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# Greener Synthesis Route for Furanic-Aliphatic Polyester: Enzymatic Polymerization in Ionic Liquids and Deep Eutectic Solvents

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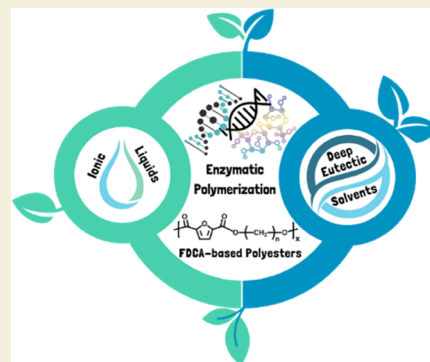
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**ABSTRACT:** The development of bio-based polymers is growing not only due to their abundance in nature but also mainly because of the current issues with fossil-based plastics. Enzymatic polymerizations are a promising way to produce such polymers since they are known to be environmentally friendly. Sustainable polymers that require a greener production process can be realized easily via this polymerization route. However, the use of organic solvents is often one of the drawbacks in developing pathways toward fully green enzymatic polymerization methods. Therefore, in the present work, a series of fully bio-based polyesters based on 2,5-furandicarboxylic acid (FDCA), namely, furanic-aliphatic polyesters (FPEs), were enzymatically synthesized using greener solvents, such as ionic liquids (ILs) and deep eutectic solvents (DESs). The enzymatic polymerization in ILs and DESs effectively leads to the FDCA-based polyesters without any byproduct, which frequently causes coloration using traditional polymerization methods. FPEs with  $M_w$  up to  $5.4 \text{ kg mol}^{-1}$  were successfully achieved by Novozyme 435-catalyzed polycondensation of dimethyl 2,5-furandicarboxylate (DMFDCA) with aliphatic diols in BMIMPF<sub>6</sub>. Polymerization in DESs was also successfully conducted, resulting in the synthesis of bio-based polyesters, which can be further functionalized. Characterization using TGA, DSC, and WAXD showed that all obtained FPEs are semi-crystalline materials, which decomposed around  $390 \text{ }^\circ\text{C}$  with a  $T_m$  of  $68\text{--}123 \text{ }^\circ\text{C}$  and  $T_g$  of  $3\text{--}12 \text{ }^\circ\text{C}$ . With this, we successfully developed more eco-friendly enzymatic synthesis routes for the production of sustainable polyesters

**KEYWORDS:** enzymatic polymerization, 2,5-furandicarboxylic acid, furan-based polymers, renewable resources, bio-based polymers, ionic liquids, deep eutectic solvents



## 1. INTRODUCTION

Over the last few decades, polymers have been developed as an essential part of our modern life. They are used in different applications, such as packaging, electronics, technology, fashion, medicine, agriculture, and many others. Hence, their production is likely to grow extensively in the future. However, the massive demand for polymeric materials is associated with extreme environmental problems. Since polymers are mainly produced from limited petrochemical feedstock and frequently they cannot be recycled efficiently after usage or naturally decomposed, they often end up causing a severe waste problem in landfills, oceans, or cluttering the landscape.<sup>1–3</sup> It is thus of critical importance to develop more sustainable polymers, both to deal with the origin of polymer building blocks and to implement a green(er) synthesis method, including the catalyst and solvent.

One of the prominent bio-based building blocks, 2,5-furandicarboxylic acid (FDCA) has been extensively studied. Properties of the synthesized polymer, namely, poly(ethylene furanoate) (PEF), resembled its petrol-based analogue, poly(ethylene terephthalate) (PET).<sup>1,4,5</sup> However, drawbacks regarding their synthetic method have been reported previously. Decarboxylation, which occurred at high polymer-

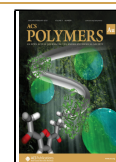
ization temperatures, frequently caused coloration of the polymer product besides the formation of carbonized sugar impurities of FDCA,<sup>1,4,6–8</sup> while metal catalysts, such as manganese, cobalt, and germanium, give results in brightly colored PEF products.<sup>9</sup> In addition, metal catalysts used in conventional polymerizations are difficult to remove. The residual metals can cause coloring, thermal instability, reduced electrical performance, and several toxicity issues.<sup>1,8,9</sup> Up until now, extensive research on FDCA-based polyesters has been conducted using various monomers and polymerization methods using nonenzyme catalysts.<sup>1,4,7</sup> The most popular nonenzyme catalysts used for FDCA-based polyester synthesis are titanium(IV) butoxide (TBT) and antimony(III) oxide (Sb<sub>2</sub>O<sub>3</sub>).<sup>1,10</sup> Synthetic routes investigated so far include several approaches to polycondensation and polytransesterification. A two-stage melt polycondensation typically involves an initial

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esterification or transesterification step, followed by a polycondensation step. Comprehensively, each synthesis parameter was optimized, i.e., starting monomer feed, temperature, and amount of catalyst used.<sup>1,4,10,11</sup> However, this polymerization is generally conducted at high temperatures and under reduced pressure, which in principle is not preferable for sustainable polymer synthesis.<sup>1,10,12</sup> Besides, as mentioned previously, high-temperature polymerization has limitations due to the coloration of FDCA-based polyester products.<sup>4,6,7</sup>

Enzymatic polymerization is renowned as a powerful method in sustainable polymer synthesis due to its selectivity, high efficiency, and sustainability.<sup>5,11,13–16</sup> Enzymatic synthesis of different polymers, including FDCA-based polyesters, has been reported in recent years.<sup>14,17–20</sup> To achieve a high molecular weight polymer product, the optimization of enzyme-catalyzed polymerization was extensively studied, i.e., using different procedures (one-step and two-step polymerization) and varying reaction temperature or pressure.<sup>11,12</sup> In addition, the effects of polymerization conditions, including oligomerization time, vacuum, catalyst dosage, the usage of several comonomers, and reaction medium, have been reported as well.<sup>11,12,14,21,22</sup> Despite this vast progress in enzymatic polymerization, there is still room for improvement, for example, the replacement of organic solvents that are considered harmful to the environment.

