduction of methyl branching, demonstrating potential for these materials in coatings applications.

KEYWORDS: bio-based polymers, 5-(chloromethyl)furfural, adipic acid, secondary alcohol diols, 2,5-furandicarboxylic acid

INTRODUCTION

Wu and Arnaud et al. reported in 2016 and 2017 the synthesis of a series of novel polyesters from secondary (2°) diol monomers derived from 5-(chloromethyl)furfural (CMF), a platform molecule obtainable in high yields directly from the polysaccharides in biomass.1,2 Various “methyl-branched” polyesters were synthesized from 2,3-butanediol (2,3-BDO), 2,5-hexanediol (2,5-HDO), 2,7-octanediol (2,7-ODO), diethyl adipate (DEA), and 2,5-furandicarboxylic acid diethyl ester (FDEE) via polycondensation. The resultant polyesters were characterized by nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC), demonstrating the potential to produce copolyesters effectively. Scheme 1 shows the common derivation of 2,5-HDO, 2,7-ODO, DEA, and FDEE from CMF. Thus, a trifurcated route starting at CMF leads either toward the rehydration product levulinic acid (path a),3 oxidation to 2,5-diformylfuran (path f),4 or reduction to 2,5-dimethylfuran (path i).5 The pathways are broken out in detail in the Scheme itself but, in general, routes a → c and a → e involve Kolbe-type electrochemical syntheses of DEA and 2,7-ODO,6,7 while f → h and i → k comprise the oxidation of CMF ultimately to FDEE or hydrolysis of 2,5-dimethylfuran and reduction of the resulting dione to 2,5-HDO, respectively.8–10 The longer chain diol 2,7-ODO was found to be the most reactive of the series, giving rise to higher molecular weight (Mw) materials, because of comparatively...
This relationship has been studied in DMSO, monoester, H BuOH, HCl, then H Isosorbide polyesters are 2,3-BDO is the simplest 2 Research Article H h. EtOH; display a melting point (S optically pure 2,5-HDO, poly(2 late con polyesters, contributing to their amorphous behavior. This was the stereo-irregularity disrupted the crystal packing of the decomposition with 10% mass loss (TD et al. H Arnaud and co- (1 h) alcohol diols. Arnaud and Boyd, in separate studies, also observed similar trends in degrees of crystallinity: polyesters of the 1° alcohol diol 1,6-HDO were highly crystalline (~60%), whereas 2,5-HDO polyesters were entirely amorphous (no melting temperature observed). In these studies, the 2,5-HDO diol was a mixture of stereoisomers, thus it was assumed that the stereo-irregularity disrupted the crystal packing of the polyesters, contributing to their amorphous behavior. This was later confirmed by van der Klis et al., who found a polyester of optically pure 2,5-HDO, poly(2,3,5,6-tetrahydroxy-1,4-butanediol) to display a melting point ($T_m$) at 200 °C, confirming it to be semicrystalline. The thermal stability of the polyesters in these earlier studies was also promising. Arnaud and co-workers showed their materials to have temperatures of decomposition with 10% mass loss (TD) to be >280 °C, while van der Klis found TD to be >250 °C for all 2,5-HDO polyesters they prepared. Polyesters from these 2° alcohol diols can be considered to be “methyl-branched” analogues of polyesters from 1° alcohol diols with the same hydroxyl group relationship but containing two fewer carbons along the backbone. 2,5-HDO is thus a methyl-branched analogue of 1,4-butanediol (1,4-BDO), and 2,7-octanediol (2,7-ODO) is a methyl-branched analogue of 1,6-HDO (Figure 1). van der Klis et al. have preliminarily examined this relationship in homopolymers of 1,4-BDO, 1,4-pentanediol (1,4-PDO), and 2,5-HDO as diols containing 0, 1, and 2 methyl branches per monomer, respectively, with succinic acid, adipic acid, and 2,5-furandicarboxylic acids. The addition of methyl branches was found to reduce polymer crystallinity, linked as noted above to the use of stereo-irregular diols. Interestingly, the introduction of methyl branching raised the $T_g$ of the amorphous regions of these materials, though multiple factors are known to affect $T_g$ beyond just steric. For example, increasing the surface area due to additional carbons in the diols will lead to more chain–chain interaction, while the free volume between the chains of the materials will also alter across the series.

However, the influence of methyl branching on the biodegradability, mechanical properties, and hydrophobicity of this family of bio-based polyesters is yet to be examined. Bio-based 2° alcohol-containing monomers are not a new concept in polymer chemistry; for example, lactic acid, 2,3-BDO, and isosorbide are all well-established materials. Poly(lactic acid) (PLA) requires ring-opening polymerization of lactide to access high $M_w$ with condensation and transesterification of LA directly resulting only in oligomers. Although a diverse range of applications are known for PLA, it is also widely recognized that its material performance is nonideal in some instances, and especially the hydrophilicity of its polyesters (native contact angle of 72°) negatively impacts serviceability in some cases. For example, the surface of PLA must be modified to make it suitable for applications such as mass loss droplet transport or reduced water ingress in crop net protection. However, these modification protocols can be laborious and require the use of various solvents and coagulants, while also being heavily influenced by the crystallinity of the PLA surface. 2,3-BDO is the simplest 2° alcohol-containing diol, though it regularly gives low-chain length polyesters when combined with aromatic diacids under transesterification conditions. Isosorbide polyesters are widely studied, and this diol increases the $T_g$ and thermal stability of the resultant materials, but also suffers from sluggish

lower steric hindrance and suppression of side reactions (e.g., dehydration to form a cyclic ether) relative to other diols in the series. The presence of methyl branches increases steric interactions between chains and thus increased glass-transition temperatures ($T_g$) compared to equivalent polymers produced using primary (1°) alcohol diols. This relationship has been studied in detail by DiStasio et al. for a series of phthalic anhydride polyesters with increasing degrees of methyl branching on the phthalate ring but not the diol. DiStasio likewise concluded that the addition of methyl groups introduced greater steric strain and thus increased $T_g$ though these groups will also likely alter other properties such as end-group composition, crystallinity, and surface energy.

