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The impact of diethyl furan-2,5-dicarboxylate as aromatic biobased monomer towards lipase-catalyzed synthesis of semi-aromatic copolyesters

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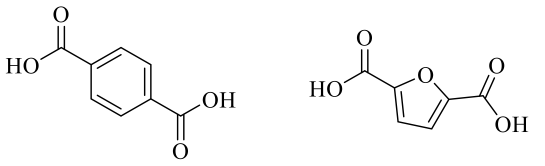
KEYWORDS: Enzymatic polymerization; polycondensation; lipase; furan; aromatic copolyesters; time course profile.

ABSTRACT: Furan-2,5-dicarboxylic acid has been introduced in the last years as a green aromatic monomer towards the design of aromatic (co)polyesters with enhanced properties, i.e. polyethylene furanoate (PEF) that can definitely compete with their petroleum-based counterpart, i.e. polyethylene terephthalate (PET). In an attempt to produce biobased semi-aromatic copolyesters in an efficient eco-friendly approach, we report herein the polycondensation of diethyl furan-2,5-dicarboxylate (DEFDC) with different aliphatic diols and diesters of variable chain-length catalyzed by an immobilized lipase from *Candida antarctica* using a two-step polymerization reaction carried out in diphenyl ether. The influence of diol and diester chain-length, the molar concentration of DEFDC, as well as the effect of enzyme loading were assessed via Nuclear Magnetic Resonance (NMR), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Wide-Angle X-ray Scattering (WAXS). With high quantities of DEFDC, significant differences in terms of $\overline{M}_n$ building-up were noticed. Only longer diols starting from octane-1,8-diol got successfully reacted with up to 90% DEFDC as opposed to only 25% DEFDC with short diols such as butane-1,4-diol. While varying the chain-length of the diester, it was evident that shorter diols such as hexane-1,6-diol have better reactivity towards longer diesters, while dodecane-1,12-diol was reactive towards all tested diesters. The incorporation of long chain fatty dimer diols such as Pripol 2033 led to polyesters with higher $\overline{M}_n$ and was successfully used to overcome the limitations of poor reactivity observed in the case of short diols in the presence of high furan content. DSC results showed a pseudo-eutectic behavior as a function of increasing the mol % of DEFDC, and a change in the crystalline phase confirmed via WAXS analysis. Finally, this work showed the successful enzyme-catalyzed synthesis of several DEFDC biobased semi-aromatic copolyesters with variable interesting properties that can be further optimized for possible applications in food packaging amongst other possibilities.

INTRODUCTION

The increasing environmental concerns of fossil fuel-based materials and their pronounced negative impact on our environment has been shifting the research focus towards a more sustainable synthetic pathway to develop polymers with adequate properties and a low carbon footprint. Such an approach is strongly supported with the increasing research works on the valorization of biomass to produce biobased polymeric materials.[1–5] In this respect, furan-2,5-dicarboxylic acid (FDCA) has been given a lot of attention in recent years as (co)monomers, due to its ease of production from biomass and its aromaticity. FDCA is a biobased monomer synthesized by oxidation of 5-hydroxymethylfurfural, which is by turn the dehydration product of hexoses such as fructose and glucose.[6–8] There are many new research works, implementing FDCA as an alternative (co)monomer to petroleum-based terephthalic acid (TPA) that is vastly used in the synthesis of aromatic polyesters, notably polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). This trend favoring FDCA stems from the structural similarities between both monomers as both are aromatic rings with two oppositely positioned carboxylic groups.[9,10] In addition, FDCA bioproduction route is easily accessible when compared to the challenging and inefficient TPA bioproduction.[11–14] The structures of both TPA and FDCA is given in Scheme 1. When polymerized, aromatic polyesters produced from FDCA instead of TPA show very competitive properties that are in some cases being considered far superior to TPA-based polyesters.[15–19]



Terephthalic acid   Furan-2,5-dicarboxylic acid

Scheme 1. Structures of terephthalic acid (TPA) and furan-2,5-dicarboxylic acid (FDCA).

In general, semi-aromatic polyesters are structurally designed on the basis of both aliphatic as well as aromatic (co)monomeric units. The incorporation of aromatic units into the polymer structure helps increasing the rigidity, hydrophobicity, and thermal properties of the polymeric backbone, whereas the aliphatic units in the form of aliphatic diacids or diols serve enhancing the flexibility of the polymeric structure and lowering its glass transition temperature (T_g).[20,21] Accordingly, the combination of aliphatic and aromatic groups in semi-aromatic polyesters such as PET, and PBT have shown a great enhancement of properties and expanded the scope of their applications, ranging from plastic bottles to synthetic fibers and food packaging.[22,23]

In recent years, many furan-based polyesters and polyamides have been synthesized,[21,24] and many research works focused on comparing them to their TPA-based counterparts.[25–27] For example, *via* a two-step polycondensation process in the presence of Titanium isopropoxide ($Ti(O\text{-}i\text{-}Pr)_4$) as catalyst, Knoop *et al.*[16] synthesized a series of polyethylene (PEF), polypropylene (PPF), and polybutylene (PBF) furanoates of medium molecular weights that are comparable to their TPA analogs, and showing less coloration. Moreover, furan-based polyesters have shown to present enhanced gas barrier properties when compared to their TPA counterparts.[28,29] Regarding their mechanical properties, PEF was found to be similar to PET in terms of its Young's modulus and maximum stress values. In contrast, PEF was shown to be significantly more brittle than PET.[30]

In another interesting study, the PBF ductility was found to significantly increase as a function of the molecular weight, reaching Young's modulus and elongation values comparable to the reported values of commercial PBT when the $\overline{M}_n$ was > 16,000 g.mol^{-1}. In contrast, lower values of Young's modulus and elongation at break were reported when the $\overline{M}_n$ was ~7,000 g.mol^{-1}. This difference was suggested to originate from the insufficient number of entanglements at lower molecular weight values.[17] Although FDCA-based polyesters are showing great promising properties, they are still prone to limitations, especially in regard to their fragility, slow crystallization, and in some cases, poor biodegradability. To address these issues, research have been trying to tune the properties of FDCA-based polymers using an array of different diols and diacids (cyclic, secondary, etc.).[21] For example, the incorporation of cyclic diols such as 1,4-cyclohexanedimethanol along with propane-1,3-diol and FDCA have shown to increase the thermal stability of the polyesters produced.[31] Moreover, the copolymerization of FDCA-based polyesters such as PEF, PPF and PBF with rigid cyclic diols such as 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol resulted in polymers with enhanced tensile strength, yet a lower elongation at break.[32,33]Enzymatic catalysis has been introduced as a greener synthetic approach towards the production of polyesters, owing to its non-toxic nature, high selectivity, and the possibility of processing under mild conditions.[34–36] When compared to current metal catalysts used for polyester synthesis, they are advantageous by avoiding any residual traces of harmful metals after synthesis and by preventing any discoloration and side reactions that can occur with metallic catalysis due to the elevated temperatures required.[37] In addition, the high selectivity of some enzymes can allow performing some reactions in minimal steps by avoiding additional steps like protection/deprotection chemistries that would otherwise require *via* these conventional catalyses.[38,39] Although the literature is rich in examples of enzyme-catalyzed polyesterification to produce aliphatic polyesters, the synthesis of aromatic polyesters remains less studied mainly due to the need to use elevated reaction temperatures when dicarboxylic aromatic (co)monomers are used. Nevertheless, several promising attempts depicted in multiple excellent review articles,[18,19] have been noted to synthesize aromatic and semi-aromatic polyesters *via* enzymatic catalysis, which can be manageable at lower temperatures by substituting diacid monomers with their methyl or ethyl diester analogous. However, such polyesters were ill-defined with their low molecular weights, mainly due to side reactions such as ether formation as well as to the low temperature used, leading to phase separation of the end-product and limited the polymer growth.[40,41] In an attempt to overcome this limitation, Jian *et al.*[34] performed a two-step polycondensation reaction in diphenyl ether, using Novozym 435 (N435) as a catalyst, which is a *Candida antarctica* lipase B (CALB) immobilized on an acrylic resin. The results obtained showed that for the polyesterification reaction between dimethyl furan-2,5-dicarboxylate (DMFDCA) and different aliphatic diols, being hexane-1,6-diol, octane-1,8-diol, and decane-1,10-diol at a temperature of 140 °C, the polyesters obtained possessed a high $\overline{M}_n$ of 41,100, 41,000, and 51,600 g.mol^{-1}, respectively. However, the high temperature used significantly impacted the activity of the recycled enzyme. Those values exceeded the values obtained at 80 °C by more than 10-folds. As enzymatic catalysis proved to be better suitable for oligomer production, several attempts to synthesize furan-based oligomers *via* enzymatic catalysis were approached in recent years, where different aromatic and semi-aromatic oligomers were produced.[42,43] Other attempts to synthesize semi-aromatic diesters via enzymatic catalysis were reported by Pellis *et al*.[44] Aliphatic diols varying in chain-length between C_4-C_8 were reacted with several aromatic monomers such as diethyl furan-2,5-dicarboxylate, diethyl terephthalate, diethyl isophthalate, in addition to different isomers of pyridine dicarboxylic acid. The results showed that the reaction between 2,4-diethyl pyridine dicarboxylate and octane-1,8-diol in diphenyl ether led to the highest molecular weight ($\overline{M}_n$ = 14,300 g.mol^{-1}). In another research work, Pellis *et al.*[45] conducted the enzyme catalyzed synthesis of furan and pyridine diol-based polyesters such as 2,5-bis(hydroxymethyl)furan (2,5-BHMF), 3,4-bis(hydroxymethyl)furan (3,4-BHMF) and 2,6-bis(hydroxymethyl)pyridine using diphenyl ether as solvent. *Via* a two-step polycondensation reaction maintained for 96 h at 85 °C, and apart from 3,4-BHMF polymers that gave low yields and M_n, all reactions tested with varying chain-length aliphatic diesters were successful with yields >65% and M_n reaching 5,000 g.mol^{-1}.