Ionic liquids (ILs) and deep eutectic solvents (DESs) were reported as green solvents and can potentially be used as a solvent for enzymatic synthesis. Both are considered to be green solvents because of their recyclability, low flammability, low volatility, and low toxicity.<sup>11,23–25</sup> Several recycling techniques are reported for these solvents, such as distillation, extraction, adsorption, membrane-based separation, and specialized techniques using a force-field separation for magnetic field-sensitive ILs.<sup>23,24,26</sup> ILs are defined as salts with a melting temperature below 100 °C, formed from conventional high-temperature melted salts. They are the first hypothetical substitute for organic solvents, which were produced from a mixture of an organic cation (typically pyridinium or imidazolium) with a wide range of anions.<sup>11,27,28</sup> They also have been reported as catalysts for various reactions.<sup>11,29–35</sup> More recently, DESs are regarded as a newer generation of ILs. DESs are generally formed by mixing an ammonium or phosphonium salt as a hydrogen-bond donor (HBD) with a hydrogen-bond acceptor (HBA) at a certain molar ratio and subsequently heated at 60–100 °C.<sup>32,36,37</sup> Both of these DESs components are typically linked by hydrogen bonds. DESs are considered as a greener solvent compared to ILs since they are less toxic, inexpensive, and more uncomplicated to produce.<sup>24,38</sup> Moreover, they are considered to be better solvent alternatives due to their potential for scaleup production.<sup>39,40</sup>

In this study, we present the synthesis of FDCA-based polyesters using Novozym 435-immobilized *Candida antartica* lipase B (CALB) known as an effective catalyst for polyester synthesis.<sup>12</sup> Intending to render enzymatic polymerizations more green, in this study, we perform enzymatic polymerizations of dimethyl 2,5-furandicarboxylate (DMFDCA) with aliphatic diols in the selected ILs, i.e., BMIMPF<sub>6</sub> and EMIMBF<sub>4</sub>, and DESs based on choline chloride (ChCl) as the HBA, and the HBD is urea and glycerol. These selected ILs and DESs were previously reported suitable for certain biocatalytic reactions. However, enzymatic polymerization of

furanic-aliphatic polyesters utilizing these solvents has not yet been reported.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Novozym 435 (N435, *Candida antartica* lipase B (CALB) immobilized on acrylic resin, 5000 + U/g), 1,6-hexanediol (1,6-HDO, 99%), 1,8-octanediol (1,8-ODO, 98%), 1,10-decanediol (1,10-DDO, 98%), 1,12-dodecanediol (1,12-DODO, 99%), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>, ≥97.0%), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>, ≥98.0%), chloroform (CHCl<sub>3</sub>, Chromasolv HPLC, ≥99.8%, amylene stabilized), deuterated chloroform (CDCl<sub>3</sub>, 99.8 atom% D), sodium chloride (NaCl), and anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were purchased from Sigma-Aldrich. Dichloromethane (DCM, amylene stabilized) was purchased from Macron Fine Chemicals. Dimethyl 2,5-furandicarboxylate (DMFDCA, 97%) was purchased from Fluorochem, U.K. Absolute methanol (MeOH, AR) was obtained from Biosolve Chemicals. Glycerol (99%) was purchased from Boom; choline chloride (99%) and urea (99.5%) were purchased from Acros Organics.

N435 was predried as reported previously.<sup>41</sup> Molecular sieves (4 Å) were preactivated at 200 °C in full vacuum. All of the other chemicals were used as received.

### 2.2. Procedure for One-Step iCALB-Catalyzed Polycondensation of DMFDCA with Various Diols

Based on our previously reported studies,<sup>42</sup> the following one-step enzymatic polymerization of FDCA-based polyester procedure was applied. As an example, the experimental polymerization of DMFDCA and 1,10-DDO is described in the following. A total amount of 1 g monomers (DMFDCA/diols = 1:1, mole ratio), predried N435, and preactivated molecular sieves (15 and 150 wt % of the total amount of the monomer, respectively) were inserted into a 25 mL round-bottom flask under a nitrogen environment. Subsequently, DMFDCA (0.5139 g, 2.79 mmol), 1,10-DDO (0.4860 g, 2.79 mmol), molecular sieve (1.5 g, 150 wt %), N435 (0.15 g, 15 wt %), and either solvent in Table 1 (5 mL) were added

**Table 1. Abbreviations of the Tested Solvents**

solvent type	solvent name		abbreviation
ionic liquid	1-butyl-3-methylimidazolium hexafluorophosphate		BMIMPF <sub>6</sub>
	1-ethyl-3-methylimidazolium tetrafluoroborate		EMIMBF <sub>4</sub>
deep eutectic solvent	hydrogen-bond donor (HBD)	hydrogen-bond acceptor (HBA)	
	1. urea	choline chloride	1. U-ChCl
	2. glycerol		2. Gly-ChCl

into the flask. The flask was magnetically stirred in an oil bath and heated to 90 °C under the nitrogen atmosphere. After a reaction time of 72 h, the reaction was allowed to cool down and stopped. Chloroform (20 mL) was added to dissolve the products under vigorous stirring. N435 and the molecular sieve were filtered by normal filtration (folded filter type 15 Munktell 240 mm) and then washed with chloroform (3 × 10 mL). All of the obtained solutions were combined and concentrated by the use of a rotary evaporator at 40 °C under a reduced pressure of 400–480 mbar. The concentrated solution was precipitated in an excess amount of methanol. The solution with the precipitated products was then stored overnight at –20 °C. After that, the precipitated product was collected by centrifugation (5 min, 4500 rpm, 4 °C) in a Thermo/Heraeus Labofuge 400 R and dried under vacuum at 40 °C for 3 days, which yielded a white powder. The powders were stored under vacuum at room temperature before analysis.

### 2.3. Procedure for Two-Step iCALB-Catalyzed Polycondensation of DMFDCA with 1,10-Decanediol

The two-step enzymatic polymerization of PDFs is conducted under two different vacuum conditions. After a two-hour reaction heated at 90 °C under a nitrogen atmosphere and continuous magnetic stirring, a second step was conducted.

- (1) The first method was performed under vacuum at 600 mmHg for 70 h.
- (2) The second method was performed by slowly applying the vacuum to 30 mmHg for 70 h.