Arnaud and Boyd, in separate studies, also observed similar trends in degrees of crystallinity: polyesters of the 1° alcohol diol 1,6-HDO were highly crystalline (~60%), whereas 2,5-HDO polyesters were entirely amorphous (no melting temperature observed). In these studies, the 2,5-HDO diol was a mixture of stereoisomers, thus it was assumed that the stereo-irregularity disrupted the crystal packing of the polyesters, contributing to their amorphous behavior. This was later confirmed by van der Klis et al., who found a polyester of optically pure 2,5-HDO, poly(2S,5S-hexylene succinate) to display a melting point ($T_m$) at 200 °C, confirming it to be semicrystalline. The thermal stability of the polyesters in these earlier studies was also promising. Arnaud and co-workers showed their materials to have temperatures of decomposition with 10% mass loss (TD) to be >280 °C,
kinetics with the added complication that reactivity differs between the two hydroxyl groups.\textsuperscript{21−23}

Polyester mechanical performance can be improved by the incorporation of rigid groups in the backbone, with furan diacids being one of the most investigated bio-based options in recent times. However, there is very little literature surrounding the effects of methyl branching on the hydrophobicity, mechanical performance, and hydrolytic stability of furandioate polymers. When researching the rates of enzymatic hydrolysis of furandioate polymers, Haernvall \textit{et al.} detected a fourfold increase in enzyme activity when 1,3-propanediol was replaced by its branched analogue, 1,2-propanediol, but the molecular weights of the polymers and their respective $T_g$s were significantly different.\textsuperscript{24} On the other hand, Ejlertsson \textit{et al.} reported that using branched alcohols to synthesize phthalic acid esters (PVC plasticizers) decreases their enzymatic hydrolysis rates.\textsuperscript{25}

In comparison to poly(1,3-propylene 2,5-furandioate) (PPF), Genovese \textit{et al.} found the methyl-branched poly(neopentyl glycol 2,5-furandioate) to be more hydrophobic, have higher $T_g$ and $T_w$ higher elastic modulus ($E$), higher stress at break ($\sigma_b$), and a similar extension at break ($\epsilon_b$).\textsuperscript{26} Subsequently, Guidotti \textit{et al.} studied a family of poly(butylene/ neopentyl 1,4-cyclohexane dicarboxylate) copolyster containing butylene-cyclohexane and neopentyl-cyclohexane units where their ratio was used to tune the polymer properties.\textsuperscript{27} Here, the methyl branches of the neopentyl moiety disrupted the formation of ordered phases, enhancing the polymer’s flexibility (increasing $\epsilon_b$), but decreasing its $E$ and $\sigma_b$ with respect to analogous polymers with no methyl branching. These researchers used the same technique to enhance the flexibility of PBS.\textsuperscript{27}

Thus, we recognized that methyl branching could be used to the same effect in linear furandioate-adipate copolysters, enhancing mechanical performance that could be of value for further commercialization of materials such as the biodegradable film-forming polyester poly(1,4-butylenediacate-co-1,4-butylenediacate 2,5-furandioate) (1,4-PBAF) as well as in coatings.\textsuperscript{28,29} A challenge remains as to how mechanical performance and hydrolytic resistance can be tuned independent of crystallinity. Innovative bio-based monomers that use methyl branching to enable this kind of control may be of strong commercial interest, particularly in the field of surfaces and coatings where combined hydrophobic control, thermal and hydrolytic stability, and mechanical strength are desirable characteristics.\textsuperscript{30,31}

Herein is described a comprehensive evaluation of the mechanical properties, enzyme-catalyzed hydrolysis, and surface hydrophobicity of methyl-branched furandioate-adipate copolysters (Figure 2) using the aforementioned \textit{2}\textsuperscript{nd} alcohol diols 1,4-PDO, 2,5-HDO, and 2,7-ODO. A comparison is made with the corresponding linear (i.e., unbranched) \textit{1}\textsuperscript{st} alcohol diols 1,4-BDO and 1,6-HDO. Of particular importance was the determination of the correct copolyester composition that produced materials capable of being formed into films, where a careful balance between the rigid furan diacid and the more flexible adipate unit would be key to success.

![Figure 2](image-url)

**Figure 2. Adipate-co-2,5-furandioate copolysters with methyl branches highlighted in blue. From top to bottom: poly(1,4-butylenediacate-co-1,4-butylenediacate 2,5-furandioate) (1,4-PBAF), poly(1,4-pentyleneadipate-co-1,4-pentylene 2,5-furandioate) (1,4-PFPA), poly(2,5-hexyleneadipate-co-2,5-hexylene 2,5-furandioate) (2,5-PFAH), poly(1,6-hexyleneadipate-co-1,6-hexylene 2,5-furandioate) (1,6-PFAH), and poly(2,7-octyleneadipate-co-2,7-octylene 2,5-furandioate) (2,7-POFAH), where ‘red F’ is the furandioate unit and ‘green A’ is the adipate unit. All copolysters were random copolysters.**

**Scheme 2. Cyclic Ether Formation from Diols**

![Scheme 2](image-url)

**Scheme 2. Cyclic Ether Formation from Diols**

Dean–Stark distillate was recovered and analyzed by \textsuperscript{1}H NMR spectroscopy (Supporting Information, Section S2).

**RESULTS AND DISCUSSION**

It has previously been reported that the thermomechanical properties and $T_g$s of aliphatic-aromatic copolysters improve with increasing fraction of aromatic units.\textsuperscript{29,32} Although high mechanical strength is often desirable, too much rigid aromatic

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and we likewise observed cyclic ether formation both for this diol and 1,6-HDO or 2,7-ODO (Scheme 3, Section S2). 2,5-PHAF0.7 (F/D = 0.7) was selected as the target polyester to optimize 2° alcohol diol polymerization via a catalyst screening (Section S12) and variation in reaction conditions (Section S13). This polyester was chosen as it produced a tough, yet flexible, nonsticky material, while higher incorporation of FDEE was found to easily under acidic conditions.15 Wu et al. found oxolane (THF) formation from 1,4-BDO under polycondensation conditions,33 and we likewise observed cyclic ether formation both for this diol and 1,4-PDO, but not for 1,6-HDO or 2,7-ODO (Scheme 3, Section S2). 2,5-PHAF0.7 (F/D = 0.7) was selected as the target polyester to optimize 2° alcohol diol polymerization via a catalyst screening (Section S12) and variation in reaction conditions (Section S13). This polyester was chosen as it produced a tough, yet flexible, nonsticky material, while higher incorporation of FDEE was found to

Scheme 3. Random Copolyesters from Diethyl 2,5-Furandioate (FDEE), Diethyl Adipate (DEA), and Various Diols

Table 1. Number-Average Molecular Weight (\(M_n\)), Weight-Average Molecular Weight (\(M_w\)), Dispersity (\(D\)), Furandioate to Total Diester Molar Fraction (F/D), End-Group Ratio (% −OH), Glass-Transition Temperature (\(T_m\)), and Melting Temperature (\(T_m^*\)) of the Isolated Polyesters

