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# Furandicarboxylate Polyesters: A Comprehensive ADMET Study of Novel Class of Furan-Based $\alpha,\omega$ -Diene Monomers

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Supporting information (SI) for this article is given via a link at the end of the document.

**Abstract:** The present research article delves into the preparation of a new class of bio-based polyesters from  $\alpha,\omega$ -diene furandicarboxylate monomers. In particular, it exploits the use of acyclic diene metathesis polymerisation (ADMET) on 2,5-furandicarboxylic acid (FDCA)-derived compounds. First, a library of furan-based  $\alpha,\omega$ -diene monomers was prepared via acid- or base-catalyzed transesterification of 2,5-furandicarboxylic acid dimethyl ester (FDME) with commercially available alcohols incorporating terminal olefins, i.e., allyl alcohol, but-3-en-1-ol, hex-5-en-1-ol and dec-9-en-1-ol. Then, the novel monomers were subject to ADMET polymerisation employing different catalysts and reaction conditions. Interestingly, first-generation Grubbs catalyst was found to be the best promoter for ADMET polymerisation. This catalyst allowed the preparation of a new family of polyesters with molecular weights up to 26.4 kDa, with good thermal stability, and adaptable cis-trans conformations. Results also revealed that the monomer structure had a direct impact on the polymerisation efficiency and the resulting thermal properties. The effect of green bio-based solvents such as Cyrene™, dimethyl isosorbide (DMI) and  $\gamma$ -valerolactone (GVL) on the polymerisation process was also studied. Data collected showed that the solvent concentration influenced both the yield and length of polymers formed. Furthermore, some co-polymerisation experiments were conducted; the successful integration of different monomers in the resulting copolymer was shown to affect the glass transition temperature ( $T_g$ ) of the resulting materials.

## Introduction

Over the last two decades, there has been a growing demand for renewable feedstock as an alternative to finite resources like petroleum. As a result, carbohydrates and their derivatives emerged as promising building blocks for the development of cost-effective and high-performance renewable materials. Among them, 5-hydroxymethylfurfural (HMF) stands out as a versatile bio-based platform chemical capable of undergoing diverse chemical transformations, including reduction,<sup>[1]</sup> hydrogenation,<sup>[2]</sup> hydrolysis,<sup>[3]</sup> esterification,<sup>[4]</sup> and oxidation<sup>[5]</sup> offering a wide range of industrially relevant compounds (Figure 1).

HMF serves as a platform molecule for the development of a wide range of bio-based monomers, such as 2,5-furandicarboxylic acid (FDCA),<sup>[6]</sup> and its esters,<sup>[6]</sup> bis(hydroxymethyl)furan (BHMF),<sup>[1]</sup> diformylfuran (DFF),<sup>[7]</sup> 5,5'(oxy-bis(methylene)bis-2-furfural (OBMF),<sup>[8]</sup> and levulinic acid.<sup>[9,10]</sup> These bio-based chemicals can, in turn, be used for the synthesis of a variety of co-polymer materials (Figure 1).<sup>[10-14]</sup> In particular, FDCA was identified as one of the top 12 high-value-added platform molecules by the US Department of Energy.<sup>[15]</sup>

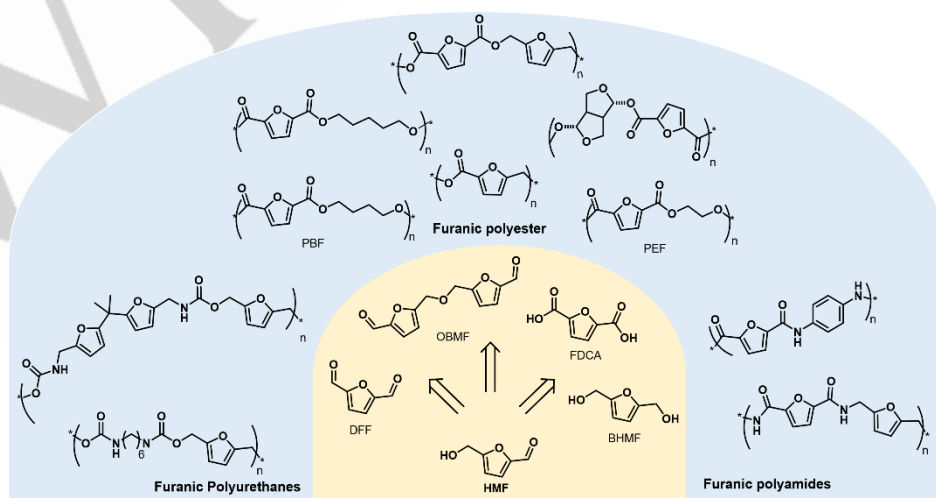
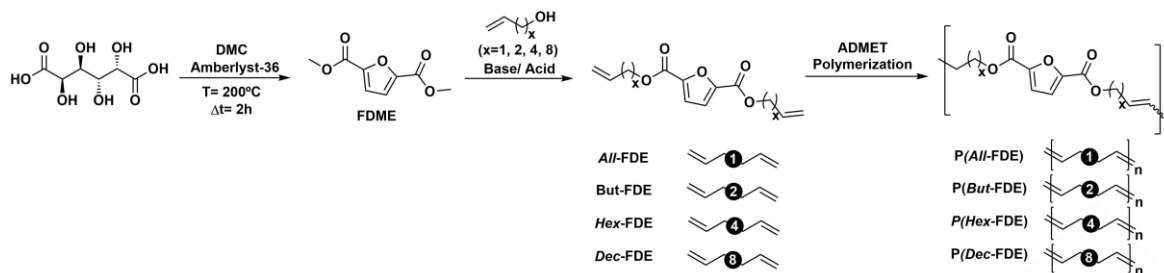


Figure 1. Examples of monomers and a polymer obtained from HMF.



**Scheme 1.** Overall scheme of this study; from the synthesis of FDME to the preparation of the polymers.

The ability of FDCA to yield polyesters such as poly(ethylene-2,5-furandicarboxylate) (PEF)<sup>[16]</sup> and poly(butylene-2,5-furandicarboxylate) (PBF)<sup>[16]</sup> showcases that they can potentially replace their petroleum-based counterparts polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), respectively. More recently, poly(propylene-2,5-furandicarboxylate) (PPF) was also studied as an alternative for poly(propylene-2,5-terephthalate) (PPT).<sup>[17]</sup> Indeed, the incorporation of furan rings in the polymer structure provides rigidity to the material,<sup>[18]</sup> resulting in a good mechanical performance, comparable thermal stability, and increased barrier properties compared to their conventional benzene-aromatic counterpart. Moreover, the polymer has a lower melting point ( $t_m$ ), which makes it easier to manipulate.<sup>[16]</sup>

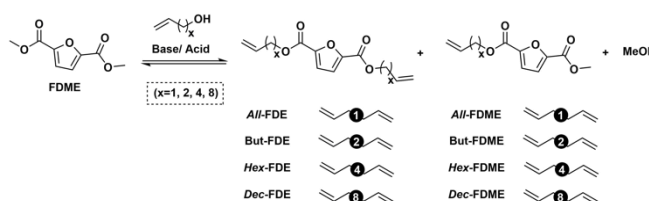
Various polycondensation methods have been used for the synthesis of furanic polyesters derived from FDCA<sup>[10,11,12]</sup> that often require harsh reaction conditions, environmentally hazardous procedures and limited control over the polymer structures.<sup>[16, 21, 22]</sup> In turn, acyclic diene metathesis (ADMET) as the advantage to synthesize polymers with precise control over polymer structures under mild conditions.<sup>[23]</sup> This technique was extensively used in the synthesis of aliphatic bio-based polyesters<sup>[23]</sup> from various biomass-derived monomers such as fatty acids,<sup>[24]</sup> castor oil derivatives,<sup>[25]</sup> ferulic<sup>[26]</sup> and sinapic acid,<sup>[27,28]</sup> and some sugar-based monomers such as isosorbide  $\alpha,\omega$ -dienes<sup>[29]</sup>. However, despite the ever-growing interest in furan-based monomers, the application of ADMET polymerisation on these compounds is still scarcely explored. To the best of our knowledge, only two studies have reported the use of ADMET polymerisation in furanic based polymers: one focusing on the preparation of co-polyesters from  $\alpha,\omega$ -dienes derived from bis(hydroxymethyl)furan (BHMF), isosorbide and glucarodilactone<sup>[30]</sup> and the other on the synthesis of BHMF based polyethers. The potential of ADMET polymerisation to produce polyesters with tailored properties renders this technique an interesting path of investigation for FDCA-derived materials.