Although semi-aromatic polyesters such as PET and PBT or their furan counterparts possess good physical properties, they are however resistant to biodegradation.[46,47] To tackle this, semi-aromatic terpolyesters such as polybutylene adipate terephthalate (PBAT) were developed, consisting of aromatic and aliphatic units, showing adequate mechanical properties while being biodegradable at the same time.[48] In fact, the biodegradation of such copolyesters was due to the presence of aliphatic repeating units such as butylene adipate (BA) in PBAT, which were more susceptible to hydrolysis and microorganism attacks than the semi-aromatic butylene terephthalate (BT).[48,49] In a study conducted by Herrera *et al.*[50] PBAT with an adipate/terephthalate ratio of 60/40 was found to degrade at a faster rate than PBAT with a higher terephthalate content (40/60). Such findings could allow for an adequate control over the properties and degradation time of semi-aromatic copolyesters such as PBAT simply by tuning the adipate/terephthalate ratio. With the biodegradability advantage of such copolyesters, in addition to the advantages of furan based polyesters, research have been focusing in recent years on developing furan based copolyesters such as polybutylene adipate furanoate (PBAF) aiming to produce biobased polymers which are also biodegradable and possess adequate properties allowing them to compete with TPA based polymers.[51–56]

Although enzymatically catalyzed synthesis of furan-based polyesters such as PBF, among other types were recently reported in the literature,[24,34,41] the enzymatic synthesis of furan-based terpolyesters, on the other hand, was less studied. Morales-Huerta *et al.*[57] synthesized poly(butylene furan-2,5-dicarboxylate-*co*-succinate) *via* the ring-opening polymerization of cyclic butylene furan-2,5-dicarboxylate and butylene succinate oligomers yielding copolyesters with a $\overline{M}_n$ ranging between 16,000 and 31,000 g.mol^{-1} where Novozym 435 was loaded at 40% w/w relative to the totality of the concentration of the monomers. On the other hand, the enzymatic polycondensation approach towards semi-aromatic copolyesters was reported by Maniar *et al.*[58] by reacting DMFDCA, 2,5-bis(hydroxymethyl)furan (BHMF), along with aliphatic linear diols and diacid ethyl esters. The highest $\overline{M}_n$ determined for precipitated polymers was achieved when using 1,8-ocatanediol reaching 16,000 g.mol^{-1} after 72 h under vacuum and a temperature varied between 80 and 95 °C.

Previously, we have introduced a statistical approach that allowed us to predict the $\overline{M}_n$ of poly(hexylene adipate) simply by tuning the values of certain parameters such as vacuum, enzyme loading and temperature.[59] In our current work, and based on the promising properties of furan-based terpolyesters, such as their excellent mechanical properties and biodegradability we investigate herein the enzyme-catalyzed synthesis of furan-based semi-aromatic terpolyesters by reacting diethyl furan-2,5-dicarboxylate (DEFDC), with variable aliphatic linear dicarboxylic esters, and primary diols. A special emphasis was made on the influence of furan loading, and the chain-length of diols and diesters, and how such factors can influence the reactivity, molecular weight, and thermal properties of the end-product. In addition, amorphous fatty dimer diol such as Pripol 2033 was tested for its influence on improving the reactivity in the system where enzymatic catalysis was limited, and its effect on the thermal behavior of such polymers. Such polymers can be used for applications in food packaging.

Materials and Methods

Materials Hexane-1,6-diol (97%), diethyl adipate (99%), sebacic acid (99%) and diphenyl ether (99%) were purchased from Sigma-Aldrich. Butane-1,4-diol (99%), octane-1,8-diol (98%), dodecane-1,12-diol (98%) were purchased from Acros Organics. Decane-1,10-diol (97%) and diethyl oxalate were purchased from Alfa Aesar. Furan-2,5-dicarboxylic acid (99.7%) was purchased from Satachem co. Pripol 2033 fatty dimer diol ((9*Z*,12*Z*)-18-[(6*Z*,9*Z*)-18-hydroxyoctadeca-6,9-dienoxy]octadeca-9,12-dien-1-ol) (≥96.5) was kindly provided by Croda Chemicals. Analytical grade methanol, absolute ethanol, and chloroform (99%) were purchased from VWR. All the reagents and solvents were used as received. Novozym 435 (N435), a *Candida antarctica* lipase B (CALB) immobilized on an acrylic resin was kindly provided by Novozymes. Chloroform D ($CDCl_3$) (99.8%) and deuterated dimethyl sulfoxide DMSO-d_6 were purchased from Euriso-Top.

Synthesis of diethyl furan-2,5-dicarboxylate (DEFDC) In general, 5 g of furan-2,5-dicarboxylic acid (FDCA) were added to 60 ml of absolute ethanol and 2 ml of sulfuric acid and refluxed overnight under continuous stirring at 100 °C. The mixture was allowed to cool followed by evaporation to remove the excess amount of ethanol. The solution was added dropwise into distilled water under continuous stirring, resulting in FDCA precipitation. The product was washed multiple times with distilled water before suspending in 100 ml H_2O solution and neutralizing by adding 5% $NaCO_3$ and finally filtering using a Buchner funnel under vacuum application. The white crystalline powder obtained was dried overnight under high vacuum and the yield by weight achieved was >75% w/w. ^1H NMR analysis confirmed the structure of diethyl furan-2,5-dicarboxylate (DEFDC) with no detectable impurities ^1H NMR ($CDCl_3$, 300 MHz): δ 7.20 (s, 2H), 4.40 (q, J = 7.1 Hz, 4H), 1.39 (t, J = 7.1 Hz, 6H) ppm (see Figure S1).

General procedure for the enzymatic synthesis of poly(alkylene alkanoate-*co*-alkylene furan-2,5-dicarboxylate)

The effect of diol length (C_4 to C_{12}) and DEFDC molar ratio Furan-based semi-aromatic copolyesters were prepared by reacting DEFDC and diethyl adipate with diols of different chain-lengths varying from C_4 to C_{12}. As an example, the synthesis of poly(hexyleneadipate-*co*-hexylene-2,5-furandicarboxylate) containing 50 mol% furan relative to the total diesters was prepared as following: hexane-1,6-diol (4 mmol), diethyl adipate (2 mmol), and DEFDC (2 mmol) were weighed and added into a schlenk tube. A predetermined amount (20% w/w) of N435 relative to the total weight of hexane-1,6-diol (4 mmol) and diethyl adipate (4 mmol) was weighed and added to the mixture. Precisely, 1 ml of diphenyl ether (6.3 mmol) was added as a solvent of choice. The reaction proceeded under atmospheric pressure for 2 h at 100 °C (using an oil bath with continuous stirring kept constant at 350 rpm). Afterwards, the schlenk tube was attached to a vacuum line, and the pressure was decreased gradually within 1 h to reach a predetermined value of 10 mbar to remove the byproduct (ethanol). The reaction was left to proceed for 24 h, then was stopped by adding an excess amount of chloroform under atmospheric pressure after a cooling step, followed by direct filtration to remove the N435 beads. The filtrate was then partially evaporated, and then added dropwise to excess amount of cold methanol under stirring to precipitate the obtained polymer. The mixture was then filtered, and the product obtained was left to dry at room temperature for 24 h before collecting and weighing. The percentage yield was calculated by dividing the actual yield (816 mg) by the theoretical yield (932 mg).

The effect of diester length (C_2-C_6-C_{10}) and DEFDC molar ratio Following the same procedure as before, the influence of diester length was examined by performing the copolymerization reaction between hexane-1,6-diol and different chain-length diesters being diethyl oxalate (C_2), diethyl adipate (C_6), and diethyl sebacate (C_{10}), at variable DEFDC molar feed percent (0-90%). The same approach was used starting from dodecane-1,12-diol.