| entry | polymer      | \(M_n\)/kDa | \(M_w\)/kDa | \(D\)^c | F/D | % −OH end groups\(^b\) | \(T_m^*\)/°C | \(T_m\)/°C |
|-------|--------------|-------------|-------------|---------|-----|---------------------|--------------|-----------|
| 1     | 1,4-PBA      | 31 (20\(^a\)) | 63          | 2       | 0   | 100^d                | −68           | 56 (47)   |
| 2     | 1,4-PBAF0.5  | 18 (9.3\(^a\)) | 28          | 1.6    | 0.51 | 100^d                | −26           | 91 [nd]   |
| 3     | 1,4-PBAF0.6  | 6.5\(^a\)   | Nd          | Nd      | 0.61 | 100^d                | −23           | 113 (25) |
| 4     | 1,4-PBAF0.7  | 10\(^a\)    | Nd          | Nd      | 0.69 | 100^d                | −13           | 132 (21) |
| 5     | 1,4-PBF      | Nd^e         | Nd^e        | Nd^e    | 15^a | 170 (46)             |              |           |
| 6     | 1,4-PPA      | 22 (9.3\(^a\)) | 37          | 1.7    | 0   | 100^d                | −50           | †         |
| 7     | 1,4-PPAF0.5  | 19 (9.5\(^a\)) | 34          | 1.8    | 0.52 | 100^d                | −10           | †         |
| 8     | 1,4-PPAF0.6  | 17 (7.1\(^a\)) | 29          | 1.6    | 0.58 | 100^d                | −3            | †         |
| 9     | 1,4-PPAF0.7  | 21 (23\(^a\)) | 37          | 1.8    | 0.70 | 100^d                | 12            | †         |
| 10    | 1,4-PPF      | 1.7 (nd^e)   | 2.9         | 1.7    | 1   | nd^e                 | 22            |           |
| 11    | 2,5-PHA      | 27 (11\(^a\)) | 45          | 1.6    | 0   | 100^d                | −34           | †         |
| 12    | 2,5-PHAF0.5  | 16 (6.7\(^a\)) | 24          | 1.5    | 0.49 | 38 [48]              | 0             | †         |
| 13    | 2,5-PHAF0.6  | 23 (13\(^a\)) | 34          | 1.5    | 0.61 | 100^d                | 19            | †         |
| 14    | 2,5-PHAF0.7  | 15 (6.8\(^a\)) | 22          | 1.5    | 0.71 | 100^d                | 27            | †         |
| 15    | 2,5-PHF      | 3.4 (2.0\(^a\)) | 5.9         | 1.7    | 1   | 91 [100]             | 37            |           |
| 16    | 1,6-PHA      | 23 (7.6\(^a\)) | 39          | 1.7    | 0   | 100^d                | †             | 57 (70)   |
| 17    | 1,6-PHAF0.5  | 3.2\(^a\)   | Nd          | Nd      | 0.51 | 100^d                | −66           | 80 (19)   |
| 18    | 1,6-PHAF0.6  | 4.2\(^a\)   | Nd          | Nd      | 0.63 | 100^d                | −37           | 97 (22)   |
| 19    | 1,6-PHAF0.7  | 6.8\(^a\)   | Nd          | Nd      | 0.72 | 100^d                | −25           | 80 (25)   |
| 20    | 1,6-PHF      | 2.8\(^a\)   | Nd          | Nd      | 1   | 100^d                | 4             | 143 (58) |
| 21    | 2,7-POA      | 21 (6.4\(^a\)) | 110         | 5.3    | 0   | 72 [0]               | −42           | †         |
| 22    | 2,7-POAF0.5  | 17 (4.8\(^a\)) | 57          | 3.5    | 0.51 | 79 [48]              | −7            | †         |
| 23    | 2,7-POAF0.6  | 11 (3.6\(^a\)) | 39          | 2.9    | 0.61 | 100^d                | −1            | †         |
| 24    | 2,7-POAF0.7  | 9.5 (2.6\(^a\)) | 21         | 2.9    | 0.71 | 88 [64]              | 4             | †         |
| 25    | 2,7-POF      | 18 (5.4\(^a\)) | 45          | 2.5    | 1   | 80 [100]             | 39            |           |

\(^a\)Determined by GPC. \(^b\)Determined by end-group analysis using \(^1\)H NMR. Value in parentheses ( ) is additional \(M_n\) determined by end-group analysis using \(^1\)H NMR. \(^c\)Determined by \(^1\)H NMR. \(F/D = \) furandioate molar fraction relative to the total diester. \(D = \) total diester molar fraction (\(F\) plus adipate, \(A\)). \(^d\)Only hydroxy end groups were detected, possibly with ethyl ester signals obscured by constitutional repeat units (CRUs), see Supporting Information section S3. \(^e\)value in brackets is % of ester end groups that are furandioate (∼4.4 ppm), as opposed to adipate (∼4.1 ppm). \(^f\)Determined by modulated DSC. \(^g\)DSC data showing the sample having a very low intensity \(T_m\) trace. nd: Not determined as the sample was insoluble in THF. nd^e: Not determined as the sample was insoluble in CDCl\(_3\). nd^a: not determined as end groups were obscured in NMR spectra. Value in braces ( ) is enthalpy of fusion (melt) in J/g, as determined by integration of the endothermic peak(s). \(^*\): No thermal transition was observed. Comparative results from other studies in the literature are given in Table S8 of the Supporting Information. Details of optimized polymerization conditions, including \(F/D\) feed ratios and time of adipate addition, are described in the Materials and Methods section and Table 4.

Table 1. Number-Average Molecular Weight (\(M_n\)), Weight-Average Molecular Weight (\(M_w\)), Dispersity (\(D\)), Furandioate to Total Diester Molar Fraction (F/D), End-Group Ratio (% −OH), Glass-Transition Temperature (\(T_m\)), and Melting Temperature (\(T_m^*\)) of the Isolated Polyesters

![Scheme 3](https://example.com/scheme3.png)

**Supporting Information**

- Section S3: Additional experimental details and figures.
- Section S2: Detailed analysis of polycondensation conditions and polymer properties.
- Table S4: Comparative data for other polyester syntheses.
- Supporting Information: Supplemental material for the manuscript.
result in materials that were too brittle. From the catalyst screening, both Ti(OiPr)_4 and Sb_2O_3 were found to be superior to other catalysts tested (Table S2), and the former was ultimately selected over the latter on the basis of elemental sustainability (Table S3) and toxicity (Table S4) considerations. When optimizing the synthesis of poly(1,4-butylenefurandioate) (1,4-PBF), Zhu et al. found that keeping the reaction temperature 30 °C below the boiling point of BDO (230 °C) yielded a maximum M_w. 2,5-HDO has a boiling point of 216–218 °C, therefore, in agreement with Zhu's recommendation, all our experiments were performed between 150 and 180 °C. Ultimately, it was found that the best way to improve chain length in the furandioate-adipate copolymers was to use a 2:1 ratio of diol to total diester and to add the faster reacting DEA after 4 h, thus allowing the furandioate bisdiol to initially form (Tables S7), an approach similar to that previously used in the synthesis of itaconate polyesters.

Furandioate-adipate copolymers using the 2° alcohol-containing diols 1,4-PDO, 2,5-HDO, and 2,7-ODO were subsequently synthesized applying the optimized conditions for 2° alcohols determined from the preliminary screening above. Full details for the optimized conditions are given in the Materials and Methods section. For each, the molar fraction of F relative to total diacid (D = F + A) was varied over the range of 0 (adipate only), 0.5, 0.6, 0.7 to 1 (furandioate only). The 1° alcohol diol equivalent polyesters were prepared from 1,4-BDO and 1,6-HDO using 1° alcohol conditions, which differ from the 2° alcohol conditions by the earlier addition of adipate (2 h rather than 4 h), and for 1,6-HDO, a lower molar excess of diol was possible (1.25:1 for 1,6-HDO as opposed to 2:1 for all other polymers).