In this view, the primary aim of this study is to explore ADMET polymerisation on novel FDCA-derived monomers (Scheme 1). Thus, a small library of different length  $\alpha,\omega$ -diene monomers was synthesized via transesterification of dimethyl furan-2,5-dicarboxylate (FDME) with several commercially available alcohols incorporating terminal olefins, i.e., allyl alcohol, but-3-en-1-ol, hex-5-en-1-ol and dec-9-en-1-ol. It is noteworthy that the FDME employed as starting material in this study was prepared according to our recently published procedure starting from galactaric acid in a one-pot procedure utilizing dimethyl carbonate (DMC) chemistry (Scheme 1).<sup>[6,31]</sup> The so-prepared monomers were then subjected to ADMET polymerisation under various conditions, offering precise control over the thermal properties of the resulting polymers. The use of green solvents in the ADMET polymerisation was also explored. Co-polymerisation experiments employing different  $\alpha,\omega$ -diene furanic monomers were then conducted in order to study their effect on the properties of the polyesters.

## Results and Discussion

### Monomer synthesis

FDME was synthesized in large scale from galactaric acid using a previously reported procedure.<sup>[6,31]</sup> Four commercially available alcohols with a terminal olefin - allyl alcohol, but-3-en-1-ol, hex-5-en-1-ol and dec-9-en-1-ol - were selected to prepare  $\alpha,\omega$ -diene monomers, by transesterification reaction. The purpose was to investigate the influence of the alkene chain length on the rigidity and thermal properties of the resulting polymers.



**Scheme 2.** Reaction scheme for the monomer synthesis.

In a typical transesterification reaction, FDME was reacted with the selected alcohol in the presence of a base or an acid. The reaction was conducted in an open vessel to allow evaporation of methanol formed as a by-product thus promoting the formation of the desired symmetric product (Scheme 2).

The synthesis of the shorter length monomer, diallyl furan-2,5-dicarboxylate (*All-FDE*), was firstly studied in consideration of the low boiling point of allyl alcohol that renders it easy to be removed from the reaction mixture once the synthesis is complete.

The transesterification was conducted at 70 °C for 5 hours using an excess of allyl alcohol (50 mol eq.). Several acid and base promoters, both homogeneous and heterogeneous, were tested (80 % (w/w) to FDME). Among the tested heterogeneous catalysts, namely Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Amberlyst-36 and Purolites (Table S1-2, SI), none showed to promote the reaction even after 24 h.

When selected homogeneous bases, i.e., 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N*-methylpyrrolidine (NMPy) (Table S1, SI), were tested in similar reaction conditions, only NMPy showed to be capable of promoting the reaction. This unexpected result cannot be ascribed solely to the basicity of NMPy, as DBU is a stronger base. Most probably there are also other factors that impact on the activity of NMPy such as base/alcohol interactions. In previous investigations,<sup>[32]</sup> it was found that NMPy - used as base in the alkylation of isosorbide - undergoes chemical transformation by reaction with dialkyl carbonates (DMC in particular) forming an ionic liquid that then acts as the real catalytic species.

As for the homogeneous acids tested, the results indicated that strong acids such as H<sub>2</sub>SO<sub>4</sub> were more effective in promoting the reaction, whereas weak acids (i.e., acetic acid) showed little or no activity. Among them, MSA was the best-performing acid in terms of selectivity toward *All-FDE*. It is noteworthy to mention that MSA is considered a greener alternative to H<sub>2</sub>SO<sub>4</sub> due to its safety, low toxicity, and overall mild environmental impact.

**Table 1.** Best promoters for the synthesis of *All-FDE*.<sup>[a]</sup>

#	Promoter	t (h)	Conv. (%)	Selectivity <sup>[b]</sup> (%)	
				<i>All-FDME</i>	<i>All-FDE</i>
1	NMPy	5	100	14	86
2	MSA	5	100	12	88
3	H <sub>2</sub> SO <sub>4</sub>	5	100	42	58

<sup>[a]</sup> Reactions conducted in reaction tubes, open to the atmosphere, with 100 mg of FDME at 70 °C, with 80 % (w/w) of promoter and 50 mol eq. of alcohol. <sup>[b]</sup> Selectivity was calculated via proton NMR.

As reported in Table 1, MSA gave similar product selectivity to NMPy. More precisely, it resulted in 88% of the desired product (*All-FDE*) and 12% of the asymmetric one (*All-FDME*), meanwhile, NMPy led to 86% of the symmetric product.

In this view, several optimization experiments were performed focussing on these best-performing promoters (Table 2- basic promoter; Table S3, SI- acidic promoters).

Further trials conducted in the presence of NMPy led to a reduction in the amount of alcohol from 50 mol eq. (#1, Table 2) to 10 mol eq. (#3, Table 2) achieving comparable product selectivity.

The amount of base used was next optimized (#5-8, Table 2). Decreasing the amount of NMPy by half, led to an increase in the selectivity of *All-FDE* up to 92%, (#6-7, Table 2). On the other hand, increasing the NMPy amount was not beneficial.

Considering the effect of the temperature on the transesterification selectivity (#9-11, Table 2); the best result was achieved when the reaction was performed at 90 °C although almost comparable selectivity toward *All-FDE* was attained at 70 and 80 °C.

Finally, the reaction time was assessed (#12-14, Table 2). After two hours (#14, Table 2), the starting material was completely converted, but there was a noticeable reduction in the reaction selectivity. Conversely, conducting the reaction for three hours (#13, Table 2) led to outcomes comparable to those achieved in five-hour experiments (#12, Table 2).

As above stated, some optimization trials were also conducted using MSA (Table S3, SI). However, in acidic conditions, attempts to reduce the amount of alcohol and catalyst resulted in a significant decrease in selectivity, thus the transesterification under acidic conditions was no further investigated.

**Table 2.** Optimization table of *All-FDE* in basic conditions.

#	Alcohol mol eq.	NMPy % (w/w)	T (°C)	t (h)	Conv. (%)	Selectivity <sup>[a]</sup> (%)	
						<i>All-FDME</i>	<i>All-FDE</i>
1	50	80	70	5	100	14	86
2	25	80	70	5	100	13	87
3	10	80	70	5	100	12	88

4	5	80	70	5	100	57	43
5	10	110	70	5	100	18	82
6	10	80	70	5	100	14	86
7	10	40	70	5	100	8	92
8	10	12	70	5	0	0	0
9	10	40	90	5	100	2	98
10	10	40	80	5	100	4	96
11	10	40	70	5	100	8	92
12	10	40	90	5	100	2	98
13	10	40	90	3	100	3	97
14	10	40	90	2	100	18	82

<sup>[a]</sup> Calculated via NMR; (All-FDE) diallyl furan-2,5-dicarboxylate, (All-FDME) 2-allyl 5-methyl furan-2,5-dicarboxylate.

In summary, the optimal conditions for the synthesis of *All-FDE* encompass the use of 40 % (w/w) of NMPy in 10 mol eq. of allyl alcohol, at 90 °C for 3 h in an open reaction tube.

The synthesis of the longer monomers (*But-FDE*, *Hex-FDE* and *Dec-FDE*) was then investigated (Scheme 1) using the aforementioned optimal conditions found for *All-FDE* (Table 3). However, performing these transesterifications at 90 °C for 3 h was not sufficient to achieve full conversion of starting FDME (#1, 4 and 7, Table 3). Thus, the reaction temperature was increased to the reflux temperature of the alcohol used, up to the limit value of 120 °C since FDME degradation starts at 130 °C (Figure S44, SI).

Additionally, all the reactions were conducted for 24 h to ensure full conversion of the starting material and increase selectivity toward the desired symmetrical product. It is worth noting that for all the above-mentioned experiments, the excess alcohol was distilled and recycled whenever feasible. This allowed us to determine the alcohol recovery rate (RR) which is also reported in Table 3 and resulted in any case quite high.