Effect of diol length on DEFDC conversion during oligomerization: "A comparison between hexane-1,6-diol and dodecane-1,12-diol based copolyesters" In the first part of this study and following the same procedure as before, different samples containing either hexane-1,6-diol or dodecane-1,12-diol, in addition to diethyl adipate and DEFDC were prepared keeping an equimolar ratio between the diol and diesters, while varying the DEFDC content from 10 to 75 %. The conversion of DEFDC into alkylene furanoate was monitored by withdrawing samples at different time intervals and exploiting the ^{1}H NMR signals at δ= (4.32-4.34) of the methylene ($-O-\underline{CH_2}-C_nH_{2n}-\underline{CH_2}-O-$) of the alkylene furanoate, δ= (4.06-4.07) of the methylene ($-O-\underline{CH_2}-C_nH_{2n}-\underline{CH_2}-O-$) of the alkylene adipate, and δ= 3.65 of the methylene ($HO-\underline{CH_2}-C_nH_{2n}-\underline{CH_2}-OH$) of the residual diol represented in equation S3. The X-furan (%) representing the evolution of furan content in oligomers produced is given *via* equation S1

In the second part of this study, hexane-1,6-diol and dodecane-1,12-diol were added into the same reaction in equimolar amounts and reacted against 75 % DEFDC and 25 % of diethyl adipate while maintaining an equimolar ratio between the diols and diesters. The conversion of DEFDC into either hexylene furanoate or dodecylene furanoate was monitored via ^{1}H NMR in the same fashion as previously mentioned and by taking advantage of the Global spectral deconvolution technique to distinguish between overlapping signals of hexylene furanoate and dodecylene furanoate. The aim was to monitor how two different chain-length diols could compete in the same reaction media.

Effect of N435 % loading Hexane-1,6-diol was chosen as a model monomer to see the effect of enzyme loading on the polymerization reaction. Similar to the general procedure mentioned above, hexane-1,6-diol was reacted with diethyl adipate and DEFDC at different molar percentages (10, 25, 50, and 75%), the N435 % loading was varied between 10 and 20%, while maintaining similar reaction conditions.

Effect of fatty dimer diol (Pripol 2033) The effect of Pripol 2033 was tested in two experimental parts. In the first experimental approach, octane-1,8-diol and Pripol 2033 were reacted with DEFDC in equimolar (diol-diester) ratios (4 mmol). Pripol 2033 was added at 10 and 20 mol% relative to the total diols in the reaction (or 13.7 and 25 wt.% relative to the total monomers), the reactions proceeded for 2 h at 100 °C in 1 ml diphenyl ether and 20% w/w N435 loading, followed by 24 h under vacuum (10 mbar). The polyesters synthesized were compared in terms of conversion, X-furan, $\overline{M}_n$ and their thermal properties.

In the second experimental procedure, butane-1,4-diol and Pripol 2033 were reacted against diethyl adipate (25 mol%) and DEFDC (75 mol%). Pripol 2033 was added at 10, 25, and 50 mol% relative to the diesters while maintaining an equimolar (diol-diester) ratio (4 mmol). The reactions proceeded for 2 h at 100 °C in 3 ml diphenyl ether and 20% w/w N435 loading, followed by 72 h under vacuum (10 mbar). The polyesters synthesized were compared in terms of conversion, X-furan, $\overline{M}_n$ and their thermal properties.

Analytical methods

Nuclear Magnetic Resonance (NMR) analysis

The ^{1}H NMR spectra of the monomers, and the recovered polymer were recorded at room temperature on a Bruker Avance 300 instrument (delay time = 3 s, number of scans = 32) at 300.13 MHz using either $CDCl_3$ or DMSO-d_6 as solvents. Chemical shifts (ppm) are given in δ-units and were calibrated using the residual signal of $CDCl_3$ and DMSO-d_6 at 7.26 ppm and 2.5 ppm, respectively. Additionally, ^{1}H NMR was used to determine the furan content in the microstructure of the polymer, confirm conversion and to determine its rate ((equations S1, S2 and S3). DOSY spectra were recorded on Avance II 400 Bruker spectrometer (9.4 T) regulated at 298 K respectively in $CDCl_3$ and toluene d8. Data acquisition and analysis were performed using the Bruker TopSpin 3.2 and MestReLab 6.0.

Gel Permeation Chromatography (GPC) analysis

Gel permeation chromatography (GPC) analysis was performed in chloroform as eluent (flow rate of 1 ml/min) at 23 °C using Alliance e2695 (Waters) apparatus and with a sample concentration around 10-15 mg/ml. A refractive index detector Optilab T-rEX (Wyatt Technology) was used as a detector, and a set of columns: HR1, HR2 and HR4 (Water Styragel) were utilized. The molecular weight calibration curve was obtained using monodisperse polystyrene standards.

Differential scanning calorimetry (DSC)

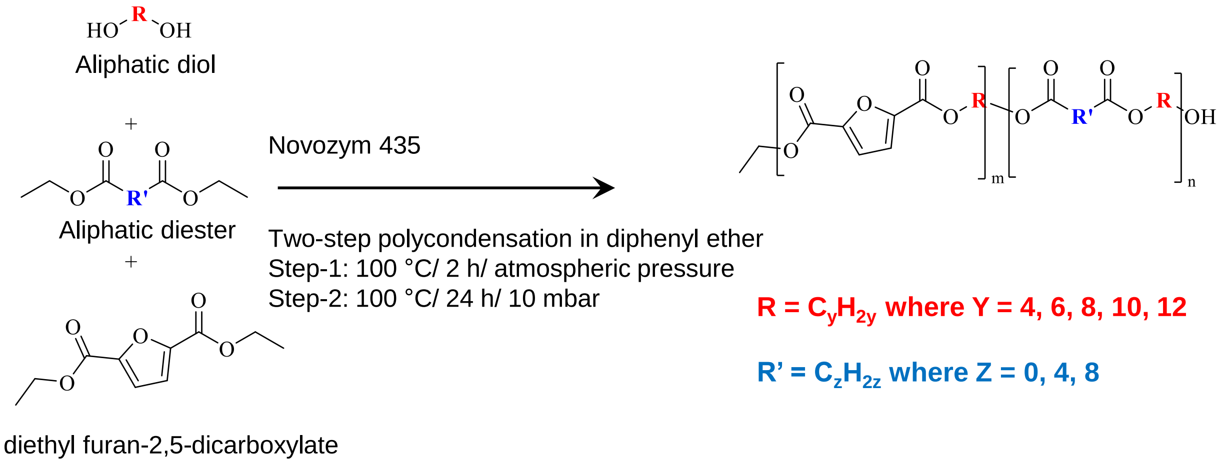
The thermal transition was recorded with a Differential Scanning Calorimetry (DSC) on a TA Discovery DSC 25 using a cooling-heating-cooling-heating method. First, samples of ~10 mg were sealed in aluminum pans, the temperature was equilibrated at - 90 °C, followed by a heating ramp of 10 °C/min to 200 °C, then a cooling ramp of 10 °C/min to - 90 °C, and a second heating ramp of 10 °C/min to 200 °C. The thermograms were analyzed using TA instruments TRIOS software.

Wide-angle X-ray scattering (WAXS)

Wide-angle X-ray scattering (WAXS) analysis were performed on a Xeuss 2.0 apparatus (Xenocs) equipped with a micro source using a Cu Kα radiation (λ= 1.54 Å) and point collimation (beam size: 500×500µm²). The sample to detector distance, around 15 cm, was calibrated using silver behenate as standard. Through view 2D diffraction patterns are recorded on a Pilatus 200k detector (Dectris). Integrated intensity profiles were computed from the 2D patterns using the Foxtrot® software. Exposure time: 15 min.

Results and discussion

Following the general procedure above, the polycondensation of different diols, with diethyl adipate and DEFDC in the presence of N435 (see Scheme 2) was conducted in diphenyl ether, as it was previously reported to be the more suitable solvent to achieve high conversion and molecular weights.[60–62] While maintaining the equimolarity between the diols and the diesters, the molar percent of DEFDC relative to the aliphatic diester was varied between 0 and 90 %. Different aliphatic diols tested as (co)monomers were butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol.



Scheme 2. Polycondensation reaction of variable diols, diethyl adipate, and DEFDC in the presence of N435 as catalyst, where n varied between 4 and 12 depending on the diol used.

The impact of the diol length and furan content on the final copolymer properties were both assessed in terms of copolymer composition (X-furan), total conversion (%), yield by weight (%), $\overline{M}_n$, dispersity (Đ$_{\mathrm{M}}$) and degree of polymerization (DP) (

Table **1**).Peak assignments and the respective calculations are given in Figure S2, and equations S1 and S2 .

Table 1. Molecular structure analysis (X-furan), % conversion, % yield, $\overline{M}_n$, Đ$_{\mathrm{M}}$ and DP of furan-based copolyesters with variable furan content and aliphatic diols.