The experimental polymerization details and monomer composition of DMFDCA and 1,10-DDO are described similarly to the aforementioned one-step method.

### 2.4. Preparation of DESs

To form DES, choline chloride (ChCl) as the hydrogen-bond acceptor (HBA) was added into a round flask and dried in full vacuum at 100 °C for approximately 4 h, and then, it was mixed with the hydrogen-bond donor (HBD), either urea (U) or glycerol (Gly) in a 1:2 molar ratio. The mixture was stirred and heated until a homogeneous solution was obtained. For Gly-ChCl, the DES formed immediately, while for U-ChCl, it mostly took an hour to form a homogeneous solution.

### 2.5. Alternative Purification Method

Furanic-aliphatic polyesters obtained from the one-step polymerization using BMIMPF<sub>6</sub> were purified by adding methanol to the crude reaction mixture containing a polymer product, BMIMPF<sub>6</sub>, enzyme, and molecular sieve. Subsequently, to separate the enzyme and molecular sieve, standard filtration using a folded filter type 15 Munktell 240 mm was conducted. The filtrate mixture was then cooled down to -20 °C for 1–2 h, which yielded two phases: a liquid phase containing methanol and BMIMPF<sub>6</sub> and a solid precipitated FPE product. The precipitated product was collected by centrifugation (5 min, 4500 rpm, 4 °C) in a Thermo/Heraeus Labofuge 400 R and dried under vacuum at 40 °C. The methanol was then separated from BMIMPF<sub>6</sub> using a rotary evaporator for additional reuse. Furan polyesters synthesized in U-ChCl were purified by adding dichloromethane (DCM) to the crude reaction mixture. The enzyme and molecular sieve were separated using standard filtering with a folded filter type 15 Munktell of 240 mm. The filtrate was then mixed with a 10 mass equivalents of distilled water containing saturated sodium chloride and subsequently vortexed for 30 s to 1 min. After that, this mixture was transferred to a separating funnel and separated into two phases, a top organic phase containing DCM and FPE products and a bottom phase containing U-ChCl and saturated salt. The organic phase was retained, while the aqueous phase was discarded. The organic phase was then dried using anhydrous sodium sulfate, followed by filtration to separate the liquid organic phase from the salt. Subsequently, the DCM was removed using a rotary evaporator and solid FPEs were obtained and dried, while the collected DCM can be reused.

### 2.6. Kinetics Study: N435-Catalyzed Polycondensation of DMFDCA and 1,10-DDO

**2.6.1. <sup>1</sup>H NMR Analysis.** DMFDCA (0.5139 g, 2.79 mmol), 1,10-DDO (0.4860 g, 2.79 mmol), preactivated molecular sieves (1.5 g, 150 wt %), and either solvent in Table 1 (5 g, 500 wt %) were added into a 25 mL flask with or without predried N435 (0.15 g, 15 wt %). The one-step method was applied according to the same procedure as described above. At selected time intervals (0, 0.5, 1, 2, 6, 9, 24, 47, and 72 h), about 70 mg of the solution mixture was withdrawn from the reaction. Subsequently, the solution mixture was dissolved by 1 g of CDCl<sub>3</sub> for <sup>1</sup>H NMR analysis.

**2.6.2. SEC Analysis.** Using a similar procedure as above, the one-step method was performed for enzymatic polycondensation of DMFDCA (0.2569 g, 2.79 mmol) and 1,10-DDO (0.243 g, 2.79 mmol) in the presence of predried N435 (0.15 g, 15 wt %) and preactivated molecular sieves (1.5 g, 150 wt %). A series of reactions were performed and stopped at certain polymerization times (2, 6, 9,

24, 47, and 72 h). After the polymerization, chloroform (10 mL) was added to dissolve the obtained products under vigorous stirring. N435 and molecular sieves were then filtered off and washed with chloroform three times. The obtained solutions were combined and then rotary evaporated at 40 °C under reduced pressure (20–40 mmHg). After that, the concentrated solution was precipitated in an excess amount of methanol. The solution with the precipitated products was then stored overnight at -20 °C. To obtain the pure product, the precipitated polymer was collected by centrifugation (30 min, 4500 rpm, 4 °C) in a Thermo/Heraeus Labofuge 400 R and dried under vacuum at 40 °C for 3 days, which yielded a white powder and finally stored in vacuo at room temperature before SEC analysis.

### 2.7. FDCA-Based Polyesters

ATR-FTIR ( $\nu$ , cm<sup>-1</sup>): 3057–3200 (=C–H stretching vibration of the furan ring); 2780–3021 (C–H stretching vibration); 1720–1724 (C=O stretching vibration of ester); 1573–1576 (aromatic C=C bending vibration); 1491–1493 and 1468–1475 (C–H deformation and wagging vibrations); 1392 (C–H rocking vibration); 1142–1144 and 1270–1284 (asymmetric and symmetric stretching vibrations of the ester C–O–C group); 1230–1234 and 1010–1016 (=C–O–C= ring vibration and furan ring); 966–977, 820–822, and 764 (=C–H out-of-plane deformation vibration, furan ring).

**2.7.1. Poly(hexamethylene-2,5-furanoate) (PHF).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.18 (2H, s, -CH=, DMFDCA), 4.32 (4H, m, -CO–O–CH<sub>2</sub>–, from 1,6-HDO), 1.77 (4H, m, -CO–O–CH<sub>2</sub>–CH<sub>2</sub>–, from 1,6-HDO), 1.47 (4H, m, -CH<sub>2</sub>–, from 1,6-HDO), 3.91 (s, -O–CH<sub>3</sub>, end group from DMFDCA), 3.64 (t, -CH<sub>2</sub>–OH, end group from 1,6-HDO).

**2.7.2. Poly(octamethylene-2,5-furanoate) (POF).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.16 (2H, s, -CH=, DMFDCA), 4.30 (4H, m, -CO–O–CH<sub>2</sub>–, from 1,8-ODO), 1.74 (4H, m, -CO–O–CH<sub>2</sub>–CH<sub>2</sub>–, from 1,8-ODO), 1.36 (4H, m, -CH<sub>2</sub>–, from 1,8-ODO), 3.90 (s, -O–CH<sub>3</sub>, end group from DMFDCA), 3.62 (t, -CH<sub>2</sub>–OH, end group from 1,8-ODO).