**Table 2.** Optimization of *But-FDE*, *Hex-FDE* and *Dec-FDE*.<sup>[a]</sup>

#	FDME (g)	NMPy % (w/w)	T (°C)	t (h)	Conv (%)	Selectivity <sup>[b]</sup> (%)		Isolated Yield (%)	RR <sup>[e]</sup> (%)
						FDME	FDE		
1	0.1	40	90	3	100	<i>But</i> -FDME 56	<i>But</i> -FDE 44	32	-
2	0.5	40	100	24	100	<i>But</i> -FDME 3	<i>But</i> -FDE 97	49	-
3	0.5	80	100	24	100	<i>But</i> -FDME 0	<i>But</i> -FDE 100	<b>75</b>	-
4	0.1	40	90	3	0	<i>Hex</i> -FDME 0	<i>Hex</i> -FDE 0	0	-
5	0.5	40	120	24	100	<i>Hex</i> -FDME 0	<i>Hex</i> -FDE 100	63	84
6	0.5	80	120	24	100	<i>Hex</i> -FDME 0	<i>Hex</i> -FDE 100	<b>53</b>	88
7	0.1	40	90	3	0	<i>Dec</i> -FDME 0	<i>Dec</i> -FDE 0	0	-
8	0.5 <sup>[c]</sup>	40	120	24	100	<i>Dec</i> -FDME 12	<i>Dec</i> -FDE 88	14 <sup>[d]</sup>	76
9	0.5 <sup>[c]</sup>	80	120	24	100	<i>Dec</i> -FDME 3	<i>Dec</i> -FDE 97	<b>41<sup>[d]</sup></b>	86

<sup>[a]</sup> Reaction conditions: 10 eq. of the indicated alcohol with NMPy as a catalyst; <sup>[b]</sup> Calculated via proton NMR; <sup>[c]</sup> 7.4 eq. of the indicated alcohol; <sup>[d]</sup> Product isolated via silica chromatography column. <sup>[e]</sup> RR (Recovery rate) = Amount of alcohol recovered by distillation / Excess alcohol used) x 100

In these conditions, the isolated yield of *But-FDE* was 49% after column chromatography. In an attempt to avoid tedious product purification, the amount of base used was further increased from 40% (w/w) to 80% (w/w) (#2-3, Table 3), leading to a 100% selectivity to the desired product and 75% isolated yield. Similar trials were carried out for the *Hex-FDE* monomer; the transesterification was conducted at 120 °C in the presence of 40% (w/w) of NMPy (#5, Table 3) resulting in the isolation of the desired compound in 63% yield.

For the longer monomer, namely *Dec*-FDE, it was necessary to further increase the amount of base to achieve a better selectivity although the isolated yield was still moderate, i.e., 41% (#9, Table 3).

### Scale up of the monomers

Gram-scale experiments were next performed in order to recover enough  $\alpha,\omega$ -diene monomers for ADMET polymerisation experiments (Table 4).

In these trials, a decrease in selectivity compared to smaller-scale reactions was observed. Interestingly, adopting an  $N_2$  flow during the synthesis of *All*-FDE and *But*-FDE led to an improvement of the reaction in larger scale most probably as a result of the easier evaporation of methanol from the reaction mixture. Conversely, for *Hex*-FDE and *Dec*-FDE, the use of  $N_2$  flow resulted in lower yields toward the desired products. These results were ascribed to the partial evaporation of the NMPy (b.p. 82 °C) due to the higher reaction temperature and also facilitated by the  $N_2$  flow.

**Table 4.** Scale up conditions for all member of the FDME-derived monomers.<sup>[a]</sup>

#	Monomer	T °C	T h	NMPy %(w/w)	Selectivity % <sup>[a]</sup>		Yield <sup>[c]</sup> %
					X-FDME	X-FDE	
1	<i>All</i> -FDE	90	3	40	1	99	46
2	<i>But</i> -FDE	100	24	80	5	95	67
3	<i>Hex</i> -FDE	120	24	40	4	96	50
4	<i>Dec</i> -FDE <sup>[d]</sup>	120	24	80	8	92	21

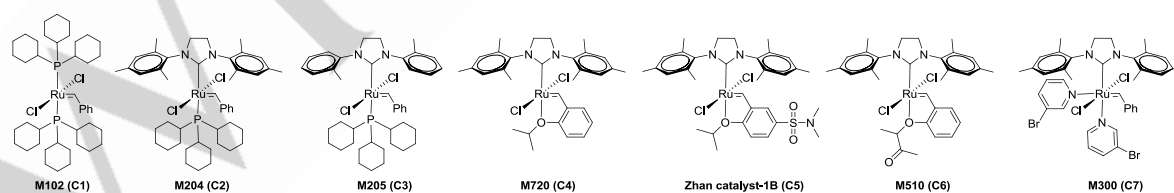
<sup>[a]</sup> Reaction conditions: 4.0 g FDME, 10 mol eq. of the appropriate alcohol; <sup>[b]</sup> Calculated via NMR; <sup>[c]</sup> Isolated yield; <sup>[d]</sup> Purified via column chromatography, 7.4 eq. of alcohol used; (X-FDE) dialkyl furan-2,5-dicarboxylate product, (X-FDME) alkyl methyl furan-2,5-dicarboxylate product;

### ADMET Polymerisation

#### Catalyst screening

ADMET polymerisation of the synthesized FDME-based  $\alpha,\omega$ -diene monomers was then performed. *Hex*-FDE was selected for the preliminary catalyst screening since previous investigations reported that monomers incorporating longer alkene chains were more efficient for the ADMET polymerisation.<sup>[27]</sup>

In this study, seven commonly used Ruthenium (Ru)-based metathesis catalyst were tested, namely, 1<sup>st</sup> generation Grubbs catalyst (C1), 2<sup>nd</sup> generation Grubbs catalyst (C2), Grubbs catalyst M205 (C3), Hoveyda–Grubbs catalyst 2<sup>nd</sup> generation (C4), Zhan catalyst-1B (C5), Grubbs catalyst M510 (C6), 3<sup>rd</sup> generation Grubbs catalyst (C7), for more information see experimental section (C1-C7, Figure 2). These Ru catalysts were selected due to their common use in metathesis transformations, their robustness and variability.



**Figure 2.** Structures of the seven tested ruthenium-based catalysts.

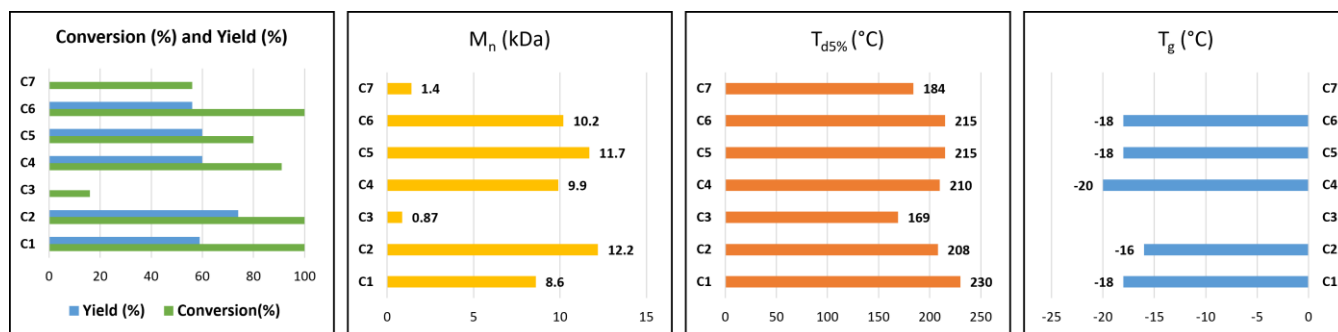


Figure 3. Results of the ADMET polymerisations of *Hex*-FDE performed using catalysts C1-C7.

The experiments were conducted in neat conditions at 80 °C in a Schleck flask under vacuum (25 mbar) in the presence of 1 mol% of Ru catalyst and 1,4-benzoquinone (3 mol eq. compared to catalyst) (Table S4, SI). Schleck line techniques were employed to consistently maintain inert conditions throughout the reaction, ensuring the removal of any generated ethylene formed by applying vacuum, thus shifting the equilibrium toward polymerisation. Additionally, 1,4-benzoquinone was used to suppress double bond isomerization, a well-known Ru-catalysed olefin metathesis side reaction,<sup>[33]</sup> increasing overall product yield and purity.

Initial trials were conducted for 1 h employing the seven selected catalysts; *Hex*-FDE conversion was then measured via proton NMR analysis. Results showed a range of substrate conversion from 16% to 100% (Figure 3) depending on the Ru-based catalyst used. Among them, three catalysts - C1, C2 and C6 - were able to quantitatively convert the monomer within 1 h. High conversion rates were also observed for C4 (91%), and C5 (80%). On the other hand, when the polymerisation was carried out in the presence of C3 and C7, poor conversions of *Hex*-FDE were observed. Even when the polymerisation time was extended, there was no significant improvement in the conversion rates.

It is important to mention that when the conversion rate was below 80%, no polymer precipitation occurred in cold methanol, and characterization had to be performed without purification. The absence of precipitation was attributed to the main formation of short oligomers that can be dissolved in methanol. Overall, very similar yields were observed for all the best performing catalysts, ca. 60%, except for the polymer synthesized with Ru-based catalyst C2 which gave a yield of 74%.