**MOLECULAR MASS AND THERMAL PROPERTIES OF POLYESTERS**

The polyesters that resulted from using the optimized reaction conditions were initially analyzed by GPC and DSC (Table 1). 1,4-PBAF0.6–0.7, 1,4-PBF, 1,6-PHAFO.5–0.7, and 1,6-PHF were insoluble in the GPC solvent (THF), so for these polymers, M_w values were calculated using end-group analysis by 1H NMR. Where possible, end-group analysis is also given for those polymers analyzed by GPC, showing a general trend of GPC values being approximately double those estimated by NMR spectroscopy. Examples of these calculations are shown in the Supporting Information (Section S3).

1,4-PBAFs and their methyl-branched equivalents (2,5-PBAFs) all show similar M_w, M_n, and dispersity (D) values. GPC traces (Supporting Information, Section S4) of all the polyesters with F/D ≤ 0.7 in Table 1 showed broad monomodal distributions. Polysters 1,4-PPF and 2,5-PHF contained many low molecular weight oligomer peaks, reflecting the lower degrees of polymerization in furandioate-only polyesters. In contrast to this, the GPC peaks from the 2,7-POAF polymers were very broad (Figure S34), which is reflected in their large D values. The same polymers synthesized by Arnaud showed much lower D values (all <2.1, Table S8). Despite their high M_w (>22 kDa), the fully aliphatic polyesters 1,4-PPA, 2,5-PHA, and 2,7-POA were all tacky gums, confirming the necessity to prepare copolyesters with aromatic units to obtain rigid film-forming materials. As was found by Arnaud et al., the M_w of the 2,7-POAF polymers were generally higher than those of the 2,5-PHAF polymers, which can be mainly attributed to reduced steric influence and the absence of oxepane formation as a side reaction (cf. Scheme 2), an issue that was observed for 2,5-HDO and 1,4-BDO (Supporting Information, Section S2). 1H NMR analysis (Supporting Information, Section S3) confirmed that the feed molar fraction of furandioate to total diester was maintained in the final isolated polyesters (F/D, Table 1). The percentage of hydroxyl end groups (% -OH) was also determined by NMR analysis, though this analysis was not possible for the 1° alcohol diol polyesters as the ethyl ester CH_2 signals (4.4 and 4.1 ppm for furan and adipate end groups, respectively) were obscured by the main polymer chain signals. The 2,5-HDO series of polyesters generally have hydroxyl-only end groups, the exceptions being 2,5-PHAFO.5 (38% hydroxyl end group) and 2,5-PHF (91%). The 2,7-ODO series showed a higher fraction of ester end groups.

As shown by Figure 3, all the polymers, as expected, show an increase in T_g with increasing furandioate unit content. The polymers also show a decrease in T_g with increasing diol chain length, representing higher chain mobility for longer diols. Methyl branching was shown to raise the T_g because of a reduction in chain flexibility. However, as these polymers vary in M_w and T_g typically increases with M_w these trends in T_g are not wholly representative of the effects of changing the polymers’ structures. For example, the 2,7-ODO diol unit imparts greater chain flexibility in comparison to 2,5-HDO, causing the 2,7-POAF series to have lower T_g than the equivalent 2,5-PHAF series. However, as the M_w of 2,7-POF is ~8 times greater than that of 2,5-PHF, it has a higher observed T_g in this dataset. Melting points (T_m) were only observed in polymers made using 1° alcohol diols (1,4-BDO and 1,6-HDO series), highlighting the semicrystalline nature of these polymers versus the 2° alcohol diol alternatives. Using the enthalpy of crystallization as a crude measure of the degree of crystallinity, it can be observed that the homopolymers of either adipate or furandioate with 1,4-BDO and 1,6-HDO are more crystalline than the copolymers. Across the 1,6-HDO copolymer series, there is an indication that the degree of crystallinity increases slightly as F/D increases from 0.5 through 0.7, though the same trend is not seen for the 1,4-BDO series. T_g values of 2,5-PHAFO.5 and 2,7-POAFO.5 are comparable to those reported by Arnaud, despite the polymers synthesized in this study having a higher M_w, 2,5-PHA and 1,4-PBA.
Table 2. Modulus, Stress at Break (σ_b), Extension at Break (ε_b), Strain at Break, and Maximum Load of Copolymers from Each Series

| entry | polymer               | M_w/kDa (D) | modulus/MPa | σ_b/MPa | ε_b/mm | strain at break/mm/mm | max load/N |
|-------|-----------------------|-------------|-------------|---------|--------|-----------------------|------------|
| 1     | 1,4-PBAF0.6           | 6.5±4       | 17.8 ± 1.0  | 4.79 ± 0.69 | 12.6 ± 4.6  | 0.63 ± 0.23           | 4.24 ± 0.60 |
| 2     | 1,4-PBAF0.7           | 19.1 ± 0.9  | 7.00 ± 0.21 | 44.5 ± 6.0  | >500 ± 0.0  | 25.0 ± 0.0            | 6.30 ± 0.19 |
| 3^a   | 1,4-PPAF0.7           | 37 (1.8)    | 0.41 ± 0.02 | 0.69 ± 0.06 | >500 ± 0.0  | 25.0 ± 0.0            | 6.2 ± 0.06   |
| 4^a   | 2,5-PHA0.6            | 34 (1.5)    | 0.24 ± 0.09 | 0.69 ± 0.11 | >500 ± 0.0  | 25.0 ± 0.0            | 6.2 ± 0.00   |
| 5     | 2,5-PHA0.7            | 67.8 ± 11.1 | 4.15 ± 0.66 | 89.7 ± 47.9 | 4.48 ± 2.39 | 4.31 ± 0.76           |            |
| 6     | 2,5-PHA0.7^b          | 41.8 ± 14.1 | 3.05 ± 0.55 | 203 ± 61    | >500 ± 0.0  | 25.0 ± 0.0            | 6.2 ± 0.00   |
| 7     | 1,6-PHA0.7            | 22.3 ± 5.0  | 5.61 ± 0.77 | 10.3 ± 4.0  | 0.52 ± 0.20 | 5.22 ± 0.72           |            |
| 8^a   | 2,7-POA0.7            | 0.006 ± 0.006 | 0.01 ± 0.01 | >500 ± 0.0  | 25.0 ± 0.0  | 0.006 ± 0.008         |            |

^aExtension at break (ε_b) given as 500 mm, which is the limit of the machine. ^b2,5-PHA0.7 was prepared using a lower diol excess compared to entry 5 (optimized synthesis), resulting in a polyester with lower M_w (21 kDa) and M_n (17 kDa). ^cDetermined by GPC, D given in parentheses, if known. ^dDetermined by 1H NMR end-group analysis, therefore they are M_w not M_n. Tensile experiment plots are presented in the Supporting Information, Section S9.