Entry	Diol[a]	DEFDC feed (%)[b]	X-furan (%)[c]	Conversion (%)[d]	Yield by weight (%)	$\overline{M}_n$ (g.mol^{-1})[e]	Đ$_M$[f]	DP[g]
1	**C_4**	**0**	0	98	85	16,000	1.80	80
2	**C_4**	10	12	86	68	4,900	1.93	24
3	**C_4**	25	27	95	62	1,300	6.9	6
4	**C_4**	50	-	-	-	-	-	-
5	**C_6**	0	0	97	91	9,200	1.80	40
6	**C_6**	10	12	95	77	9,400	1.61	41
7	**C_6**	25	27	98	82	11,100	2.13	48
8	**C_6**	50	51	98	87	9,600	2.09	41
9	**C_6**	75	75	96	90	3,800	1.91	16
10	**C_6**	90	78	48	0	-	-	-
11	**C_8**	0	0	94	88	9,000	1.94	35
12	**C_8**	10	12	95	87	10,900	1.82	42
13	**C_8**	25	27	95	86	8,900	1.75	34
14	**C_8**	50	49	91	74	9,900	1.91	38
15	**C_8**	75	75	96	84	7,500	2.14	28

16	**C_8**	90	87	96	87	4,700	1.85	18
17	**C_{10}**	0	0	95	98	9,100	2.05	32
18	**C_{10}**	10	12	95	93	8,300	1.91	29
19	**C_{10}**	25	27	95	92	8,600	1.78	30
20	**C_{10}**	50	50	94	83	10,300	1.84	35
21	**C_{10}**	75	74	95	92	7,300	2.04	35
22	**C_{10}**	90	89	97	99	8,500	2.27	29
23	**C_{12}**	0	0	95	98	7,700	2.07	25
24	**C_{12}**	10	11	95	97	9,900	2.01	31
25	**C_{12}**	25	26	96	93	9,700	2.21	31
26	**C_{12}**	50	50	95	95	8,700	1.97	27
27	**C_{12}**	75	74	95	89	6,300	1.98	20
28	**C_{12}**	90	88	97	100	7,300	2.19	23

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a C_4 = butane-1,4-diol, C_6 = hexane-1,6-diol, C_8 = octane-1,8-diol, C_{10} = decane-1,10-diol, C_{12} = dodecane-1,12-diol.

b DEFDC feed (%) = represents the molar percentage of diethyl 2,5-furandicarboxylate added, relative to the total diester amount.

c X-furan (%) = defined as the molar fraction of alkylene furan-2,5-dicarboxylate repeating unit in the copolymer and determined *via* ^{1}H NMR as per equation S1.

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d Conversion (expressed in %) =represents the total amount of reacted diols in relative to the overall diols in the system and was calculated by ^{1}H NMR *via* equation S2.

e The number average molecular weight ($\overline{M}_n$) was obtained from GPC analyses ($CHCl_3$, 23 °C, polystyrene standards). $\overline{M}_n$values might be skewed to higher values for longer chain comonomers.

f Molar mass dispersity $Đ_M$ = $\overline{M}_W$ /$\overline{M}_n$ was obtained from GPC analyses ($CHCl_3$, 23 °C, polystyrene standards). $Đ_M$ might be skewed to lower values due to fractionation (precipitation).

g D.P. = degree of polymerization = $\overline{M}_n$ /M_0 where M_0 is the molecular weight of the repeating unit.

From

Table **1**, it was observed that the increase in DEFDC content had a negative impact on X-furan, conversion, yield, $\overline{M}_n$, and DP of copolymers synthesized from shorter diols. The maximum quantities of furan successfully incorporated into copolymers based on butane-1,4-diol and hexane-1,6-diol were 27 and 75 mol%, achieving yields of 62 and 90% (as observed in entries 3 and 9), respectively. Increasing the feed molar percentage of DEFDC with these short diols limited the copolymer growth and led to a failure in precipitation, which was assumed to result from the low reactivity and the formation of short oligoesters that did not precipitate in methanol. No detectable conversion or yield were observed (see entry 4), when the DEFDC feed was increased to 50%, while only 48% conversion was calculated when the DEFDC feed was increased to 90% (as observed in entry 10); without any detectable yield. Similarly, the DP of the copolymers prepared with butane-1,4-diol was highly influenced by DEFDC feed, where increasing the DEFDC feed by only 10% led to a drop in DP from 80 (entry 1) to 24 (entry 2), and further decreased to 6 (entry 3) with 25% DEFDC. On the other hand, copolymers based on octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol showed a stable conversion (>90%) and high yields without any noticeable variations as a function of DEFDC feed increase. The DP of copolymers based on octane-1,8-diol was partially affected at high DEFDC content, decreasing from 38 to 28 to 18 with the increase in DEFDC feed from 50 to 75 to 90%. Longer diols were not significantly affected by the increase in DEFDC feed %, where copolymers based on decane-1,10-diol and dodecane-1,12-diol maintained a relatively stable D.P. at high DEFDC feed. The formation of poly(alkylene alkanoate-*co*-alkylene furan-2,5-dicarboxylate) rather than poly(alkylene alkanoate) and poly(alkylene furan-2,5-dicarboxylate) homopolymers was confirmed by performing DOSY NMR scans. The spectrum provided in Figure S3 shows a single diffusion coefficient for the produced poly(dodecylene adipate-*co*-dodecylene furan-2,5-dicarboxylate) representing entry 26.

What was generally noticed from these results is that the limitation imposed by the increase in DEFDC feed became less significant as a function of increasing the diol length, where up to 90% DEFDC were successfully incorporated into the copolyesters based on octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol. The superior catalytic efficiency of N435 or CALB catalysts towards longer diols in the presence of high furan content agreed well with the previously documented results by Jiang *et al.*[34] They suggested that besides the better selectivity of CALB towards longer diols, furan-based polyesters based on longer diols showed higher solubility in the reaction media (diphenyl ether), and lower melting points compared to those produced from shorter diols which precipitated rapidly due to the reasons mentioned above and prevented polymer growth. In another study, Bazin *et al.*[63]assumed that the limited polymer growth detected in terpolymers synthesized in diphenyl ether based on hexane-1,6-diol, diethyl adipate and dimethyl furan-2,5-dicarboxylate was mainly a solubility limitation, rather than a catalytic one, where high furan content (90%) leads to early precipitation and limited polymer growth. Surprisingly though, in our work, and contrary to previous results in the literature (performed under similar conditions in diphenyl ether or bulk),[61] increasing the diol length in the absence of DEFDC, did not seem to cause any increase in the DP of the corresponding aliphatic polyesters. On the contrary, the polymer based on butane-1,4-diol and diethyl adipate (entry 1) was found to possess the highest DP (80) amongst the aliphatic polyesters, while the DP was maintained within a range of (25-40) for polymers based on hexane-1,6-diol (entry 5), octane-1,8-diol (entry 11), decane-1,10-diol (entry 17) and dodecane-1,12-diol (entry 23). However, it should be noted that the limitations in polymer growth could have stemmed from the diminishing in the mixing speed due to the increase in the viscosity of the samples, which might have posed a negative effect on the heat and mass transfer. In fact, it was observed that the mixing efficiency decreased rapidly in the reactions containing long diols, while it took more time to notice the same decrease when shorter diols were used. This observation could further justify the limited DP values with long diols.

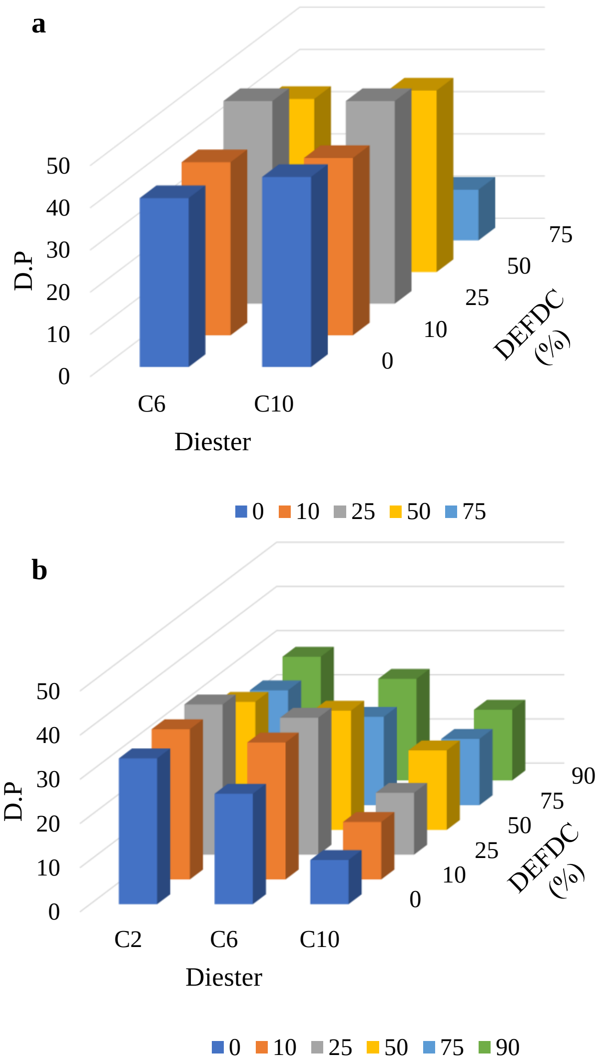


Figure 1. (a) the variation in DP of furan-based copolyesters with variable furan content based on hexane-1,6-diol and different aliphatic diesters. (b) the variation in DP of furan-based copolyesters with variable furan content based on dodecane-1,12-diol and different aliphatic diesters, where (C_2=1,2-diethyl oxalate), (C_6=1,6-diethyl adipate), and (C_{10}=1,10-diethyl sebacate).

The influence of the diester length was examined by comparing 1,2-diethyl oxalate (C_2), 1,6-diethyl adipate (C_6), and 1,10-diethyl sebacate (C_{10}). The results showing the evolution of DP as a function of diester length is given in Figure 1, and further results concerning the X-furan, conversion (%), yield (%), $\overline{M}_n$ (g.mol^{-1}), Đ$_M$, and DP are stated in Table S1.