NMR spectroscopy was used to confirm the structure of all the isolated polymers formed starting from *Hex*-FDE namely *P*(*Hex*-FDE). The peaks attributed to the terminal olefins of *Hex*-FDE (5.8 and 5.1–4.86 ppm) disappeared as the signals corresponding to the internal olefins formed during the metathesis reaction emerged at 5.40 ppm. According to NMR analysis, no side products resulting from monomer isomerization or ring-closing metathesis (RCM) were detected. This is because, when employing monomers with longer alkene chains, polymerisation is more likely to occur rather than RCM.<sup>[27]</sup> Interestingly, for the polymers synthesized with C1, both *trans* and *cis* conformations were observed in the NMR spectra. Using deconvolution techniques in NMR,<sup>[34,35]</sup> it was possible to identify that 13% of the polymer appeared to be in *cis* conformation. This may lead to a more folded polymer chain that may confer to the *P*(*Hex*-FDE) extra thermal stability (vide infra).

The synthesized *P*(*Hex*-FDE) polymers were then analysed by size-exclusion chromatography (SEC) to determine the number average molecular weight ( $M_n$ ) and dispersity ( $D$ ) of the polymer chains (Figure 3). A unimodal distribution was observed for all precipitated polymers. As expected, higher  $M_n$  values were observed for C1 (8.6 kDa), C2 (12.2 kDa), C4 (9.9 kDa), C5 (11.7 kDa) and C6 (10.2 kDa), compared to those obtained for C3 (0.87 kDa) and C7 (1.3 kDa).

Thermal properties of the polymers synthesized starting from *Hex*-FDE were determined using TGA and DSC analysis, as shown in Figure 3. The results revealed that the longer polymers, obtained with C1, C2, C4, C5, and C6, exhibited good thermal stability, with a  $T_{d5\%}$  value greater than 200 °C. A drop of thermal stability below 200 °C was observed for shorter polymers (C7 and C3). It is important to note that the thermal stability of the novel polyester is influenced not only by its molecular weight, but also by its dispersity. This is obvious when comparing the polymer with the highest thermal stability (8.6 kDa,  $D = 1.8$ ) which, despite not being the longest, exhibits the highest homogeneity (#1; Table 5). Additionally, the DSC analysis revealed that all the synthesized polymers were amorphous, with similar glass transition temperatures ( $T_g$ ) of approximately -18 °C. This is consistent with expectations for aliphatic polymers, as their flexibility allows for a  $T_g$  below room temperature.<sup>[34]</sup>

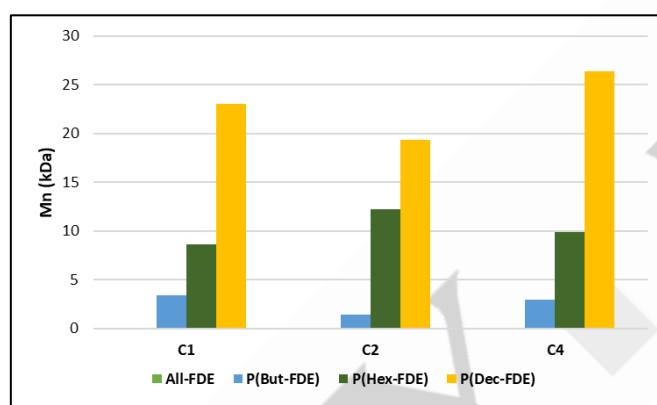
According to the above discussed data, C1, and C2 were selected as the best performing catalysts for additional testing; C4 was also chosen for further investigations being a frequently used catalyst for ADMET polymerisation.<sup>[37]</sup> Although C5 and C6 presented very promising results, they were not selected for further study as they resulted in similar results to C2 and C1, respectively, and are considerably more expensive.

### Catalyst loading

Different catalyst loadings of C1, C2 and C4, ranging from 0.1 to 10 mol%, were evaluated for *Hex*-FDE ADMET polymerisation (Table 5). The reactions were run once again in neat conditions at 80 °C and monitored by <sup>1</sup>H NMR analysis to ensure complete conversion of the substrate, with a maximum duration of 24 h. Increasing the loading of C1 to 2 mol% (#2; Table 5) led to the synthesis of a polymer with a higher molecular weight (18.3 kDa). A further increase in the amount of catalyst to 10 mol% (#3; Table 5) resulted in a lower molecular weight P(*Hex*-FDE) and a longer reaction time. This result was ascribed to the considerable increase in viscosity already visible after a few minutes, inhibiting stirring and rendering the polymerisation more challenging. Trials were also conducted up- and downloading the amount of C2 (#4-8; Table 5).

During the downloading process, the reaction did not reach full completion even after 24 h, leading to the formation of shorter polymers that did not precipitate. Similarly, increasing the catalyst amount from 1 mol% up to 10 mol% led to a considerable decrease in polymerisation efficiency, forming shorter polymers and higher dispersity, resulting in lower thermal stability.

Attempts in lowering the C4 loading were then conducted also in consideration that this catalyst is a very efficient promoter for ADMET polymerisation (#9-11; Table 5).<sup>[27]</sup> Reducing the catalyst amount from 1 mol% to 0.2 mol% led to a higher conversion (94%) although it required 2 h to reach full completion.



**Figure 4.** Comparison of molecular weights generated from 3 different catalyst (1 mol%), C1, C2 and C3 when polymerising the different members of the family.

**Table 3.** Catalyst loading for solvent-free polymerisation of *Hex*-FDE, with C1, C2 and C4 at 80 °C.

#	Catalyst	Time <sup>[a]</sup> (h)	Cat. (mol%)	Conv. <sup>[b]</sup> (%)	Yield <sup>[c]</sup> (%)	M <sub>n</sub> <sup>[d]</sup> (kDa)	Đ <sup>[e]</sup>	T <sub>d5%</sub> <sup>[f]</sup> (°C)	T <sub>g</sub> <sup>[g]</sup> (°C)
1	C1	1	1	100	59	8.6	1.8	230	-18
2		1	2	100	86	18.3	1.9	224	-15
3		2	10	100	85	11.7	1.9	215	-18
4	C2	24	0.1	87	0 <sup>[h]</sup>	1.52	1.1	181	-
5		1	1	100	74	12.2	2.1	208	-16
6		1	2	100	56	6.4	1.9	185	-
7		0.5	5	100	78	7.3	2.2	194	-17
8		0.5	10	100	76	4.6	2.3	197	-17
9	C4	24	0.1	71	0 <sup>[h]</sup>	2.5	1.2	- <sup>[b]</sup>	- <sup>[b]</sup>
10		2	0.2	100	77	7.13	1.8	234	-18
11		1	1	91	60	9.9	2.1	209	-20

<sup>[a]</sup> Duration required to attain full conversion as determined by <sup>1</sup>H NMR, with maximum time of 24 h; <sup>[b]</sup> Conversion was calculated through NMR; <sup>[c]</sup> Isolated yield after purification and drying, yield = (isolated mass/theoretical mass) × 100; <sup>[d]</sup> Determined by SEC in THF (10 mM LiBr) at 50 °C; <sup>[e]</sup> Đ = dispersity. <sup>[f]</sup> TGA degradation temperatures at which 5% (T<sub>d5%</sub>) mass loss was observed under nitrogen; <sup>[g]</sup> Glass transition temperature determined by DSC, temperature ramp 10 °C min<sup>-1</sup>; <sup>[h]</sup> The polymer did not precipitate.



Further reducing to 0.1 mol% resulted in only 71% conversion after 24 h with the formation of a short polymer (2.5 kDa,  $\bar{D} = 1.22$ ). Overall, downloading the catalyst led to a decrease in molecular weight and dispersity, resulting in the formation of a more uniform polymer at 0.2 mol% with a higher  $T_{d5\%}$  value.

It should be also mentioned that in all these trials, no significant variation was detected in glass transition values of the P(*Hex*-FDE) polymers (Table 5).

It is worth mentioning that our amorphous polymer has lower thermostability in comparison to a similar polyester known as polyhexamethylenefuranoate (PHF) that possesses a crystalline structure. This supports the existing literature that suggests the crystalline structure of a polymer can be seen as a form of physical cross-linking, which restricts chain movement therefore contributing to higher  $T_g$  and  $T_{d5\%}$  values.<sup>[38]</sup>

According to the results collected, C1 seems to be the best catalyst for *Hex*-FDME ADMET polymerisation. However, as several factors, including the alkene chain length, might influence the catalyst activity, we decided to test all the best performing catalysts, i.e., C1, C2 and C4 in the polymerisation of the other FDME-based monomers (Figure 4, Table S5, SI). These experiments were conducted in neat conditions at 80 °C in a Schleck flask under vacuum (25 mbar) in the presence of 1 mol% of Ru catalyst and 1,4-benzoquinone (3 mol eq. compared to the amount of catalyst used). The shortest member, *All*-FDE, showed no conversion even after 24 h. *But*-FDE, on the other hand, was converted between 35% to 81% after 24 h, with the best performing catalyst being C1 leading to a molecular weight of 3.4 kDa. Conversely, *Dec*-FDE was fully converted in 30 min using all of the tested catalysts; the longest polymer was attained when ruthenium-based catalyst C4 was used (26.4 kDa). However, due to its higher dispersity ( $\bar{D} = 2.48$ ), P(*Dec*-FDE) seems less thermally stable than the one synthesized with C1 (23 kDa,  $\bar{D} = 1.99$ ). Additionally, some experiments on catalyst up- and downloading of C1 were conducted (Table S5). By decreasing the amount of catalyst to 0.1 mol% (10.6 kDa,  $\bar{D} = 1.61$ ) and 0.5 mol% (15.1 kDa,  $\bar{D} = 1.73$ ), shorter polymers with better dispersity and high thermal stability ( $T_{d5\%} = 325$  °C) were obtained. However, when increasing to 10 mol%, the polymers seemed to have lower thermal stability, likely due to some remaining catalyst in the polymer even after several purification attempts.