**2.7.3. Poly(decamethylene-2,5-furanoate) (PDF).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.17 (2H, s, -CH=, DMFDCA), 4.28 (4H, m, -CO–O–CH<sub>2</sub>–, from 1,10-DDO), 1.73 (4H, m, -CO–O–CH<sub>2</sub>–CH<sub>2</sub>–, from 1,10-DDO), 1.38 (4H, m, -CH<sub>2</sub>–, from 1,10-DDO), 3.91 (s, -O–CH<sub>3</sub>, end group from DMFDCA), 3.63 (t, -CH<sub>2</sub>–OH, end group from 1,10-DDO).

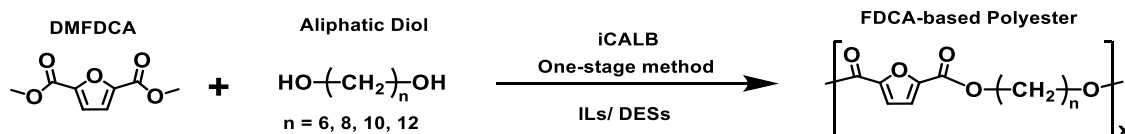
**2.7.4. Poly(dodecamethylene-2,5-furanoate) (PDF).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.17 (2H, s, -CH=, DMFDCA), 4.28 (4H, m, -CO–O–CH<sub>2</sub>–, from 1,12-DODO), 1.73 (4H, m, -CO–O–CH<sub>2</sub>–CH<sub>2</sub>–, from 1,12-DODO), 1.38 (4H, m, -CH<sub>2</sub>–, from 1,12-DODO), 3.91 (s, -O–CH<sub>3</sub>, end group from DMFDCA), 3.63 (t, -CH<sub>2</sub>–OH, end group from 1,12-DODO).

### 2.8. Analytics

Proton nuclear magnetic resonance (<sup>1</sup>H NMR; 400 MHz) spectra were recorded on a Varian VXR spectrometer, using CDCl<sub>3</sub> as the solvent. Attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra were recorded on a Bruker VERTEX 70 spectrometer equipped with an ATR diamond single reflection accessory. The measurement resolution was 4 cm<sup>-1</sup>, and the spectra were collected in the range of 4000–400 cm<sup>-1</sup>, with 16 scans for each sample. Atmospheric compensation and baseline correction were applied to the collected spectra using OPUS spectroscopy software (v7.0) (Bruker Optics).

Molecular weights (number-average,  $\bar{M}_n$ , and weight-average,  $\bar{M}_w$ ) of FPEs were determined by size exclusion chromatography (SEC) equipped with a triple detector, consisting of a Viscotec 270 Malvern Dual detector and Schambeck RI2012, a refractive index detector. The separation was carried out using two PLgel 5  $\mu$ m MIXED-C 300 mm columns from Agilent Technologies at 35 °C. Chloroform of HPLC grade was used as the eluent, with a flow rate of 0.5 mL/min. Data acquisition and calculations were performed using Viscotec OmniSec software version 5.0. Molecular weights were determined based on a conventional calibration curve generated from narrow

## Scheme 1. Enzymatic Synthesis of Furanic-Aliphatic Polyesters



dispersity polystyrene standards (Agilent and Polymer Laboratories,  $\bar{M}_w = 645 - 3\,001\,000$  g/mol). The samples were filtered over a 0.2  $\mu\text{m}$  PTFE filter before injection.

The analysis of the thermal properties was performed on a TA Instruments Q1000 DSC, which was calibrated on indium as a standard. The heating rate was 10  $^{\circ}\text{C min}^{-1}$  under nitrogen flow. Melting points ( $T_m$ ) of FPEs were measured by a second heating scan. The glass transition temperatures ( $T_g$ ) were measured by a temperature-modulated DSC (TMDSC) at 2  $^{\circ}\text{C min}^{-1}$  with a temperature modulation of  $\pm 0.50$   $^{\circ}\text{C}$  for every 60 s.

The thermal stability and degradation temperatures were analyzed by thermogravimetric analysis (TGA) on a TA Instruments Discovery TGA 5500 using a heating rate of 10  $^{\circ}\text{C min}^{-1}$  in a nitrogen environment.

Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.1542$  nm) in the angular range of 5–50 $^{\circ}$  ( $2\theta$ ) at room temperature.

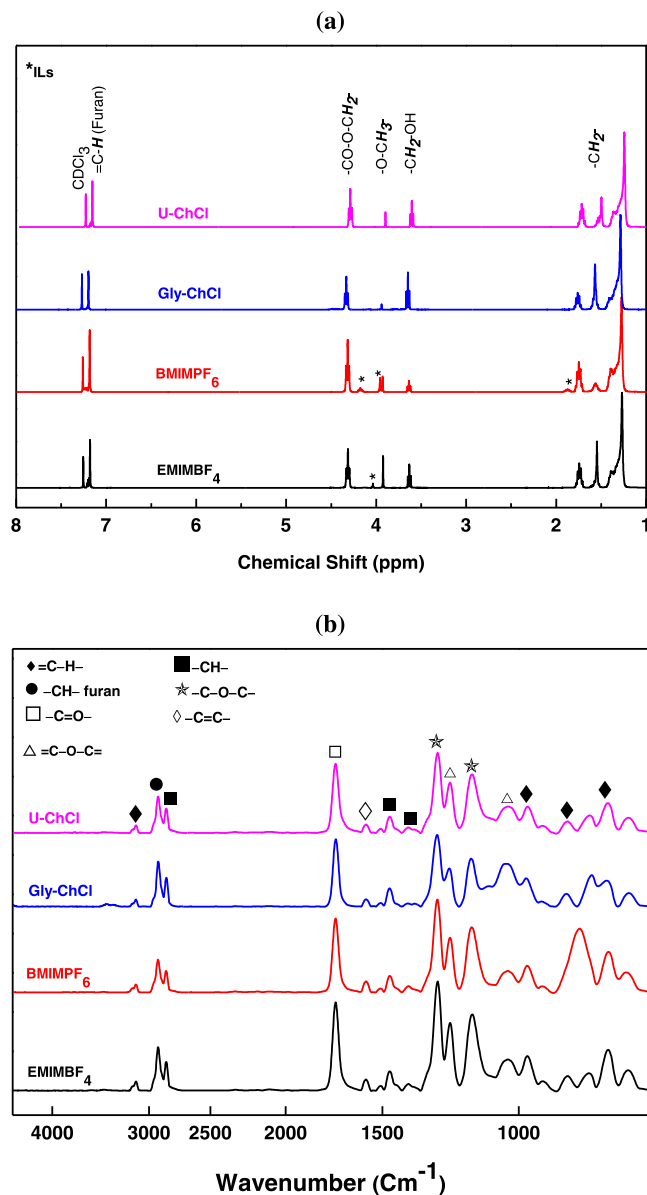
### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and Structural Characterization of Furanic-Aliphatic Polyesters