With the exception of 1,2-diethyl oxalate that did not yield any polymers when reacted against hexane-1,6-diol, the increase in the diester length from C_6 to C_{10} did not have a significant impact on the molecular weight of the copolymers produced as observed in Figure 1 (a). On the other hand, in Figure 1 (b), reacting dodecane-1,12-diol with diethyl oxalate (C_2) in the presence or absence of DEFDC led to copolymers with a DP ranging between 26 and 34. The DP decreased on average with increasing the diester length down to a DP (20-31) with diethyl adipate (C_6) and a further decrease in DP down to (10-18) with diethyl sebacate (C_{10}). However, as mentioned before, the decrease in DP with longer diesters could have resulted from the high viscosity built up in the system that could have limited polymer growth. Moreover, unlike copolyesters based on hexane-1,6-diol, copolyesters based on dodecane-1,12-diol and regardless of the aliphatic diester used, did not show significant variations in term of conversion, yield, and DP as a function of increasing the DEFDC feed.

Taking advantage of the difference in reactivity between different chain-length diols, a time course study was performed comparing hexane-1,6-diol and dodecane-1,12-diol in terms of conversion during the oligomerization step as a function of DEFDC content in the feed. The results showing the evolution of conversion in addition to X-furan representing the furan content (%) in the oligomers produced is given in Figure 2.

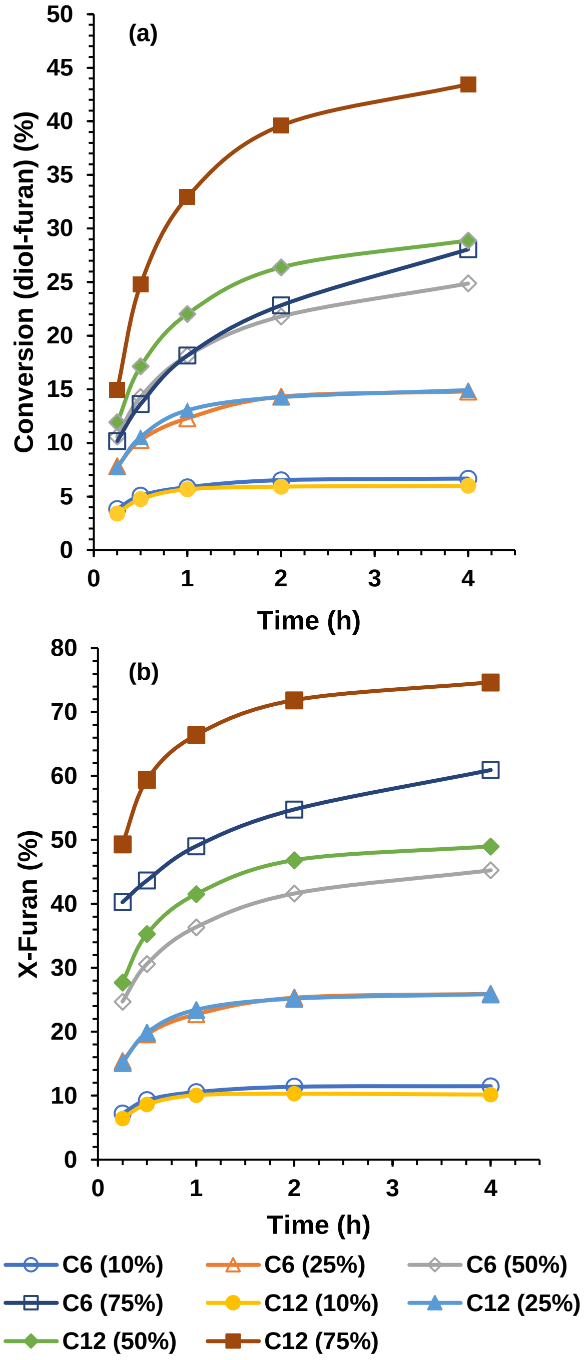


Figure 2. (a) Conversion of diols to furan-esters (expressed in mol %) during oligomerization, determined *via* ^{1}H NMR. Medium: diphenyl ether, N435: 20% w/w, temperature: 100 °C. (b) Composition of copolyesters during oligomerization showing the evolution of furan content in

oligomers produced, determined *via* ^{1}H NMR. Medium: diphenyl ether, N435: 20% w/w, temperature: 100 °C.

From Figure 2, the reactions of two diols showed similar time course profiles at 10 and 25% DEFDC in the feed, where in both cases, the conversion representing the total amount of diols that reacted with DEFDC reached within a 2 h interval a constant value of 6% for C_6 (10%) and C_{12} (10%), and 14% with C_6 (25%) and C_{12} (25%). Similarly, the amount of furan (X-furan) in the copolymer structure was similar with both diols reaching 10% with C_6 (10%) and C_{12} (10%), and 25% with C_6 (25%) and C_{12} (25%), respectively. Such values represented accurately the DEFDC in the feed. However, as the DEFDC feed content increased to 50% and 75%, variations in terms of conversion and X-furan were observed when comparing hexane-1,6-diol to dodecane-1,12-diol-based oligoesters, where at 50% DEFDC feed content, the conversion calculated for C_6 (50%) and C_{12} (50%) reached values of 25 and 29%, and the X-furan values were 45 and 49%, respectively. The superior reactivity of dodecane-1,12-diol with DEFDC was further confirmed at higher DEFDC content (75%), where for C_6 (75%), conversion did not increase beyond 29% after 4 h oligomerization time, compared to 43% with C_{12} (75%) within the same time limit. Similarly, the X-furan was limited to 61% with C_6 (75%) but was equivalent to the DEFDC feed percentage with C_{12} (75%) with a X-furan value of 75%. These results further confirmed the results obtained in

Table **1**, suggesting that in the presence of N435 as a catalyst, longer diols were more reactive towards DEFDC than their shorter counterparts. However, at low DEFDC content (<25%), and in the presence of diethyl adipate, the conversion of both seemed to proceed at a very similar rate regardless of the diol length.

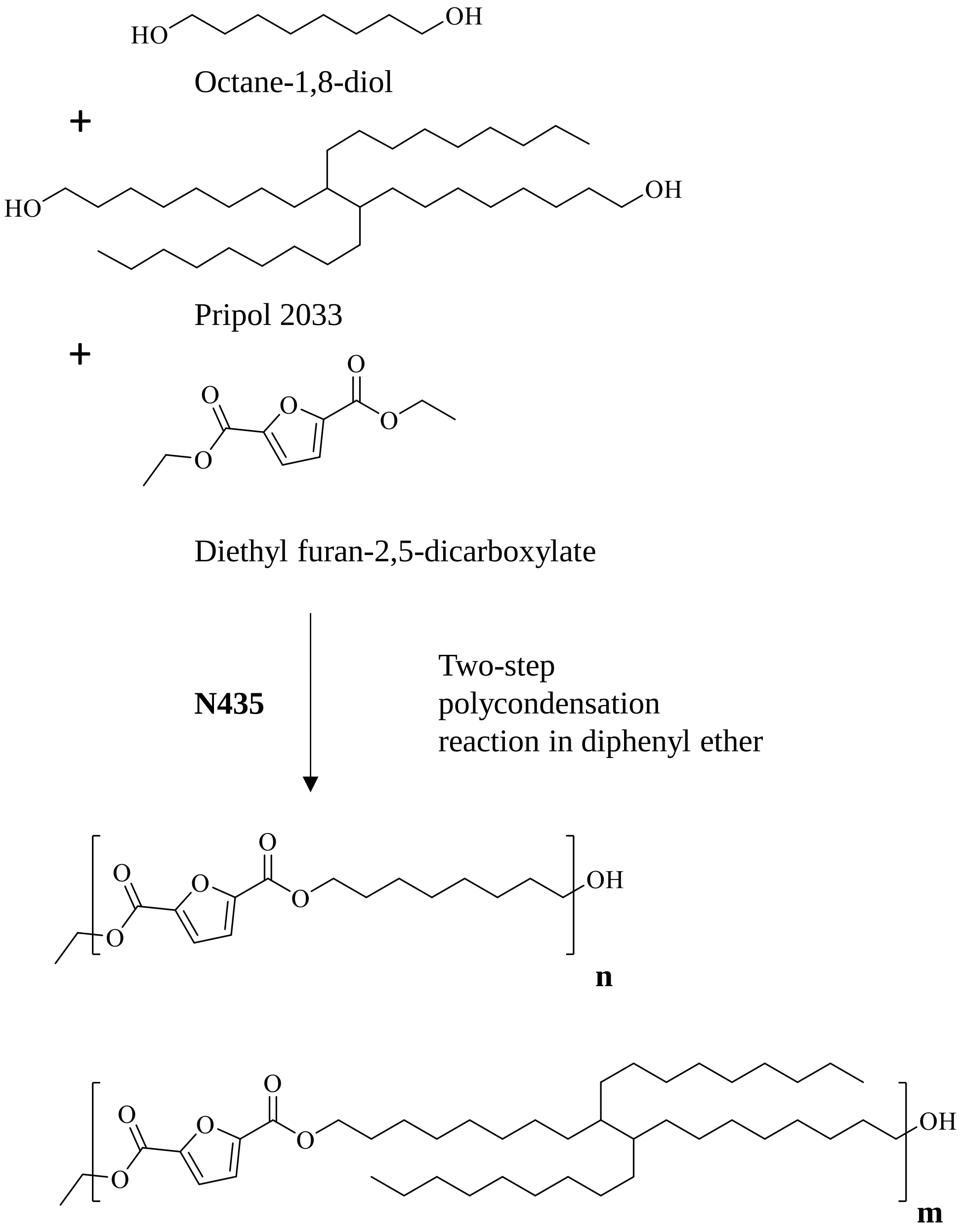
As the reactivity differences between hexane-1,6-diol and dodecane-1,12-diol appeared to be more significant in the presence of high amounts of DEFDC, another time course study was performed comparing hexane-1,6-diol and dodecane-1,12-diol reactivity using the same system as detailed under the experimental section. The evolution of X-furan and X-adipate for both hexane-1,6-diol and dodecane-1,12-diol are given in Figure S4.