As for P(*Hex*-FDE), the structures of P(*But*-FDE) and P(*Dec*-FDE) polymers so formed were confirmed using NMR spectroscopy. Once again, no evidence of RCM was detected for any of the members of the  $\alpha,\omega$ -diene monomers. However, *But*-FDE led to some isomerization side product, resulting in lower polymerisation yield. Furthermore, around 20% *cis* conformation was detected in P(*Dec*-FDE). Notably, only *trans* conformation was observed for P(*But*-FDE), demonstrating that more flexible polymers have a higher tendency to have *cis* conformation in their chains (Figure 5).

Considering all the data, it becomes evident that C1, although not the best performing catalyst for all members of the family individually, is the best overall choice. This catalyst consistently produces high molecular weight polymers with excellent thermal resistance. In addition, from an economic perspective, the lower prices of the 1<sup>st</sup> Grubbs generation catalyst (C1), compared to the other metathesis catalysts, offer significant advantages. Therefore, C1 was selected to be exploited in further experiments such as investigating the impact of temperature on the ADMET polymerisation.

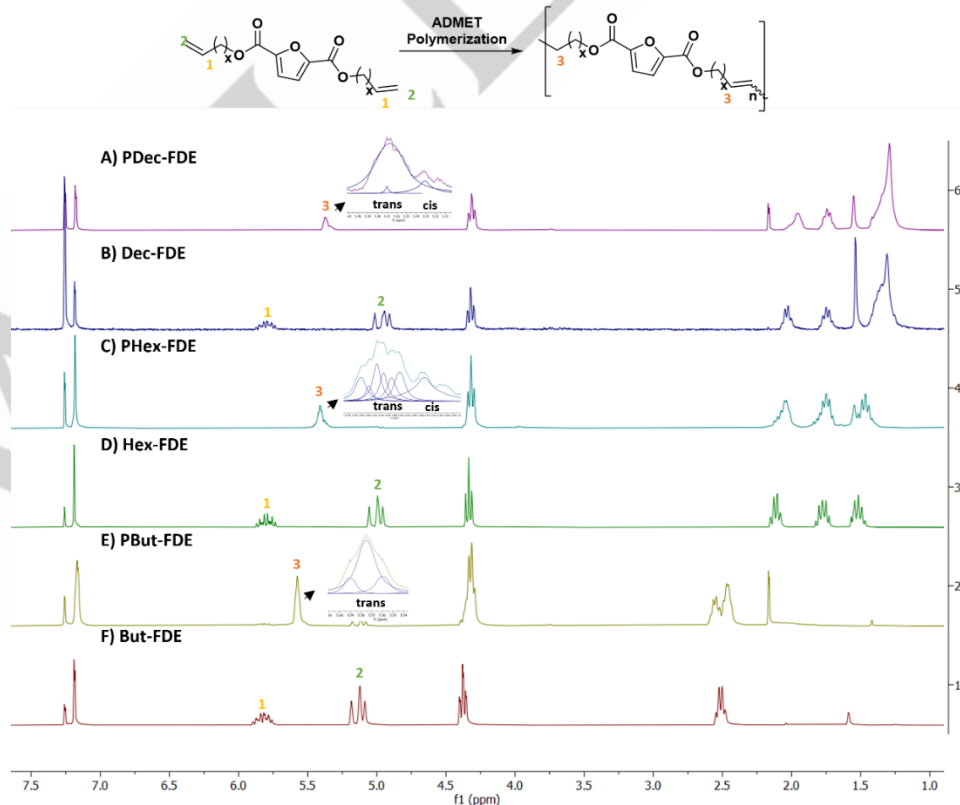


Figure 5. <sup>1</sup>H NMR spectroscopy of the polymer and their respective monomer.

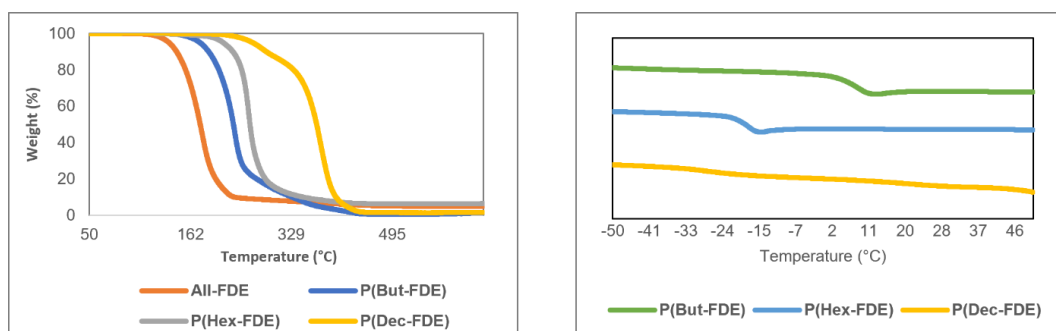


Figure 6. Thermograms for some polymers synthesized: Left) comparison of TGA analysis; Right) Comparison of DSC analysis (Table S5, #1, 4, 7 and 10, SI)

Polymerisation experiments were conducted employing *Hex*-FDE in the presence of 1 mol% of C1 at both 60 °C and 100 °C for 1 hour (Table S6, SI).

When the reaction was conducted at 60 °C, the conversion dropped to 66% and polymer with a low molecular weight of 5.09 kDa, and a dispersity of 1.36 were obtained. On the other hand, increasing the temperature to 100 °C led to the complete conversion of the monomer, however, shorter *P(Hex-FDE)* formed with a molecular weight of 7.88 kDa, and a dispersity of 1.6. Moreover, both increasing and decreasing the temperature caused an increase of *cis* conformation in the polymer chain by 20% (60 °C) and 17 % (100 °C), respectively. Consequently, 80 °C was determined as the optimal temperature for achieving a fast and efficient polymerisation.

Data indicate that monomers with longer dienes lead to faster and more efficient polymerisation, resulting in substantially higher molecular weight polymers in less time. Existing literature supports the idea that the effectiveness of Ru-catalysed metathesis polymerisation is directly related to the length of the alkene chain in the starting monomer.<sup>[27]</sup>

Moreover, when analysing the thermal properties of the polymers using TGA and DSC (Figure 6), certain trends can be observed. All polyesters showed an amorphous structure with no melting temperature ( $T_m$ ) observed in the DSC thermograms within the analysed temperature range (-70 °C to 150 °C), except for *P(Dec-FDE)* which exhibited a  $T_m$  of 70 °C. While no correlation between the polymer molecular weight and the  $T_g$  was observed for all polymers, a strong dependence of  $T_g$  on the alkyl chain lengths of the initial monomer is detected, consistent with previous literature.<sup>[26,27,36]</sup> Comparing the polymers synthesized with 1 mol% of C1, it was found that  $T_g$  (*PDec-FDE*) <  $T_g$  (*PHex-FDE*) <  $T_g$  (*PBut-FDE*). This is because alkene chains of different lengths provide the polyester with different levels of flexibility. Furthermore, TGA analysis, revealed that longer alkenes result in more thermally stable polymer.

### ADMET polymerisation employing green solvents

A drawback of solvent-free polymerisations is the potential for generating reaction media with a high viscosity, which can make handling and processing the polymers more difficult. Thus, some experiments for *Hex*-FDE and *Dec*-FDE were conducted using bio-based green solvents having a boiling point higher than 200 °C, such as Cyrene™,<sup>[27,35]</sup> dimethyl isosorbide (DMI), and  $\gamma$ -valerolactone (GVL).<sup>[34]</sup>

Table 6. ADMET polymerisation employing green solvents, using C1 at 80 °C for 18 h.