The two 2,5-PHA0.7 samples synthesized under different diol excesses (2:1 and 3:1 diol/diester, the diester being both FDEE and DEA at a ratio of 0.7:0.3) showed noticeable variation in their mechanical performance (Table 2, entries 5 and 6). These differences were attributed to a number of factors, the first being M_w with a lower modulus and σ_b (41.6 and 3.05 Mpa, respectively, for the 17 kDa polymer, entry 6) seen for the samples with a lower M_w compared with the better performing 2,5-PHA0.7 (67.8 and 4.15 Mpa for the 22 kDa polymer, entry 5). However, tensile values for each 2,5-PHA0.7 sample had high standard deviations (Figure 4). This was because not all runs of each sample came from the same film, so the thickness varied slightly. Because of their brittleness, the 2,5-PHA0.7 films frequently broke while specimens were punched. These films were therefore first heated on a warmed Petri dish to raise their temperature above their T_g to make them soft enough to punch. This meant each sample was pressed and punched numerous times to obtain enough data points. The brittleness of the 2,5-PHA0.7 films can be explained by the two methyl branches in the diol unit raising T_g (27 °C) to above room temperature. Indeed, this near room temperature T_g of entry 5 may also explain the lower mechanical performance for entry 6, where the drop in M_w subsequently caused a drop in T_g (19 °C) to below the temperature at which the measurements were performed. This does, however, highlight the potential that these 2° alcohol diol monomers give to tuning the polymer performance towards the range of being thermally responsive at room or body temperature.

2,5-PHA0.7 displayed a superior modulus to 1,4-PBA0.7 (67.8 and 19.1 Mpa, respectively), suggesting that the former is a stiffer material, again a clear effect of methyl branching. This is in agreement with the results of Genovese et al., who observed that the methyl-branched poly(neopentyl furandioate) displayed a higher modulus than its linear analogue, poly(1,3-propyl furandioate).^10 1,4-PBA0.7 showed slightly higher σ_b than 2,5-PHA0.7, demonstrating the former to be a stiffer material, which appears to be a result of its semicrystalline nature. Considering their brittleness and higher modulus, it was surprising to see that both 2,5-PHA0.7s also displayed superior ε_b to 1,4-PBA0.7, suggesting better flexibility. The increased ε_b of 2,5-PHA0.7 could be explained by decreased crystallinity (no T_m) compared to 1,4-PBA0.7, indicating that the introduction of stereo-irregular methyl branching can improve processability when totally amorphous materials are desired. However, another plausible rationale is T_g with 1,4-PBA0.7 being in its rubbery state (T_g = 13 °C), while 2,5-PHA0.7 was in its glassy state (27 °C). The same trends were not observed in 2,5-PHA0.6 and 1,4-PBA0.6. Here, 2,5-PHA0.6 displayed a much lower modulus and σ_b, but a higher...
than 1,4-PBAF0.6, showing 2,5-PHAF0.6 to be more flexible than 1,4-PBAF0.6. In this study, 1,4-PBAF0.6 displayed a lower modulus, lower $\sigma_b$, and lower $\epsilon_f$ than 1,4-PBAF0.7, while in previous studies, these two polymers exhibited a similar modulus and $\sigma_b$, although 1,4-PBAF0.7 displayed a higher $\epsilon_f$.\(^{29}\)

Compared to the literature values, the recorded tensile properties of the PBAFs are low, which is expected because of their lower $M_w$.\(^{37}\)

In comparison to 2,5-PHAF0.7, 2,5-PHAF0.6 had much lower modulus and $\sigma_b$ but higher $\epsilon_f$. This result was expected due to the reduced flexibility of the rigid furandioate unit in comparison to the aliphatic adipate unit. 2,5-PHAF0.6 samples extended to 500 mm (the instrument’s maximum extension), at which point they were unbroken but extremely thin (Figure 5). The same occurred with samples of 1,4-PPAF0.7 and 2,7-POAF0.7. This is presumably a result of their entirely amorphous structures.

**Figure 5.** Photograph showing untested (A) and recovered tested (B) samples of 2,5-PHAF0.6 (top) and 1,4-PBAF0.6 (bottom) following tensile measurements.

2,7-POAF0.7 displayed the lowest modulus, 0.006 MPa, a value so low that it is likely to have been influenced by instrument limitations. The poor performance of this polymer is attributed primarily to a low chain length ($M_w = 22$ kDa), though it could also be affected by having a larger $D$ (2.9) compared to the other tested samples (1.5–1.8). This polymer was also the only material from the tensile strength study to be soluble in the GPC solvent (THF).

**Table 3.** WCAs of All Polymers Tested\(^{a,b,c,d}\)

| entry | polymer     | $M_w$/kDa$^e$ | WCA/°C |
|-------|-------------|---------------|---------|
| 1     | 1,4-PBAF0.5 | 28            | 83.0 ± 1.8 |
| 2     | 1,4-PBAF0.6 | Nd            | 87.8 ± 4.7 |
| 3     | 1,4-PBAF0.7 | Nd            | 103.6 ± 1.3 |
| 4     | 1,4-PPAF0.5 | 34            | 99.4 ± 2.8 |
| 5     | 1,4-PPAF0.6 | 29            | 88.4 ± 3.2 |
| 6     | 1,4-PPAF0.7 | 37            | 104.8 ± 4.4 |
| 7     | 2,5-PHAF0.5 | 24            | 95.8 ± 1.7 |
| 8     | 2,5-PHAF0.6 | 34            | 95.0 ± 3.3 |
| 9     | 2,5-PHAF0.7 | 22            | 112.3 ± 4.1 |
| 10$^f$| 2,5-PHAF0.7 (low $M_w$) | 17 | 91.0 ± 6.2 |
| 11    | 1,6-PHAF0.5 | Nd            | 78.5 ± 4.0 |
| 12    | 1,6-PHAF0.6 | Nd            | 88.5 ± 3.1 |
| 13    | 1,6-PHAF0.7 | Nd            | 93.2 ± 4.6 |
| 14    | 2,7-POAF0.5 | 57            | 106.9 ± 1.4 |
| 15    | 2,7-POAF0.6 | 39            | 100.9 ± 1.4 |
| 16    | 2,7-POAF0.7 | 21            | 96.9 ± 1.9 |

$^a$Errors represent standard deviations. $^b$Static measurements of the WCA using the sessile drop method at ambient temperature and pressure. Films were prepared as detailed in the Materials and Methods section; with use of a polyimide film a consistent smooth surface was produced. Droplets were allowed to stand for 10 s before being recorded for 3 s at a rate of 3 frames per second. Analysis was done using the Young–Laplace equation. At least five measurements were taken for drops in different areas of the film and their average and standard deviation were determined accordingly. $^c$2,5-PBAF0.7 in entry 10 was prepared using a lower diol excess compared to entry 9 (optimized synthesis), resulting in a polyester with a lower $M_w$ (12 kDa) and $M_n$ (17 kDa). $^d$Determined by GPC, nd shows samples not soluble in the GPC solvent (THF).

method on the films described above (Figure 6). Considering first the polyesters with no methyl branching (1,4-PBAFs entries 1–3 and 1,6-PHAFs entries 11–13), we note that increasing diol chain length resulted in a lower contact angle for like-for-like F/D ratios. Jiang et al. also observed this phenomenon when comparing the furan homopolymers 1,4-

**Figure 6.** Examples of static WCA photographs demonstrating the (A) influence of increasing F:D over the 1,4-PBAF series and (B) influence of introducing methyl branching. Values shown are single points of data, while the values in Table 3 are averages of multiple static values.