It was evident from Figure S4 that after only 15 mins from the start of the reaction, the oligoester structures were dominated by hexanediol-adipate and dodecanediol-adipate ester units recording 32 and 36% respectively, relative to the total esters formed in the system, while hexanediol-furan and dodecanediol-furan esters were limited to 13 and 19 %, respectively. The domination of diol-adipate esters during the first minutes of the reaction resulted from the higher reactivity of diols towards aliphatic diesters under N435 mediated catalysis. As the reaction proceeds, the X-adipate for both diols started to decrease gradually while the X-furan increased simultaneously, where after 4 h, the X-adipate(hexane-1,6-diol) and X-adipate(dodecane-1,12-diol) decreased to reach values of 13 and 18 %, whereas the X-furan(hexane-1,6-diol) and X-furan (dodecane-1,12-diol) increased to reach 33 and 37 %, respectively. Unlike what was observed in Figure 2 in the case of hexane-1,6-diol; where the X-furan was limited to 61 % after 4 h, the presence of the two diols in the same system allowed the oligoesters' composition to rearrange as the reaction proceeds to reach after 4 to 6 h a composition that accurately represent the feed ratio of diols and esters based on the summation of X-furan of both hexane-1,6-diol and dodecane-1,12-diol.

These two time course studies showed how N435 showed minimal catalytic differences between hexane-1,6-diol and dodecane-1,12-diol at low DEFDC content, which is evident from the conversion profiles presented in Figure 2. On the other hand, it was also clear how in the presence of an aromatic group such as DEFDC, N435 tended to catalyze the transesterification reaction between dodecane-1,12-diol and DEFDC at a faster rate compared to similar reactions with hexane-1,6-diol. These observations suggest that in enzymatic catalysis based on N435, longer diols are better suitable to react against high furan content.

The impact of % N435 w/w loading was tested by comparing the polycondensation reaction of hexane-1,6-diol with diethyl adipate and DEFDC at 10 and 20% w/w N435 enzyme loading. The results in Table S2**Erreur ! Source du renvoi introuvable.** showed modest variations in results at low DEFDC % (entries 22' and 26'). However, as the DEFDC feed content increased, it became evident that a higher enzyme loading was necessary for conducting the reaction, where copolymers based on 10% N435 (see entries 24' and 25' in table S2) had a minute amount of furan in their structures (3-4%), and a low conversion of 24 and 17%, respectively. While elevated conversions and yields were persistent in copolymers based on 20% N435 loading.

As the reactivity of diols and the M_n of the copolyesters tend to decrease with high amounts of DEFDC, especially with shorter diols, small amounts of Pripol 2033 were incorporated in the reaction media as mentioned in the experimental section and observed in Scheme 3 in an attempt to overcome the limitations of producing copolyesters with high aromatic content *via* enzymatic catalysis.



Scheme 3. Enzyme-catalyzed polycondensation reaction of octane-1,8-diol, Pripol 2033 and DEFDC.

As observed in Table S3, the yield by weight and M_n increased significantly with the addition of Pripol 2033 from 68 % and 2,700 g.mol^{-1} up to 90 % and 5,300 g.mol^{-1} upon the addition of 10 and 20 % of Pripol 2033 relative to DEFDC. The formation of a single copolyester rather than two homopolymers was confirmed by performing a DOSY NMR analysis for entry 32', the spectrum showing a single diffusion coefficient for the concerned peaks is provided in Figure S5.

As semi-aromatic copolyesters based on small diols such as butane-1,4-diol were limited to small amounts of DEFDC (~25 %) and to small molecular weights and yields, Pripol 2033 was used in a similar approach as before to enhance the polycondensation reaction in the presence of butane-1,4-diol. The reactions proceeded as observed in Scheme S1 in equimolar ratios between the diols and the diesters, where Pripol 2033 was added at 10, 25, and 50 % relative to the diesters. Similar to what was observed before in the case of butane-1,4-diol at high DEFDC loading, and even after extending the reaction time for 72 h and increasing the volume of diphenyl ether up to 3 ml to avoid mixing issues, butane-1,4-diol did not react with DEFDC when the latter was added at 75 % relative to the total diesters in the reaction, and no copolyesters were collected (entry 40, Table 2). In fact, the ^{1}H-NMR of the sample collected from the reaction media after 72 h did not show any peaks representing the formation of an ester bond between butane-1,4-diol and DEFDC. The same observation continued upon the addition of 10 % Pripol 2033 (entry 41, Table 2), with no detected changes in the reactivity towards DEFDC whether for butane-1,4-diol or for Pripol 2033. However, upon further increase in Pripol 2033 molar loading up to 25 %, the X-furan detected in the ^{1}H NMR sample was equivalent to the DEFDC molar feed percent (75 %), with 56 % resulting from the esterification of butane-1,4-diol and DEFDC and 19 % of Pripol 2033 and DEFDC, and a high conversion ~99 % (entry 42, Table 2). Likewise, when butane-1,4-diol and Pripol 2033 were in equimolar amounts, the reaction proceeded to reach a high conversion, and the X-furan reached 75 % divided equally between butane-1,4-diol and Pripol 2033(entry 43, Table

2). The increase in Pripol 2033 feed ratio had a positive impact on reactivity and as a result, a higher $\overline{M}_n$ was achieved, reaching 7,700 and 12,000 g.mol^{-1} with 25 and 50 % Pripol 2033.

Table 2. X-furan, % conversion, % yield and $\overline{M}_n$, of copolyesters based on butane-1,4-diol and DEFDC with or without Pripol 2033.

Entry	**Pripol 2033 (%)**[a]	**X-furan (1,4-BD) (%)**[b]	**X-furan (Pripol) (%)**[c]	**X-furan (total) (%)**[d]	**Conversion (%)**[e]	**Yield by weight (%)**	$\overline{M}_n$ **(g.mol^{-1})**[f]
29	0	0	0	0	-	-	-
30	10	0	0	0	-	-	-
31	25	56	19	75	99	88	7,700
32	50	37	38	75	99	91	12,000

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[a] Pripol 2033 (%) = represents the molar percentage of Pripol 2033 added, relative to the total diester amount.

[b] X-furan (1,4-BD) (%) = Molar percent of butylene furandicarboxylate unit in the copolymer, calculated *via* equation S1.

[c] X-furan (Pripol) (%) = Molar percent of pripol-furandicarboxylate unit in the copolymer, calculated *via* equation S1.

[d] X-furan total (%) = Molar percent of alkylene furandicarboxylate unit in the copolymer, equal to the summation of X-furan (1,4-BD) and X-furan (Pripol).

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[e] Conversion (expressed in %) calculated *via* ^{1}H NMR, calculated *via* equation S2.

[f] The number average molecular weight ($\overline{M}_n$) was obtained from GPC analyses ($CHCl_3$, 23 °C, polystyrene standards).

The DSC profiles of the prepared polymers were determined following the protocol stated in the experimental section. The results given in Figure 3 representing the entries in Table 1 showed the evolution of major melting endotherms (T_m) and crystallization enthalpies (ΔH_c) during the second heating cycle as a function of DEFDC molar ratio and diol length. Up to 25 mol% DEFDC feed, the melting endotherms of the copolymers showed a gradual decrease as a function of the increase in DEFDC molar content, where longer diols showed higher melting endotherms. However, as the DEFDC content increased beyond 25 mol%, the melting endotherms started increasing. Copolymers based on hexane-1,6-diol showed an increase in their melting endotherms from 34 °C at 25 mol% DEFDC up to 81 and 119 °C at 50 and 75 mol% DEFDC content. Similarly, copolymers based on octane-1,8-diol showed a similar increase in their melting endotherms exceeding that of hexane-1,6-diol based copolymers, where T_m increased from 49 °C at 25 mol% DEFDC up to 92, 124, and 134 °C for 50, 75, and 90 mol% DEFDC feed ratios. Although the increase in DEFDC molar content also resulted in a positive shift in the melting endotherms of copolymers based on C_{10} and C_{12} diols, this increase was not as significant as those for shorter diols. It is to be noted that copolymers based on C_8, C_{10}, and C_{12} diols showed a second but minor melting endotherm at 50 mol% DEFDC which appeared to fall within close proximity to the main endothermic peaks suggesting the coexistence of two crystalline structures. In fact, the thermal behavior of these copolyesters represented in Figure 3 and showing a decrease followed by an increase in the melting endotherms, and the coexistence of two crystalline phases at certain molar ratios, suggests a pseudo-eutectic behavior and isodimorphic cocrystallization.[64,65] The crystallization enthalpy, which was higher for aliphatic copolymers based on longer diols, showed a gradual decrease as a function of DEFDC feed ratio until reaching a transitional point (~50 mol% DEFDC), followed by an increase upon further DEFDC addition (>50% DEFDC). In fact, the pseudo-eutectic point in copolymers that is usually characterized by the coexistence of two crystalline phases and represents the minimal crystalline value, usually falls around equimolar monomer ratios, but it can vary according to the nature of the repeating unit.[64,66] The different crystal phases were later confirmed *via* WAXS analysis.