#	Monomer	Solvent	Conc (mol/L)	Cat (mol%)	Conv. <sup>[a]</sup> (%)	Yield <sup>[b]</sup> (%)	$M_n$ <sup>[c]</sup> (kDa)	$D$ <sup>[d]</sup>	$T_{d5\%}$ <sup>[e]</sup> (°C)	$T_g$ <sup>[f]</sup> (°C)
1		Cyrene™	2	1	86	22	4.2	1.2	— <sup>[g]</sup>	— <sup>[g]</sup>
2		Cyrene™	4	1	100	55	5.1	1.4	245	-21
3	<i>Hex</i> -FDE	Cyrene™	4	2	100	56	4.4	1.5	238	-23
4		DMI	4	1	88	48	4.3	1.4	233	-24
5		GVL	4	1	75	— <sup>[h]</sup>	1.5	1	177	— <sup>[i]</sup>
6		Cyrene™	4	1	100	68	4.3	1.3	210	— <sup>[i]</sup>
7	<i>Dec</i> -FDE	DMI	4	1	100	84	9.4	1.7	265	-26
8		GVL	4	1	100	80	12.1	1.6	320	-27

<sup>[a]</sup> Conversion was calculated through NMR; <sup>[b]</sup> Isolated yield after purification and drying,  $\text{yield} = (\text{isolated mass}/\text{theoretical mass}) \times 100$ ; <sup>[c]</sup> Determined by SEC in THF (10 mM LiBr) at 50 °C, <sup>[d]</sup>  $\mathcal{D}$  = dispersity; <sup>[e]</sup> TGA degradation temperatures at which 5% ( $T_{d5\%}$ ) mass loss was observed under nitrogen; <sup>[f]</sup> Glass transition temperature determined by DSC, temperature ramp 10 °C  $\text{min}^{-1}$ ; <sup>[g]</sup> not enough product was recovered to proceed with this analysis; <sup>[h]</sup> The polymer did not precipitate; <sup>[i]</sup> No  $T_g$  was detected

The experiments were conducted with two different concentrations (2 and 4  $\text{mol}\cdot\text{L}^{-1}$ ) in the presence of 1 mol% of C1 for 18 h. In a first trial, *Hex*-FDE ADMET polymerisation was performed using Cyrene™ (#1-3; Table 6). Results demonstrated that high monomer concentration resulted in polymers with high molecular weight, however, a considerable reduction in molecular weight was observed when compared with the neat reaction. Performing the polymerisation with 2 mol% of C1 resulted in similar results (#3; Table 6). Overall, full conversion for *Hex*-FDE took place only for the polymer synthesized in Cyrene™ (#2, Table 6) providing polymers with high thermal stability. GVL-mediated polymerisation led only to the formation of small oligomers (#4, Table 6). Reactions performed *Dec*-FDE led to full conversion regardless of the green solvent used (#6-8; Table 6). However, for this monomer, the polymerisation conducted in GVL led to higher molecular weight (#8, Table 6). It is worth noting that the P(*Dec*-FDE) polymers showed a 9% increase in *cis* conformation compared to the neat synthesized polymers which can be attributed to the solvation effect

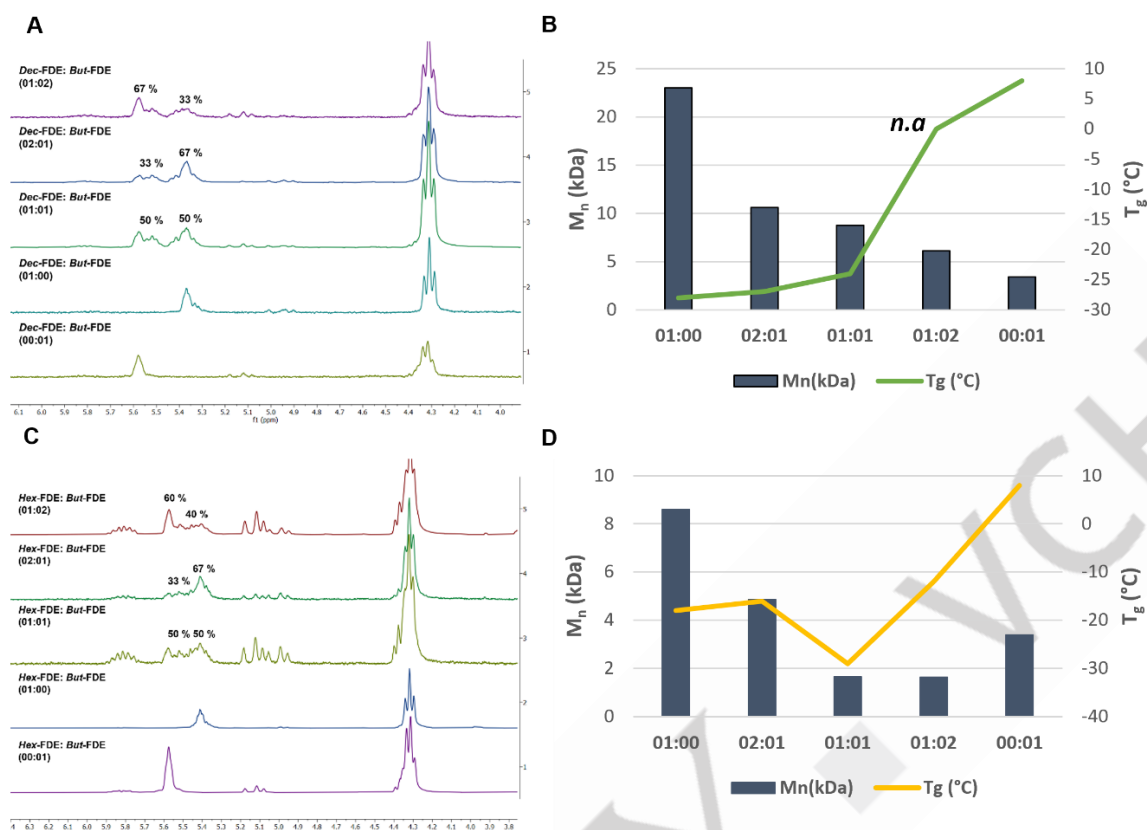
### ADMET co-polymerisation of *Hex*-FDE and *Dec*-FDE with *But*-FDE

A general approach to enhance the properties of a homopolymer is employ co-polymerisation techniques with different monomer units.<sup>[39]</sup> In this view we also conducted selected co-polymerisation experiments on the longer members of the FDME  $\alpha,\omega$ -Diene Monomers family – namely *Hex*-FDE and *Dec*-FDE - with *But*-FDE.

Three different ratios of longer monomer to *But*-FDE were attempted (01:01, 01:02, and 02:01, Figure 7, A, B, C and D) using the same conditions as in solvent-free reactions for homopolymers (Table S7, SI). <sup>1</sup>H NMR analysis showed that both monomers were successfully incorporated into the copolymer, maintaining the related ratio in the final product (Figure 7, A, C).

Co-polymerisation experiments of *But*-FDE with *Hex*-FDE were more challenging than the one with *Dec*-FDE. In fact, the initial monomers were not fully converted even after 24 h leading to short-chain polymers (between 1.64 kDa to 4.87 kDa), that could not be isolated through precipitation in cold methanol. This result was ascribed to the lower reactivity of *Hex*-FDE compared to the *Dec*-FDE monomer.

As expected,  $T_g$  values increased considerably with the increase of *But*-FDE in the polymeric chain (Figure 7, B, D) due to the decrease in flexibility of the resulting polyesters, with values ranging from -18 °C to 8 °C for *Hex*-FDE:*But*-FDE (Figure 7, D) and -28 °C to 8 °C for *Dec*-FDE:*But*-FDE (Figure 7, B). With the exception of *Hex*-FDE:*But*-FDE (01:01) that decreased the  $T_g$  value.



**Figure 7.** <sup>1</sup>H NMR spectra for both synthesized copolymers with respective monomer ratios calculated through NMR (A- Dec-FDE: But-FDE; C- Hex-FDE: But-FDE); Graphical comparison of  $M_n$  and  $T_g$  between the different synthesized co-polymers (B, D); *n.a.* = value not available.

## Conclusion

In this study, a novel class of different length  $\alpha,\omega$ -diene furanic monomers derived from FDME were synthesized through transesterification using different commercial alcohols with a terminal olefin. Reaction conditions were optimized and the synthesis was performed on multi-gram scale.

ADMET polymerisation was then carried out on these novel monomers using 7 different ruthenium catalysts. Surprisingly, the 1<sup>st</sup> generation Grubbs catalyst (C1) emerged as the best option overall, despite not being the top-performing catalyst for each member of the family. This catalyst led to polymers with molecular-weight up to 26.4 KDa that exhibited good thermal resistance. NMR analysis demonstrated that the polymerisation reaction catalyzed by C1 formed both *cis* and *trans* conformations in the polymeric chain, resulting in increased thermal stability. The more flexible polymer, P(*Dec*-FDE), tends to incorporate a higher percentage of *cis* conformation in its chains. Previous research suggested that the length of the initial monomer can impact both the effectiveness of polymerisation and the thermal properties of the resulting polymer. When comparing P(*Dec*-FDE) to P(*But*-FDE), there was a significant increase in  $T_g$  values and a decrease in  $T_{d5\%}$ .