Various furanic-aliphatic polyesters were successfully synthesized via two approaches in different media, as outlined in Scheme 1. In this work, furan polyesters were prepared by the N435-catalyzed reaction between DMFDCA and diols. Different reaction media (listed in Table 1) were used to evaluate their influence on the enzymatic synthesis of furanic-aliphatic polyesters. The synthesized polyester varies in the number of methylene units ( $n$ ) of the aliphatic linear diols as 6, 8, 10, and 12. These are defined as the carbon chain length of the used aliphatic linear monomers of the polyester's synthesis.

$^1\text{H NMR}$  and ATR-FTIR spectra (Figures 1, S1, and S8) showed the successful enzymatic synthesis of the FPEs. The presence of a  $-\text{CO}-\text{O}-\text{CH}_2-$  signal at 4.3 ppm confirmed the formation of the polyester. Additionally, ATR-FTIR spectra prove the ester linkage formation by the occurrence of a sharp band around 1650  $\text{cm}^{-1}$ , corresponding to the  $\text{C}=\text{O}$  stretching vibration of the ester groups.<sup>21,43</sup> The detailed assignment of the NMR and IR peaks are specified in the Materials and Methods section. As shown in the  $^1\text{H NMR}$  peaks (see Figure 1a), weak signals corresponding to the ILs were observed. However, different from our previous work on the FDCA-based poly(ester amide)s,<sup>17</sup> no coloration was observed in the product—see below.

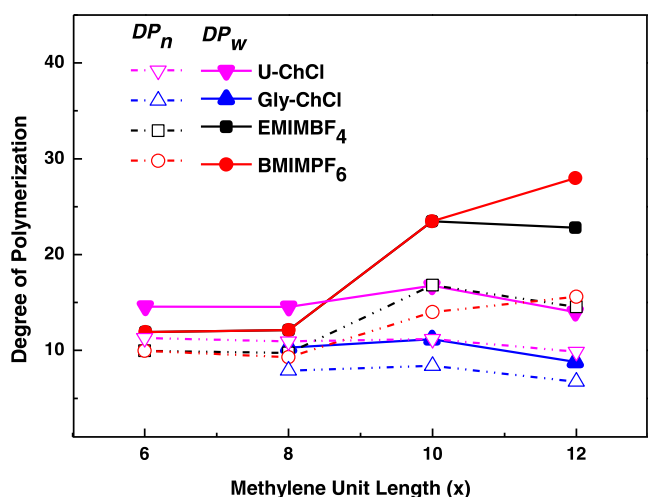
We found that when these ILs and DESs were used as the medium, the polymerization of DMFDCA and diol can also be performed without N435 as the catalyst. This result confirmed that ILs and DESs can be used as both the medium and catalyst in the polymerization, as previously reported.<sup>6,11,26,44–46</sup> Among the tested solvents, U-ChCl shows the best performance in terms of the yield and molecular weight (Table S2). However, based on the kinetic study, the N435-catalyzed polymerization of DMFDCA and 1,10-DDO in U-ChCl still gives a higher molecular weight,  $\bar{M}_n = 2300$  g  $\text{mol}^{-1}$  and  $\bar{M}_w = 3400$  g  $\text{mol}^{-1}$ , compared to the nonenzymatic polymerization,  $\bar{M}_n = 1750$  g  $\text{mol}^{-1}$  and



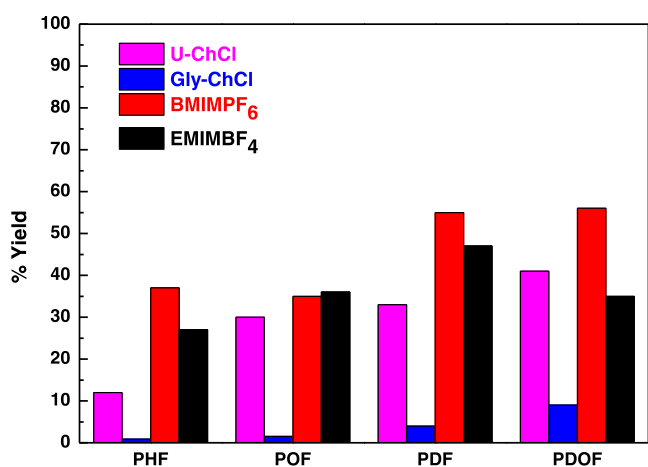
**Figure 1.** (a)  $^1\text{H NMR}$  spectra of PDOF obtained in different solvents and (b) ATR-FTIR spectra of PDOF obtained in different solvents.

$\bar{M}_w = 2400$  g  $\text{mol}^{-1}$  (see Table S3). Nonenzymatic polymerization of DMFDCA and 1,10-DDO for 47 and 72 h resulted in PDF with a relatively similar molecular weight,  $\bar{M}_w = 2200$  g  $\text{mol}^{-1}$  and  $\bar{M}_w = 2400$  g  $\text{mol}^{-1}$ , respectively. These findings show that the polymerization was indeed significantly catalyzed by the enzyme.