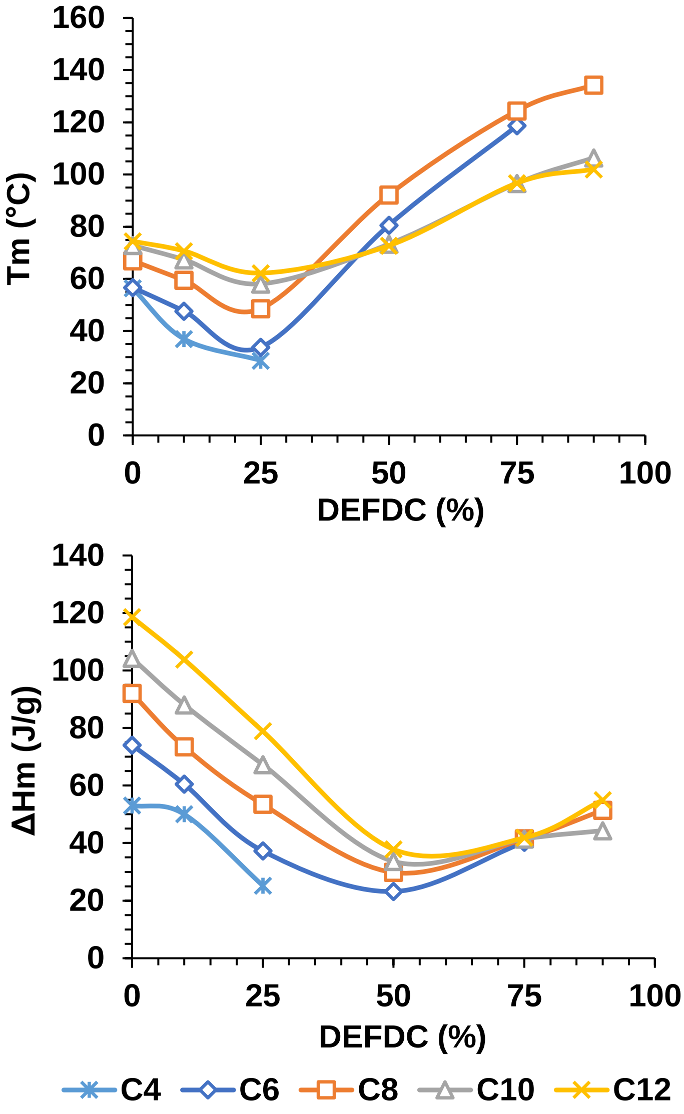

Figure 3. Variations in melting endotherms (°C) and crystallization enthalpies (J/g) as a function of diol length and furan content.

Regarding the glass transition temperature (T_g), Table S4 depicts its evolution as a function of diol length and DEFDC molar content. Due to the high crystallinity in some samples, the T_g was not detected in all copolyesters. As observed in Table S4, the T_g appeared to increase as a function of increasing DEFDC mol% with all tested copolymers, but no specific pattern that relates the length of the tested diols to the value of T_g was observed. During the first heating cycle, and at 50 mol% DEFDC feed, the polymer based on C_6 (entry 8) showed a glass transition temperature at -47 and a premelting point at 43 °C belonging to adipate-rich and furan-rich blocks, respectively. However, during the second heating cycle, the premelting point at 43 °C disappears and only a T_g at -40 °C is observed. The same observation was noticed at 75 mol% DEFDC (entry 9). Similarly, polymers based on C_8 diol showed similar behavior at 50 and 75 mol% DEFDC feed (entries 14 and 15), but at 90 mol% DEFDC (entry 16), only a premelting point at 45 °C appeared during the first heating cycle, while no changes were observed during the second heating cycle. The polymers based on C_{10} diol showed a T_g of -44 and -35 °C at 50 and 75 mol% DEFDC during the second heating cycle, while polymers based on C_{12} did not show any T_g with 75 and 90 mol% DEFDC (entries 27 and 28). What was noticeable from these results was that although changes in the melting endotherms as a function of furan content were observed for all copolymers, their change was more pronounced with copolymers based on shorter diols achieving higher T_m values at high DEFDC content, which comes in agreement with previous reports in the literature associating the decrease in T_m to the increase in the number of methylene groups.[10,34] Regarding the influence of diester length on the DSC profiles of the copolymers produced, (Figure S6) shows the evolution of both the melting endotherms and crystallinity as a function of both DEFDC mol% and diester length. The increase in mol% DEFDC showed a similar effect on the DSC profiles as what was observed in Figure 3Figure **3.** Variations in melting endotherms (°C) and crystallization enthalpies (J/g) as a function of diol length and furan content. However, no direct relation was found relating the evolution of the DSC profiles as a function of the diester length.

Regarding the thermal properties of the copolyesters based on Pripol 2033, octane-1,8-diol and DEFDC depicted in Scheme 3, and during the second heating cycle (see Table S3), all polymers showed an endothermic peak that gradually decreased as a function of increasing Pripol 2033 content, from 140 °C in entry 30' in the absence of Pripol 2033, down to 135 and 129 °C with 10 and 20 % Pripol 2033, respectively. Similarly, the crystallinity also decreased from 66 to 38 J/g.

The incorporation of Pripol 2033 at 25% along with butane-1,4-diol, diethyl adipate, and DEFDC as depicted in Table 2 resulted in a highly viscous yellow sticky liquid, which during the first heating cycle of the DSC (Figure 4), the copolymer given in entry 31, showed a T_g at -36 °C and a broad melting endotherm peaking at 110 °C with an enthalpy of 16 J/g. The cooling cycle did not show any recrystallization peaks. During the second heating cycle, the first T_g increased by 6 °C up to -30 °C, followed by a cold crystallization peak at 39 °C. The T_m peaked at 109 °C with a slight decrease in enthalpy from 16 to12 J/g. The decrease in crystallinity might have risen from the incomplete crystallization during the second heating cycle and the close proximity between the crystallization and melting point. Regarding entry 32, the increase in Pripol 2033 feed to 50 mol% led to the formation of a copolyester with a T_g appearing at -47 °C during the first heating cycle, and a T_m at 51 °C with an enthalpy not exceeding 5.5 J/g. During the second heating cycle, the T_g shifted slightly towards 43 °C, followed by a cold crystallization peak at 46 °C. Directly after crystallization, the T_m peaked at 77 °C, with minimal enthalpy that did not exceed 1 J/g. The big shift in the T_m peak from 51 °C during the first heating cycle to 77 °C on the second cycle, could have resulted from the presence of the cold crystallization and the melting peaks in very close quarters, masking any melting that might have occurred at similar intervals. The copolymer in entry 32 appeared as a white flexible film. The decrease in T_g as a function of increasing Pripol 2033 content reflects an increase in the flexibility of the polymer structure and increases the distance between the rigid blocks which subsequently decreases the crystallinity and the crystallization rate.[67]

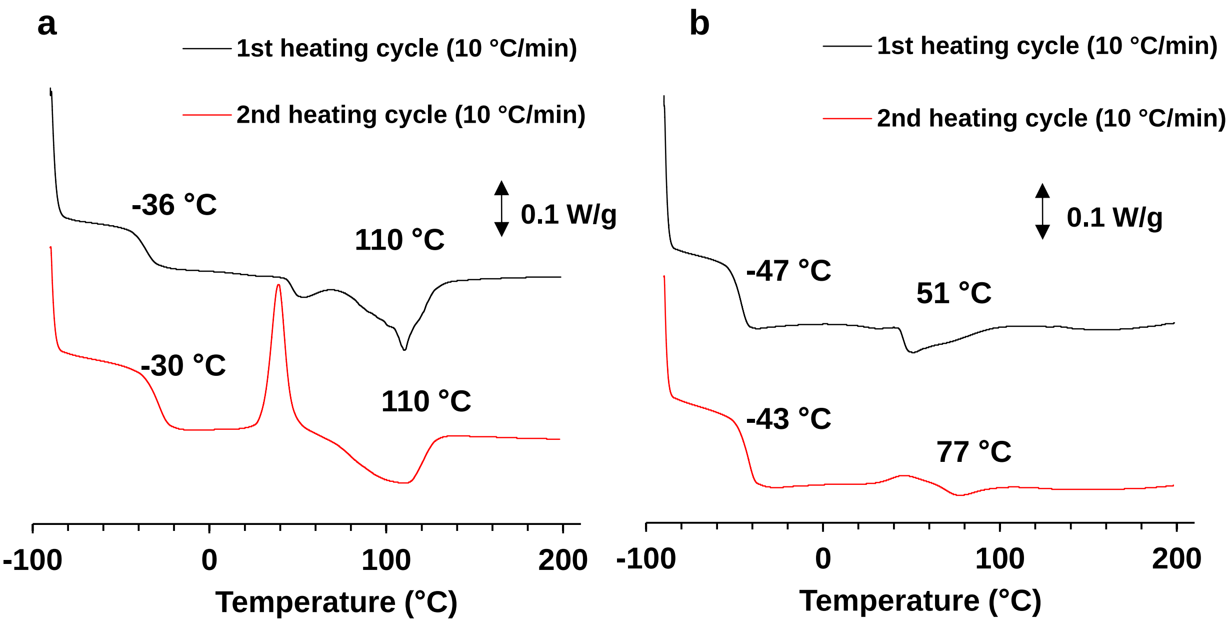

Figure 4. DSC profiles of entries 31 (a) and 32 (b) showing the 1st and 2nd heating cycle.