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PBF and 1,6-PHF, the latter being more hydrophilic.\(^{38}\) One possible explanation for this is that the furandioate is the greater contributor to surface hydrophobicity and thus longer linear diols increase spacing between the furans. Indeed, Mathers’ comprehensive study of functional group identity on polymer hydrophilicity does not necessarily follow an order of influence based on the simple C/O ratio.\(^{39}\) Another possible reason is that 1,6-HDO is more likely to possess alcohol end groups as it does not easily form the cyclic ether byproduct during polycondensation, thus maintaining a higher OH to CO\(_2\)Et end-group ratio. Mathers showed supporting evidence of the significant influence of polyester chain length on hydrophobicity when alcohol end groups are present, where shorter chains reduced hydrophobicity, and especially in cases with degrees of polymerization <8.\(^{39}\)

As a general trend, hydrophobicity increased as \(F/D\) increased for both the methyl-branched and conventional linear furandioate-adipate copolymers. However, as Figure S73 shows, 1,4-PPAF0.6 and 2,5-PHAF0.6 were more hydrophilic than 1,4-PPAF0.5 and 2,5-PHAF0.5. Of note is that 2,5-PHAF0.5 had a markedly lower number of \(-\text{OH}\) end groups (38\%, Table 1, entry 12) relative to 2,5-PHAF0.6 (all end groups were \(-\text{OH}\)). It is reasonable that a greater proportion of ester end groups will result in a more hydrophobic surface and would therefore explain the deviation in the trend seen for the 2,5-HDO series. The lower contact angle of 1,4-PPAF0.6 could be due to it having a lower \(M_w\) than 1,4-PPAF0.5 (29 and 34 kDa, respectively), as a lower \(M_w\) results in a greater number of hydrophilic OH end groups. This theory was confirmed by measuring the contact angle of low \(M_w\) 2,5-PHAF0.7 (Table 3, entry 10, 91.0\(^{\circ}\), 17 kDa), which displayed lower hydrophobicity than that of a higher \(M_w\) 2,5-PHAF0.7 (entry 9, 112. 3\(^{\circ}\), 22 kDa). Another unexpected result was the decrease in hydrophobicity as the \(F/D\) ratio increased for the 2,7-POAF polyesters. Again, this was proposed to be a matter of \(M_w\) as this dramatically decreases across this series. While no literature is available with which these values can be compared, the WCAs of 1,4-PBAFs and 1,6-PHAFs were expected to lie below the published values of the homopolymers 1,4-PBF (83.7\(^{\circ}\)) and 1,6-PHF (80.4\(^{\circ}\)).\(^{38}\) Many of the values for the furandioate-adipate copolyesters were higher than this, possibly because of differences in experimental technique or \(M_w\) and thus the influence of chain ends. Overall, these data strongly indicate that the addition of methyl branches from 2\(^{\circ}\) alcohol diols increases the surface hydrophobicity in furandioate-adipate copolyesters. Of particular note is that the most hydrophobic material, 2,5-PBAF0.7, was also the best performing material in terms of modulus.

### ENZYME-CATALYZED HYDROLYSIS

An initial study on the hydrolysis rates of 1,4-PBAF0.5, 1,4-PPAF0.5, and 2,5-PHAF0.5 was carried out to determine the timescale over which these polymers biodegrade and to show how methyl branching affects the rate. For these experiments, a commercial cutinase from *Humicola insolens* (HiC) was used as the biocatalyst as this was previously reported to efficiently hydrolize both aliphatic and aromatic polyesters containing benzene and furan moieties.\(^{40−42}\) Figure 7 shows that methyl branching decreases the enzymatic hydrolysis rate. In fact, after 24 h of incubation with HiC, 1,4-PBAF0.5 was completely degraded into soluble compounds, while for the methyl-branched 1,4-PPAF0.5 (one methyl branch) and 2,5-PHAF0.5 (two methyl branches), the measured weight loss was 5 and 21\%, respectively.

In order to better understand how the hydrolysis rate changes over time, additional hydrolysis studies using polymers containing a higher furandioate unit content (\(F/D = 0.7\) for all) were undertaken. The enzymatic hydrolysis rates of 1,4-PBAF0.7, 2,5-PHAF0.7, 1,6-PHAF0.7, and 2,7-POAF0.7 were measured over a time course reaction. Using copolymers containing a higher furandioate unit content enabled the rates to be examined over 48 h. As Figure 8 shows, this study confirmed that the rate of enzymatic hydrolysis was slowed by

![Figure 7](image1.png)

*Figure 7.* Weight loss of 1,4-PBAF0.5, 1,4-PPAF0.5, and 2,5-PHAF0.5 after 24 h of enzymatic degradation in 1 mL of 5 \(\mu\)M *H. insolens* cutinase in 1 M KPO buffer at pH 8. All samples were run in triplicate alongside a blank reaction (buffer only) that showed no significant weight loss. Error bars represent the standard deviations of triplicate samples. WCA = water contact angle (see Table 3).

![Figure 8](image2.png)