Preliminary trials on ADMET polymerisation using environmentally friendly solvents like Cyrene™, dimethyl isosorbide (DMI), and  $\gamma$ -valerolactone (GVL) were also conducted. *Hex*-FDE and *Dec*-FDE - the best-performing monomers - were employed as substrates in these experiments. The results showed that a higher concentration of solvents produced more consistent and longer polymers with greater yields. Cyrene resulted in the best media for *Hex*-FDE, meanwhile, GVL gave the best results in the case of *Dec*-FDE. We also observed a decrease in molecular weight compared to the bulk reaction.

Finally, some co-polymerisation trials were conducted mixing different amounts of *Hex*-FDE or *Dec*-FDE with *But*-FDE. Data collected showed that both monomers were incorporated into the copolymer while maintaining their related ratio in the final product. Interestingly, an increase in the amount of *But*-FDE resulted in an increase of  $T_g$ .

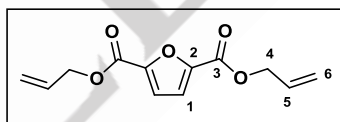
## Experimental Section

### Materials and Methods

All reagents and solvents were purchased from Sigma-Aldrich and employed without any further purification. Purolite-type catalysts were kindly provided by Purolite®. All heterogeneous solid catalysts tested for the monomer synthesis were dried in the oven at 100 °C overnight before use. Reactions were done in either silicon bath or in Drysyn at the required temperature, measured with a thermocouple. Reactions were monitored by TLC on an aluminum strip coated with silica gel 60 F254 from Merck, revealed under UV light (254 nm) and in the presence of permanganate staining solution, and using GC-MS Agilent Technologies (GC System 6890 N; Agilent Technologies Mass Selective Detector 5973) with a silica column (HP-5MS), where compounds were injected through a Hamilton micro-syringe (10 µL). <sup>1</sup>H NMR spectra of all monomers was done through a spectrometer Bruker 400 MHz in CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra were recorded on Bruker Fourier 400 (101 MHz) in CDCl<sub>3</sub>. Chromatographic purification was conducted using ca 20 cm of silica. Polymerisation was conducted under inert conditions using standard Schlenk techniques on a dual manifold line, on a high-vacuum line. All catalyst used for the polymerisation experiments were stored in an air-dried container at 2 °C. All ruthenium catalyst were purchased from Sigma-Aldrich (Merck) including the following: Grubbs catalyst first generation (C1), Grubbs catalyst second generation (C2), dichloro[1,3-bis(2-methylphenyl)-2-imidazolidinylidene] (benzylidene) (tricyclohexylphosphine) ruthenium (II) (Grubbs catalyst M205) (C3), Hoveyda–Grubbs catalyst second generation (C4), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][[5-[(dimethylamino)sulfonyl]-2-(1-methylethoxy-O)phenyl]methylene-C] ruthenium(II) (Zhan catalyst-1B) (C5), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][[2-(1-methylacetoxo)phenyl]methylene} ruthenium(II) (Grubbs catalyst) M510 (C6), and Grubbs catalyst third generation (C7). Polymers were analysed by <sup>1</sup>H NMR in CDCl<sub>3</sub> using a Bruker Fourier 300 (300 MHz) and were calibrated using the residual sign of CDCl<sub>3</sub> at 7.26 ppm. <sup>13</sup>C NMR spectra were recorded on Bruker Fourier 300 (75MHz) in CDCl<sub>3</sub> and calibrated using the solvent peak at 77.16 ppm. Additionally, 2D experiments were conducted, namely <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HMBC, and <sup>1</sup>H-<sup>13</sup>C HSQC spectra, to assign the peaks. Size-exclusion chromatography (SEC) was performed on an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector and two PLgel columns (5 µm MIXED-D 300 x 7.5 mm) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min at 50 °C. Calibration was performed with polystyrene standards from Agilent Technologies. Thermogravimetric Analysis (TGA) was measured with a TGA Q500 (TA Instruments). 5 to 10 mg of dried sample was equilibrated at 50 °C for 5 min and was flushed with highly pure nitrogen gas. All the experiments were performed with a heating rate of 10 °C/min up to 600 °C. The reported values of T<sub>d5%</sub> represent the temperature at which 5 % of the product mass is lost. Differential Scanning Calorimetry (DSC) was performed with a DSC Q20 (TA Instruments); 8 to 14 mg of sample were placed in a sealed pan, flushed with highly pure nitrogen gas and passed through a heat-cool-heat cycle at 10 °C/min in a temperature range of -70 °C to 150 °C. Three heat/cool cycles were done for each sample, where the last two cycles were used to analyse the heat flow of the sample after being cooled in controlled conditions. The T<sub>g</sub> values recorded herein are those obtained from the third cycle.

## Monomer Synthesis

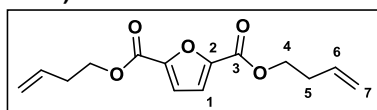
### Diallyl furan-2,5-dicarboxylate (*All-FDE*):



FDME (100 mg, 0.54 mmol, 1 eq. mol) was added to a test tube, with allyl alcohol (0.32 g, 5.43 mmol, 10 eq. mol) and NMPy (40% w/w) equipped with a magnetic stirrer. The test tube was heated in oil bath to 90 °C once the temperature was reached it was kept at this temperature for 3 h. The reaction crude was filtered over acidic silica and washed with dichloromethane; the solvent was then evaporated under reduced pressure. The white solid product was quantified by NMR (68% yield with 97% selectivity,  $T_m = 36.9 \pm 0.12$  °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm): δ 7.26 (2H, s, H1), 6.04 (2H, m, H5), 5.44 (2H, dt, J = 17.2, 1.6 Hz, H6), 5.34 (2H, dq, J = 10.4, 1.5 Hz, H6), 4.86 (4H, dq, 4.85, J = 5.9, 1.6 Hz, H4); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) (ppm): δ 157.7 (C3), 146.8 (C2), 131.5 (C5), 119.2 (C1), 118.6 (C6), 66.1 (C4).

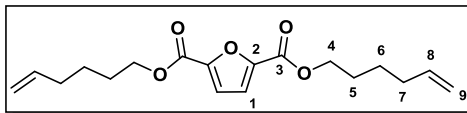
### Di(but-3-en-1-yl)-furan-2,5-dicarboxylate (*But-FDE*):



FDME (400 mg, 2.17 mmol., 1 eq. mol), was added to a test tube, with but-3-en-1-ol (1.57 g 21.80 mmol., 10 eq. mol) and NMPy (80 % (w/w)) equipped with a magnetic stirrer. The tube was heated in an oil bath to 100 °C once the temperature was reached, it was kept at this temperature for 24 h. The reaction crude was filtered over acidic silica and washed with dichloromethane; the solvent was evaporated under reduced pressure. The product was obtained in 75% yield (light-yellow oil).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm):** δ 7.21 (2H, s, H1), 5.86 (2H, m, H6), 5.19 (2H, d, H7), 5.13 (2H, d, H7), 4.41 (4H, t, J = 6.8 Hz, H4), 2.54 (4H, m, H5); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) (ppm):** δ 158.0 (C3), 146.9 (C2), 133.5 (C6), 118.3 (C1), 117.7 (C7), 64.5 (C4), 33.0 (C5).

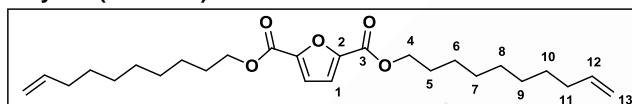
#### Di(hex-5-en-1-yl)-furan-2,5-dicarboxylate (*Hex-FDE*):



FDME (500 mg, 2.71 mmol., 1 eq. mol) was added to a test tube, with hex-5-en-1-ol (2.70 g 27.10 mmol., 10 eq. mol) and NMPy (40 % (w/w)) equipped with a magnetic stirrer. The test tube was heated in an oil bath to 120 °C once the temperature is reached, it was kept at this temperature for 24 h. The reaction crude is filtered over acidic silica and washed with dichloromethane; the solvent was evaporated under reduced pressure. Then excess hex-5-en-1-ol was distilled by vacuum distillation (0.05 bar) with a recovery rate (RR) of 84%. The pure product was obtained in 63% yield (yellow oil).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm):** δ 7.21 (2H, s, H1), 5.83 (2H, m, H8), 5.06 (2H, d, H9), 5.00 (2H, d, H9), 4.36 (4H, t, J = 6.7 Hz, H4), 2.14 (4H, m, H7), 1.80 (4H, m, H3 (C1), 115.0 (C9), 65.5 (C4), 33.2 (C7), 28.0 (C6), 25.1 (C5); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) (ppm):** δ 158.16 (C3), 146.93 (C2), 138.20 (C8), 118.25 (C1), 114.99 (C9), 65.48 (C4), 33.24 (C7), 28.02 (C6), 25.11 (C5).