The influence of the lengths of aliphatic linear monomers on the enzymatic synthesis of furanic-aliphatic polyesters was investigated. As shown in Figure 2, the results indicate that *Candida antarctica* lipase B (CALB) prefers longer linear diols



**Figure 2.**  $\overline{DP}_n$  and  $\overline{DP}_w$  of the furanic-aliphatic polyesters synthesized in different solvents plotted against the chain length of the linear monomers using the one-step method.



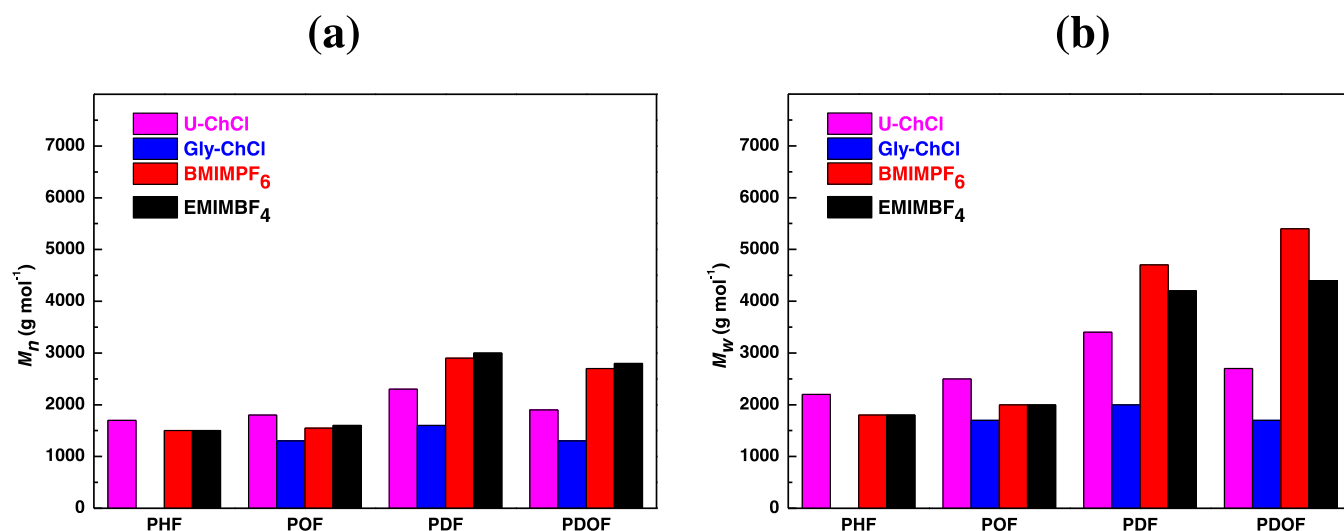
**Figure 3.** Yield of the furanic-aliphatic polyesters synthesized in different solvents using the one-step method.

( $n = 10$  and  $12$ ) over shorter linear diols ( $n = 6$  and  $8$ ). This result is in line with our previous findings that CALB consistently prefers aliphatic monomers with longer chains.<sup>21,43</sup> The results showed that the weight-average degree of polymerization ( $\overline{DP}_w$ ) of the obtained FPEs synthesized in BMIMPF<sub>6</sub> was increased from 12 to 24 upon increasing the chain length of the diols from  $n = 8$  to  $10$ . Similarly,  $\overline{DP}_w$  of FPEs synthesized in U-ChCl was increased from 15 to 17. A slight decrease was observed when the diol length was increased to  $n = 12$ . As illustrated in Figure 2, the tendency toward a certain diol chain length is similar, regardless of the solvent type. CALB was reported to have better activity in solvents bearing fluorinated anions, and this explains the higher DP obtained in both ILs, EMIMBF<sub>4</sub> and BMIMPF<sub>4</sub>, especially at a longer alkyl chain length  $n > 8$ .<sup>6,47,48</sup> However, no significant difference was observed in the polymerization in DESs despite the increase in the chain length of the used diol. This is in agreement with Durand et al. who reported that immobilized CALB possess the best activity in DESs containing ChCl, regardless of the alcohol chain length used in transesterification of vinyl laurate with alcohols.<sup>49</sup>

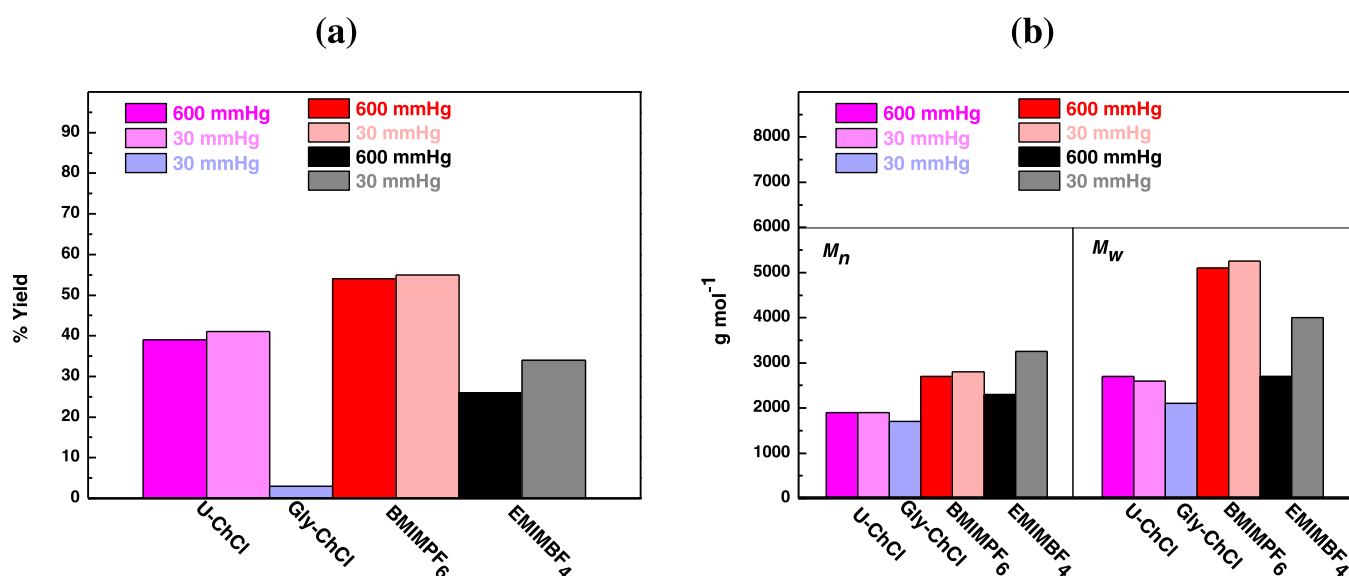
### 3.2. Influence of the Solvent on the Enzymatic synthesis of the Furanic-Aliphatic Polyesters