*Figure 8.* Weight loss of 1,4-PBAF0.7, 2,5-PHAF0.7, 1,6-PHAF, and 2,7-POAF0.7 over a 48 h time course enzymatic degradation in 1 mL of 5 \(\mu\)M *H. insolens* cutinase in 1 M KPO buffer at pH 8, 65 \(^{\circ}\)C. All samples were run in triplicate alongside the blank reaction (buffer only) that showed no significant weight loss. Error bars represent the standard deviations of triplicate samples, and those with no error bars had standard deviations that were too small to display. WCA = water contact angle.
the more crystalline 1,4-PBAFs were anticipated to degrade more slowly than their methyl-branched analogues. However, this was not the case, and methyl branching was seen to be a significant factor in the enzyme hydrolysis rate. We expected that the rate of hydrolysis might also be linked to the surface energy, with the more hydrophobic surfaces being slower to hydrolyze. A closer inspection of the relationship between WCA (values next to series legends in Figure 8) and the rate of enzymatic hydrolysis instead suggests that the hydrolytic stability seen for the 2,5-PHAF0.7 and 2,7-POAF0.7 polyesters was predominately a result of steric hindrance around the ester bonds in the polymer backbone. Based on the WCA alone, we would have predicted the order of enzyme hydrolytic stability to be 2,5-PHAF0.7 > 1,4-PBAF0.7 > 2,7-POAF0.7 > 1,6PHAF0.7, yet the order clearly shows the methyl-branched polyesters to be significantly more resilient to hydrolysis. An explicit reason for the slower degradation could therefore be that methyl branching sterically encumbers the ester group, reducing the degree of interaction with the enzyme’s active site. In fact, when using Candida antarctica lipase B as the catalyst for transesterification, low degrees of polymerization (leading to only short oligomers) were observed when attempting to synthesize 2,5-PHA and 2,7-POA (Table S10 for the complete set of data on enzymatic polymerization of methyl-branched diols). These data are fully supported by previous reports on the inhibition of esterification of 2° and tertiary alcohols with enzymes belonging to the serin-hydrolase family. It is also known that the enzymatic hydrolysis of aliphatic polyesters such as PLA and PBS is usually faster than the degradation of aromatic–aliphatic polyesters such as PBAT and aromatic polyesters such as PET. This indicates that steric hindrance derived from the monomers has a greater impact than crystallinity on the enzymatic degradation of these materials, although further studies would be needed to confirm this. For example, the significant shift in $\theta_{w}$ from the aliphatic polyesters to the aromatic-containing polyesters makes direct comparisons challenging, while the aliphatic polyester PLA has a relatively slow rate of hydrolysis because of its high $\theta_{c}$ and semicrystalline character.

As it is known that $M_n$ greatly impacts the rate of biodegradation, it is important to ensure that the samples being tested were of similar $M_n$. GPC analysis confirmed 1,4-PBAF0.5, 1,4-PPAF0.5, and 2,5-PHAF0.5 all to be of comparable $M_n$ and $M_w$ (Table 1). While the rate of enzymatic hydrolysis typically decreases with increasing $M_n$, differences in chain length can be discounted from affecting the observed trends. During the hydrolysis studies, a few hours after incubation, all film samples of the methyl-branched copolyesters from 2° diols lost their shape, turning from flat 0.5 × 1.0 cm rectangles into beads (Figure 9). These tests were carried out at 65 °C, well above the $T_g$ values of all the polymers. As the methyl-branched polyesters were entirely amorphous (no $T_g$ observed in DSC), they were soft and deformable at this temperature. Combining this with their high hydrophobicity, the samples formed spheres in order to reduce their surface area in contact with the aqueous buffer solution. This impacted the hydrolysis data, as a lower surface area sample has less contact with the enzyme, resulting in a lower degradation rate.

It is clear from these results that both methyl branching and a higher furan content in the polymer chain reduced the rate of enzyme hydrolysis in furandioate-adipate copolyesters. This study thus demonstrates that the use of methyl-branched diols is an effective means in improving the hydrolytic stability of a polyester, a benefit in applications where the service lifetime of a plastic needs to be long, or for hydrolytically more stable coatings and surfaces.

## MATERIALS AND METHODS

1,4-Butanediol (1,4-BDO), 2,3-butanediol (2,3-BDO), 1,4-pentanediol (1,4-PDO), 1,6-hexanediol (1,6-HDO), 2,5-hexanediol (2,5-HDO), diethyl adipate (DEA), levulinic acid, titanium isopropoxide (Ti(OiPr)$_3$), buffer solutions, THF (analytical grade, degassed), ReadyCal polystyrene standards, tetradeacne standard, and deuterated chloroform (CDCl$_3$) were purchased from Sigma-Aldrich and used as received. 2,5-Furandicarboxylic acid diethyl ester (FDEE, >99%) was purchased from Carbosynth and used as received. Cutinase from H. insolens (HiC) was purchased from Strem Chemicals and stored under vacuum following lyophilization. 10% PD/C and La(OTf)$_3$ were purchased from Strem Chemicals. 2,7-Octanediol (2,7-ODO) was prepared using a previously reported method. Diols were dried over molecular sieves prior to use in polymerizations. A Kaption HN polyimide sheet (Dupont) was used between the heated plates and samples for pressing films for WCA measurements.

### 1 Alcohol Conditions: Preparation of Copolyesters from 1° Alcohol Diols. A mixture of diol (12.5 mmol), FDEE (total diester feed of 10 mmol) and Ti(OiPr)$_3$ (1 mol % relative to total diester) was introduced into a 25 mL wide-neck round-bottom flask equipped with a stirrer bar. This was attached to a Dean–Stark condenser and a Schlenk line. The system was evacuated and back-filled with argon/nitrogen four times, heated to 150 °C, and stirred at 300 rpm. After 2 h, DEA (total diester was 10 mmol) was added. After a further 2 h, the temperature was increased to 180 °C. The distillate was collected.

### 2 Alcohol Optimized Conditions: Preparation of Copolyesters from 2° Alcohol Diols. A mixture of diol (20 mmol), FDEE (total diester was 10 mmol), and Ti(OiPr)$_3$ (1 mol % relative to total diester) was introduced into a wide-neck round-bottom flask equipped with a stirrer bar. This was attached to a Dean–Stark condenser and a Schlenk line. The system was evacuated and back-filled with argon/nitrogen four times, heated to 150 °C, and stirred at 300 rpm. After 4 h, DEA (total diester was 10 mmol) was added and
after a further 2 h, the temperature was raised to 180 °C. The distillate was collected from the Dean–Stark trap a further hour (7 h total) into the experiment and the pressure was reduced to 200 mbar. After another ~15 h, the pressure was further reduced to 4 mbar, and 30 min later full vacuum was applied (~1 mbar). The stirring rate was reduced as the mixture thickened. The reaction was performed until the Weissenberg effect emerged (~4–7 h later). The system was then back-filled with argon/nitrogen and the polymer was removed while in the molten state. The polymer samples were analyzed as collected.

Optimized Procedure for the Preparation of Homo-Polyesters. A mixture of diol (12.5 mmol using DEA) (20.0 mmol using FDEE), diester (total 10 mmol), and Ti(OiPr)4 (1 mol % relative to total diester) was introduced into a wide-neck round-bottom flask equipped with a stirrer bar. This was attached to a Dean–Stark condenser and a Schlenk line. The system was evacuated and back-filled with argon/nitrogen four times, heated to 150 °C, and stirred at 300 rpm. After 2 h, the temperature was raised to 180 °C. The distillate was collected from the Dean–Stark trap a further hour into the experiment and the pressure was reduced to 200 mbar. After another ~15 h, the pressure was further reduced to 4 mbar, and 30 min later full vacuum was applied (~1 mbar). The stirring rate was then reduced as the mixture thickened. The reaction was performed until the Weissenberg effect emerged (~4–7 h later). The system was then back-filled with argon/nitrogen and the polymer was removed while in a molten state. When using 2° diols, the system was left for 3–4 h at the initial 150 °C before increasing the temperature to 180 °C. The polymer samples were analyzed as collected.