#### Di(dec-9-en-1-yl)-furan-2,5-dicarboxylate (*Dec-FDE*):



FDME (500 mg, 2.71 mmol., 1 eq. mol), was added to a test tube, with dec-9-en-1-ol (3.12 g 20.00 mmol., 7.38 eq. mol) and NMPy (80 % (w/w)) equipped with a magnetic stirrer. The tube was heated in an oil bath to 120 °C once the temperature was reached, it was kept at this temperature for 24 h. The reaction crude was filtered over acid silica and washed with dichloromethane; the solvent was evaporated under reduced pressure. Then excess dec-9-en-1-ol was distilled by vacuum distillation (0.05 bar) with a recovery rate (RR) of 86%. The product was quantified by NMR (43% yield with 97% selectivity). To insure the purity of the monomer a chromatography column on silica (8:2 hexane:ethyl acetate). The pure product was obtained in 41% yield (white solid,  $T_m = 39.8 \pm 0.6$  °C).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm):** δ 7.21 (2H, s, H1), 5.83 (2H, m, H12), 5.01 (2H, d, H13), 4.95 (2H, d, H13), 4.35 (4H, t, J = 6.9 Hz, H4), 2.06 (4H, m, H11), 1.78 (4H, m, H5), 1.37 (20H, m, H6, 7, 8, 9, 10); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) (ppm):** δ 158.2 (C3), 147.0 (C2), 139.2 (C12), 118.2 (C1), 114.2 (C13), 65.7 (C4), 33.8 (C11), 29.3 (C5), 29.2 (C8), 29.0 (C9), 28.9 (C10), 28.6 (C7), 25.8 (C6).

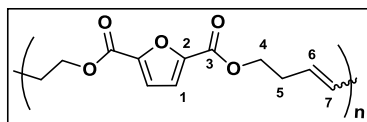
**Monomer scale up:** The scale up procedure followed the same methods described for each monomer, with the addition of working with a dean stark and N<sub>2</sub> flow for the synthesis of *All-FDE* and *But-FDE*. All monomers were purified by chromatography column, with hexane: ethyl acetate (8:2) as eluent.

## Polymer Synthesis

**Solvent free ADMET polymerisation of homopolymers general procedure:** The selected monomer (250 mg) was added in a 25 mL Schleck flask with p-benzoquinone (3 mol eq. compared to the catalyst), the flask was purged with 3 cycles of 15 min vacuum followed by N<sub>2</sub>. After the purge was completed the appropriate amount of catalyst was added followed by the magnetic stirrer. The flask was then placed in a pre-heated Drysyn at 80 °C and put under vacuum (25 mbar). Aliquots were taken at different time intervals, dissolved in CDCl<sub>3</sub> and analysed through <sup>1</sup>H NMR to monitor the progress of the reaction. The reaction was quenched with a solution of ethyl vinyl ether/THF (1:9) for 1 h. The crude product was then reprecipitated in cold methanol. Separation of the precipitated product was done based on the state of the polymer formed. For sticky low molecular weight polymers, a minimum amount of a low boiling point solvent (acetone, CH<sub>2</sub>Cl<sub>2</sub>) was used to recover the product. For solid polymers, the polymer was filtrated and washed with cold methanol. Both types of polymers were then dried under vacuum for 24 h.

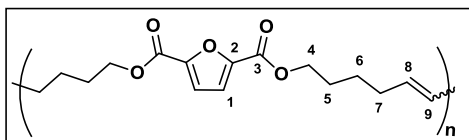
**Solution ADMET polymerisation of homopolymers general procedure:** The selected monomer (250 mg) was added in a 25 mL Schleck flask with p-benzoquinone (3 molar equivalents to the catalyst), the flask was purged with 3 cycles of 15 min vacuum followed by N<sub>2</sub>. After the purge was completed, the monomer was dissolved in the desired solvent (4 or 2 mol/L) and placed in a pre-heated Drysyn at 80 °C, for 15 min. The 1 mol% of C1 was then added, and the reaction was continued under vacuum (25 mbar) for 18 h. The reaction was quenched with a solution of ethyl vinyl ether/THF (1:9) for 1 h. The crude product was then reprecipitated in cold methanol. The purified polymer was isolated as described above for solvent-free polymerisation.

### *But-FDE*-based polymers P(*But-FDE*)



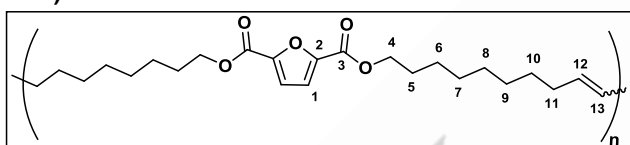
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  7.17 (2H, s, H1), 5.58 (2H, s, H6, 7), 4.31 (4H, d,  $J = 6.8$  Hz, H4), 2.50 (4H, m, H5);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  158.0 (C3), 146.8 (C2), 128.3 (C6), 127.4 (C7), 118.4 (C1), 64.7 (C4), 32.0 (C5), 26.9.

#### Hex-FDE-based polymers P(Hex-FDE)



$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  7.19 (2H, s, H1), 5.41 (2H, s, H6, 7), 4.33 (4H, td,  $J = 6.7, 1.6$  Hz, H4), 2.05 (4H, m, H7), 1.75 (4H, m, H5), 1.48 (4H, m, H6);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  158.1 (C3), 146.9 (C2), 130.3 (C8), 129.7 (C9), 118.2 (C1), 65.5 (C4), 32.1 (C7), 28.1 (C6), 25.7 (C5).

#### Dec-FDE-based polymers P(Dec-FDE)



$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  7.19 (2H, s, H1), 5.37 (2H, m, H12, 13), 4.31 (4H, td,  $J = 6.8, 2.2$  Hz, H4), 1.95 (4H, m, H11), 1.75 (4H, m, H5), 1.33 (20H, m, H6,7,8,9,10);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  158.2, (C3) 147.0 (C2), 130.3 (C12, 13), 118.2 (C1), 65.7 (C4), 32.6 (C11), 29.6 (C5), 29.4 (C8), 29.2 (C9), 29.1 (C10), 28.6 (C7), 25.8 (C6).

**Solvent free ADMET polymerisation of co-polymers general procedure:** Hex-FDE and Dec-FDE were mixed in molar ratio of 2:1, 1:1 and 1:2 with *But*-FDE (total 0.6mmol), then 1.94 mg of *p*-benzoquinone (3 molar equivalents to the catalyst) was added. The reaction mixture was purged with 3 cycles of 15 min vacuum follow by  $\text{N}_2$ . After the purge was completed the appropriate amount of C1 (1 mol%) was added followed by the magnetic stirrer. The flask was then put in a pre-heated Drysyn at 80 °C and put under vacuum (25 mbar). Aliquots were taken at different time intervals, dissolved in  $\text{CDCl}_3$  and analysed through  $^1\text{H NMR}$  to monitor the progress of the reaction. The reaction was quenched with a solution of ethyl vinyl ether/THF (1:9) for 1 h. The crude product was then reprecipitated in cold methanol. The purified polymer was isolated as described above for solvent-free polymerisation.

#### Hex-FDE: *But*-FDE-based co-polymers (1:1, 1:2, 2:2)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  7.18 (2H, s), 5.56 (2H, s), 5.39 (2H, s), 4.32 (4H, t), 2.47 (4H, m), 2.06 (4H, m), 1.48 (4H, m);

#### Dec-FDE: *But*-FDE-based co-polymers (1:1, 1:2, 2:2)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  7.17 (2H, s), 5.54 (2H, s), 5.36 (2H, s), 4.32 (4H, m), 2.47 (4H, dq,  $J = 20.0, 7.2$  Hz), 1.97 (4H, dt,  $J = 21.4, 6.8$  Hz), 1.73 (4H, p,  $J = 6.9$  Hz), 1.29 (20H, s);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  158.2, 147.0, 134.1, 130.3, 124.4, 118.2, 77.4, 77.0, 76.6, 65.7, 32.6, 32.0, 29.6, 29.3, 29.2, 29.1, 28.6, 25.8.

## Supporting Information

The authors have cited additional references within the Supporting Information.

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ADMET polymerisation experiments was efficiently carried out on a novel family of different length  $\alpha,\omega$ -diene furanic monomers. 1st Generation Grubbs catalyst emerged as the best polymerisation promoter leading to high molecular-weight polyesters that exhibited exceptional thermal resistance. Preliminary trials were also conducted on ADMET polymerisation using green solvents as well as on co-polymerisations mixing different amounts of the best performing monomers.

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