Aside from their green characteristics, ILs and DESs were chosen as solvents due to their typical solubility for organic and inorganic materials. Their ability as a lipase stabilizer solvent was reported previously.<sup>50,51</sup> In this work, two types of ILs, i.e., BMIMPF<sub>6</sub> and EMIMBF<sub>4</sub>, were used. It was previously reported that CALB showed higher activity in ILs containing fluorinated anions; hence, these two ILs were selected.<sup>17,47</sup> Similarly, U-ChCl and Gly-ChCl have been reported as appropriate DESs for good lipase activity.<sup>26,32,49,52–54</sup>

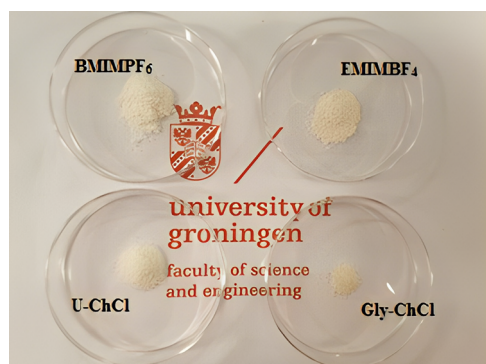
We have successfully synthesized FPEs in ILs with a relatively high yield and molecular weight. We observed that there is no significant difference in the resulting yield and molecular weight of the polyester obtained from the two ILs: BMIMPF<sub>6</sub> and EMIMBF<sub>4</sub>. As listed in Table S1, POF synthesized in BMIMPF<sub>6</sub> has a yield of 35% and  $\overline{M}_n$  of 1550 g mol<sup>-1</sup>, while for EMIMBF<sub>4</sub>, the corresponding values



**Figure 4.** (a) Number-average molecular weight  $\overline{M}_n$  and (b) weight-average molecular weight  $\overline{M}_w$  of the furanic-aliphatic polyesters synthesized in different solvents using the one-step method.



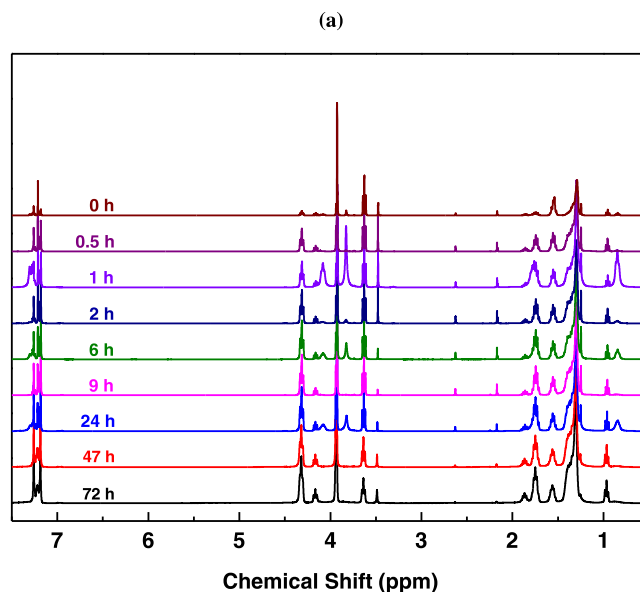
**Figure 5.** (a) Yield of PDFs and (b) number-average molecular weight  $\bar{M}_n$  and weight-average molecular weight  $\bar{M}_w$  of PDFs synthesized in different solvents using the two-step method.



**Figure 6.** Poly(decamethylene-2,5-furanoate) (PDOF) synthesized in different media. Logo by University of Groningen used with permission.