To further study the influence of the DEFDC molar content and diol length on the crystallinity of the copolymers, Wide-angle X-ray scattering (WAXS) was employed following the protocol stated under the experimental section. Regarding the influence of DEFDC feed %, copolymers based on octane-1,8-diol with DEFDC content varying between 0 and 90% were examined and compared (see Figure 5). For C_8 (0%), the WAXS profile was dominated by two major peaks at 22 ° and 25 ° which appeared to be very similar to the profiles of similar aliphatic polymers tested in the literature such as the case of poly(hexylene succinate).[68] Up to 25% DEFDC feed, the crystallinity continued to be dominated by poly(octylene adipate) crystals. However, upon the increase in DEFDC to 50 %, a new peak started appearing at 17 ° with a significant decrease in the intensity of the peak at 22°, suggesting a mixture of poly(octylene adipate) and poly(octylene furanoate) crystal phases. Upon further increase in DEFDC mol% up to 75 and 90 %, the peak at 20 ° completely disappears. These WAXS profiles of furan rich copolymers were very similar in pattern to what was previously reported in the literature with poly(octylene furanoate), suggesting that at high furan content; regardless of the presence of small amounts of diethyl adipate, the crystalline structures of the copolymers is dominated by the poly(octylene furanoate) crystal phase.[34]The pseudo-eutectic behavior of these copolyesters is thus confirmed by the WAXS results, and is a characterstic of isodimorphic copolymers showing adipate-rich crysalline phase at one side of the pseudo-eutectic region, furan-rich crystalline phase at the other, and the coexistance of both crystalline phases at the pseudo-eutectic point which is observed in the case of C_8 (50 mol%) in Figure 5. This does not mean that only one of the crystalline phases can exist at either sides of the pseudo-eutectic region, but rather that the two crystalline phases coexist at any given ratio of the two repeating unit, but appear as a single crystalline phase resembling that of the repeating unit present in abundance.[21,64,69]

The influence of diol length was studied by comparing the WAXS profiles of copolymers based on hexane-1,6-diol, octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol at a constant 50 mol% DEFDC ratio as observed in Figure S7. All tested copolymers appeared to be semi-crystalline in nature, where C_6 (50 mol%) showed dominating peaks at 17 ° and 25 ° belonging to furan-rich blocks, in addition to a minor peak at 14 ° that appeared to move gradually to lower theta angles as a function of increasing the diol length, reaching 10 ° with C_{12} (50 mol%), while maintaining a stable intensity. As the diol length increased, peaks at 17 ° started to diminish and new crystalline peaks at 21 ° belonging to the adipate-rich blocks started appearing, where C_8 (50 mol%) showed a mixture of both poly(octylene adipate) and poly(octylene furanoate) crystal blocks, C_{10} (50 mol%) was dominated by poly(decylene adipate) crystals and small quantities of poly(decylene furanoate). However, with the longer dodecane-1,12-diol, the peak belonging to poly(dodecylene furanoate) disappeared, and the WAXS spectra was dominated with peaks at 21 ° and 25 ° suggesting the domination of poly(dodecylene adipate) blocks. From these results, it appeared that at equimolar DEFDC: diethyl adipate ratio, copolymers based on longer diols had a stronger tendency to form poly(alkylene adipate) rather than poly(alkylene furanoate) crystals, as opposed to copolymers based on shorter diols that had a quicker tendency to form the opposite. What was generally observed in our work, was that shorter diols reach the pseudo-eutectic transitional point at lower quantities of DEFDC, whereas evident in Figure S7, at 50 mol% DEFDC, polymers based on smaller diols such as hexane-1,6-diol had already shifted towards furan-rich crystalline structures, octane-1,8-diol-based polymers appeared to be in very close proximity to the pseudo-eutectic point, while polymers based on decane-1,10-diol and dodecane-1,12-diol maintained an adipate-rich crystalline structures even at 50% DEFDC.

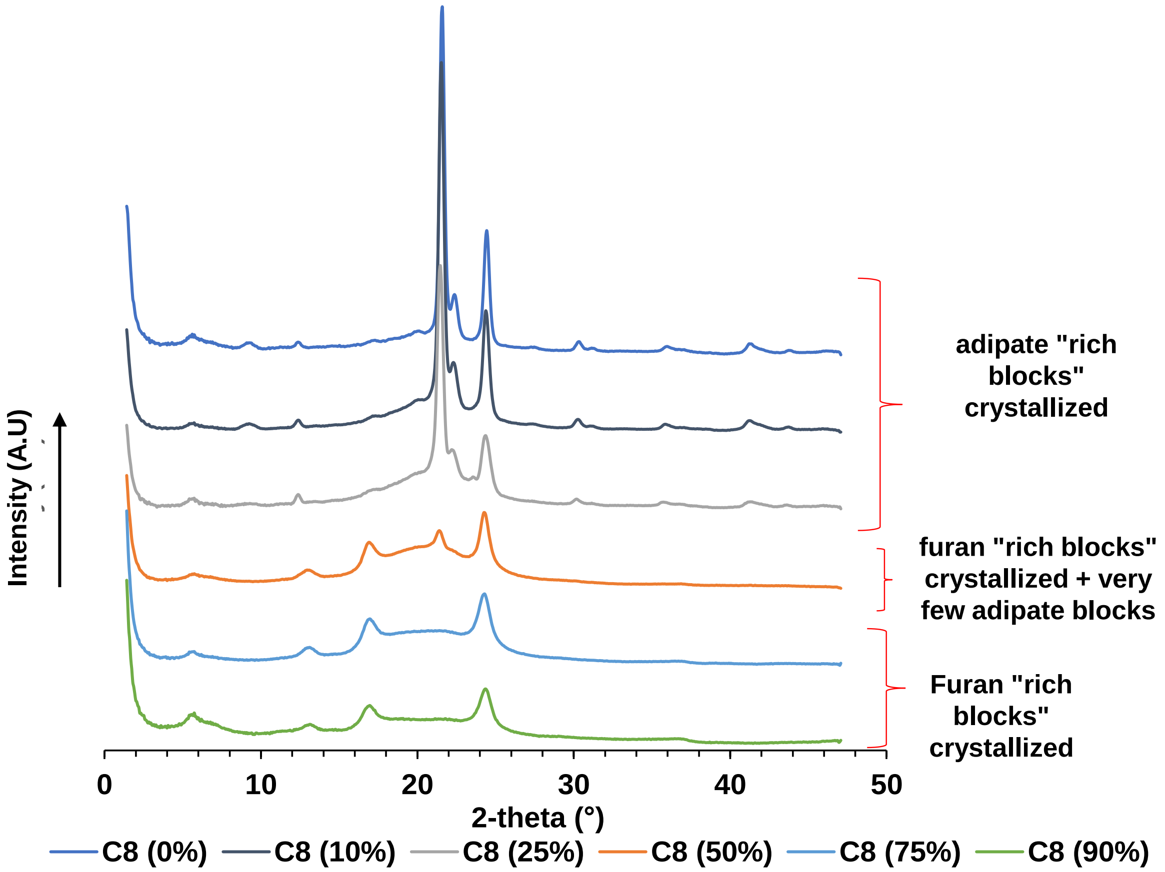

Figure 5. WAXS profiles of poly(octyleneadipate-*co*-octylenefuranoate) as a function of increasing the DEFDC content.

Conclusion

The polycondensation reactions of different chain-length aliphatic diols and diesters at a variable content of diethyl furan-2,5-dicarboxylate (DEFDC) were studied using Novozym 435 as biocatalyst. In agreement with previous reports in the literature, increasing the diol length was essential to allow better reactivity towards DEFDC. However, adding aliphatic diesters to synthesize terpolymers rather than biopolymers was found to be better suited for CALB-mediated catalysis yielding polymers with M_n as high as 10,000 g.mol^{-1} even at elevated DEFDC content, without the need for extreme temperatures and long reaction times. On the other hand, reacting dodecane-1,12-diol with different aliphatic diesters in presence of DEFDC showed no variations as a function of DEFDC feed. Surprisingly though, copolymers produced in the presence of long aliphatic diesters such as diethyl sebacate had low M_n when compared to reactions with diethyl oxalate and diethyl adipate that were relatively similar in results. The introduction of the amorphous Pripol 2033 improved the polymerization reaction in systems containing high furan content and butane-1,4-diol which otherwise did not yield any polymers without the long chain fatty dimer diol. The use of such long fatty acid diols adjacently with short chained diols could be a promising approach playing an important role in future work to overcome some major limitations in enzymatic catalysis towards the synthesis of semi-aromatic polymers. Such polymers can be used for food packaging, and this work has introduced a green method to produce semi-aromatic furan based copolyesters that could be further optimized, studied, and compared with other semi-aromatic copolyesters already on the market such as polybutylene adipate terephthalate.

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Notes

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SYNOPSIS sustainable polyesters synthesized *via* enzymatic catalysis.