1H NMR Spectroscopy. NMR spectra were obtained on a Jeol 400 spectrometer (400 MHz) using CDCl3 as a solvent and TMS as the internal standard. Samples were prepared by dissolving 10–20 mg of sample in CDCl3.

Gel Permeation Chromatography. GPC was carried out using a set (PSS SDV High) of three analytical columns (300 x 8 mm, particle diameter: 5 μm) of 1000, 105, and 106 Å pore sizes and a guard column, supplied by Polymer Standards Service GmbH (PSS) installed in a PSS SECurity SEC system. Elution was with THF at 1 mL/min at a column temperature of 30 °C and detection was done by refractive index. 20 μL of a 1 mg/mL sample in THF, with a small quantity of toluene added as a flow marker, was injected for each measurement and eluted for 45 min. Calibration was carried out in the molecular weight range 400 to 2 x 10^4 Da using ReadyCal polystyrene standards (Sigma Aldrich) and referenced to the toluene peak.

Differential Scanning Calorimetry. DSC experiments were performed on a TA Instruments Q2000 DSC. Samples were scanned under a nitrogen atmosphere over a temperature range of −80 to 200 °C and at a heating rate of 10 °C min⁻¹. Samples of mass ~10 mg were used. Tg values were reported from the second heating scans.

Film Preparation of Polymers. Films were prepared using a hot-press. Samples were placed between Teflon sheets and plates were positioned on either side of the polymer (~4 cm apart). Polymers prepared from 1,4-PDO, 2,5-HDO, and 2,7-DOA were heated to 100 °C and then pressed for 30 s at 10 tonnes. Polymers prepared from 1,4-BDO and 1,6-HDO were heated to 150 °C and then pressed at 1 tonne for 10 s. Films of a thickness of 0.3 ± 0.03 mm were obtained. The reported thickness (Table S9) represents the mean of 10 measurements taken using a micrometer at different points of the polymer film. For the contact angle measurements, films were prepared using a polyimide film (bottom layer) and a smooth Teflon film (top layer). The Teflon film was removed just before taking measurements.

Tensile Measurements of Polymers. Tensile properties were measured using an Instron 3367 machine. Dumbbell-shaped specimens (0.3 mm in thickness (the thickness range is available in Table S9), 20 mm in length, and 3 mm in width with a 10 x 10 mm square for gripping at each end were punched from the prepared films. Samples were tested at a rate of 5 mm/min at ambient temperature and pressure using screw action rubber grip claws and a 100 N (max) static load cell. For each sample, at least four specimens were tested.

Enzyme-Catalyzed Hydrolysis of Polyester Films. This was done based on a previously reported method.69 Consistent 0.5 × 1.0 cm pieces were cut from 0.3 mm deep films, washed to remove surface impurities (5 g/L Triton X-100, 100 mM Na2CO3 and deionized H2O, each for 30 min at 40 °C), and dried overnight in a vacuum oven. The film pieces were then weighed, placed in a weighed 2 mL Eppendorf tube, and incubated with 1.0 mL of 5 μM H. insolens cutinase (HiC) in a 1 M pH 8 KH2PO4/KH2PO4 buffer solution. Incubation was carried out in an Eppendorf ThermoMixer at 65 °C and 300 rpm. After the required time, samples were removed, washed repeatedly with deionized water, dried in a vacuum oven overnight, and weighed. All samples were run in triplicate alongside a blank (incubated as stated but without the HiC). The degradation rate was calculated from the weight loss using eq 1

\[
W = \frac{m_0 - m_1}{m_0} \times 100\%
\]

where W is the weight loss/%, \(m_0\) is the mass before/g, and \(m_1\) is the mass after/g.

WCA Measurements of Films. Static measurements of the WCA were performed on an Attension ThetaLite101 goniometer using the sessile drop method at RTP. The water droplets were allowed to stand for 10 s before being recorded for 3 s at a rate of 3 frames per second. Analysis was performed using the Young–Laplace equation. At least five measurements were taken of drops in different areas of the film and their average and standard deviation were recorded.

CONCLUSIONS

High Mw (>20 kDa) furandioate-adipate copolyesters from 2° alcohol diols (1,4-PDO, 2,5-HDO, and 2,7-DOA) with a furan/adipate molar ratio in the 0.5–0.7 range were synthesized via melt polycondensation using Ti(OiPr)4, as the catalyst. Loss of diol to oxolane formation prevented the formation of high Mw copolyesters in some cases. Increasing the diol/diester load ratio from 1.25:1 to 2:1 partially overcame this issue.

For the first time, the mechanical properties, hydrolytic stability, and WCA of methyl-branched copolyesters from bio-based 2° diols (1,4-PFA, 2,5-PFAF, and 2,7-POAF) could be compared to their linear equivalents from 1° diols (1,4-PBFAF and 1,6-PHAF). As has been previously observed, methyl-branched copolyesters displayed higher Tg's than their equivalents from 1° alcohol diols. As expected, across the series, Tg increased with increasing furandioate unit content. All copolyesters from 2° diols were entirely amorphous (displayed no melting points by DSC) whereas those from 1° diols were semicrystalline (distinct melting points detected). This reduced crystallinity gave these methyl-branched polymers increased flexibility (higher extension at break), indicating easier processability. Methyl-branched 2,5-PHAF0.7 displayed a modulus three times that of 1,4-PBFA0.7 (67.8 MPa vs 19.1 MPa, respectively), thus comprising a stiffer material. In apparent contradiction to this, the methyl-branched polyester also showed a far superior extension at break (89.7 vs 44.5 %), indicative of a more flexible material. The high modulus of 2,5-PHAF0.7 in comparison to the low modulus of all other methyl-branched materials is attributed to differences in Tg, with 2,5-PHAF0.7 being only copolyester to have a Tg (27 °C) above the test temperature. WCA measurements revealed that the methyl-branched copolyesters were generally more hydrophobic than their linear 1° alcohol diol equivalents, with some influence of alcohol end groups also observed. H. insolens cutinase-catalyzed ester hydrolysis studies showed that methyl branching slows the rate of enzymatic hydrolysis, indicating slower biodegradation (on the
order of 5 times after 24 h of incubation for 1,4-PBAF vs 2,5-PHAF) and thereby a longer service life for materials that would benefit from greater robustness. Steric influence around the ester appears to be the major contributing factor to the marked difference in behavior between these polyesters.

In conclusion, 100% bio-based copolyesters of methyl-branched diols are shown to have great potential both in terms of material performance (thermomechanical and water resistance) and the ability to tune their useful service life where this may be a commercial advantage, such as uses in coatings.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04513.

Preliminary investigation of suitable conditions of furandioate-adipate copolyesters with 2,5-HDO, analysis of distillate collected during polycondensation, 1H NMR spectra, GPC chromatograms, tabulated literature values for GPC and DSC analysis, DSC analysis, photographs of polyester samples, film thickness, tensile analysis of polyester films, graph of trends in WCA and furan content, and polyester synthesis using CaLB enzyme as a catalyst (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Notes

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Research Article

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