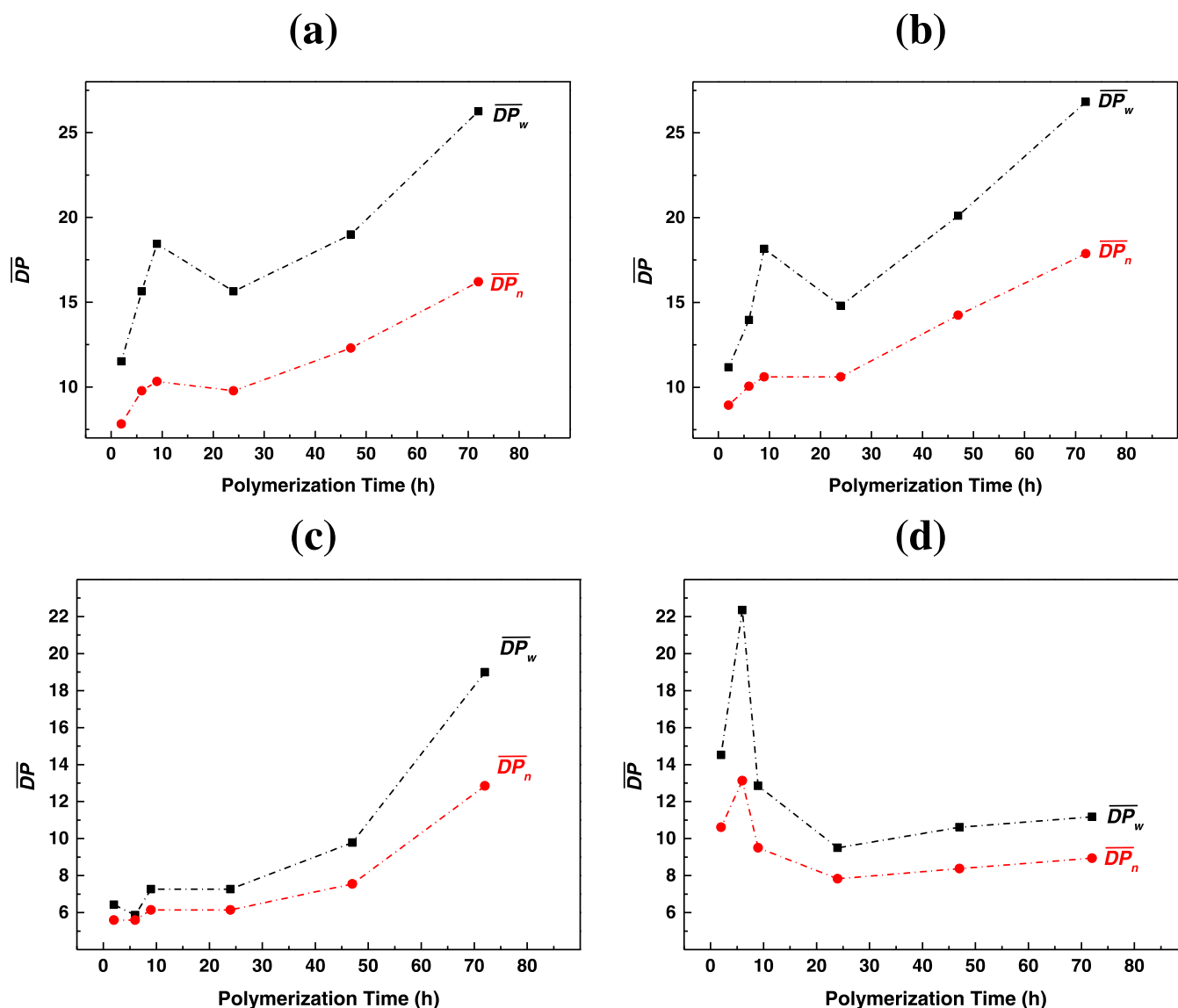
are 36% and 1600 g mol<sup>-1</sup>. A similar result, which shows that synthesis in EMIMBF<sub>4</sub> renders a high product yield and molecular weight, was observed in PHF, PDF, and PDOF as well. These results agreed with a nonenzymatic study by Qu et al., in which EMIMBF<sub>4</sub> was reported as the most preferred solvent–catalyst for FPEs due to the stronger electronegativity and proton donating ability.<sup>6</sup> In contrast, this result did not agree well with our previous report on furan poly(ester amide)s (PEAFs). In PEAF synthesis, BMIMPF<sub>4</sub> gives a better yield and higher molecular weight compared to EMIMBF<sub>4</sub>.<sup>17</sup> This can be explained due to the different solubility of PEAFs and FPEs in both solvents.

Lipase was reported as an active catalyst in two DES, namely, U-ChCl and Gly-ChCl.<sup>26,32,52–55</sup> The DESs are prepared typically using a 1:2 molar ratio of the ChCl as the halide salt to the hydrogen-bond donor (HBD), i.e., urea and glycerol.<sup>32,54,56</sup> In this study, we used those two DESs as the reaction media and we found that they give significantly different reaction yields (Figure 3). The enzymatic polymerization in U-ChCl results in a higher yield compared to Gly-ChCl. In addition, as depicted in Figure 4 and listed in Table S1, the polyesters synthesized in U-ChCl also possess higher  $\bar{M}_n$  and  $\bar{M}_w$ . These results suggest that U-ChCl is a more



**Figure 7.** <sup>1</sup>H NMR spectra of the solution mixture from the N435-catalyzed polycondensation of DMFDCA and 1,10-DDO at 90 °C in BMIMPF<sub>6</sub>.

preferable DES to Gly-ChCl for the tested polymerization. This might be due to the reduced activity of the enzymes in Gly-ChCl. As seen by the kinetic analysis in Figure 8d, the molecular weight of PDF dropped after a 9-h reaction. Glycerol was reported to have a negative effect on lipase activity and stability due to its ability to be adsorbed onto the lipase. This can potentially limit the substrate and water diffusion into the enzyme that is crucial for the enzyme catalytic activity.<sup>49,57,58</sup> In addition, glycerol was found to compete with the alcohol substrate; as reported by Bubalo et al.<sup>59</sup> and Gorke et al.,<sup>54</sup> alcohol could act as hydrogen-donor and then interact with Gly-ChCl as the solvent or linked to the ester substrate. This might explain the molecular mass decreases after 6 h of reaction times (see Figure S4b), which correspond to the potential transesterification involving



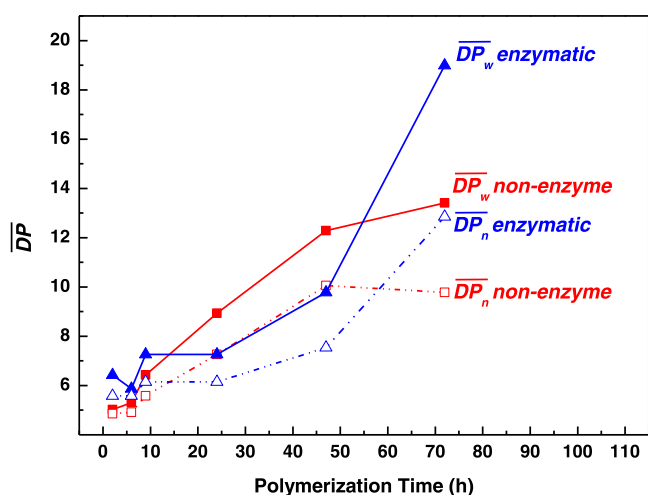
**Figure 8.**  $\overline{DP}_n$  and  $\overline{DP}_w$  of the obtained PDF determined by SEC as a function of polymerization times in (a) BMIMPF<sub>6</sub>, (b) EMIMBF<sub>4</sub>, (c) U-ChCl, and (d) Gly-ChCl.

glycerol. While Xu et al. studied ethanolysis of rapeseed oil using immobilized lipase in the presence of glycerol, they successfully prevented glycerol blocking and achieved 90% conversion using agitation in their reaction.<sup>57</sup> In another study, Durand et al.<sup>49</sup> found that iCALB has better long-term stability in U-ChCl compared to Gly-ChCl. They observed that iCALB activity rate only reduced to 5% after one-day incubation and less than 38% after 5 days in U-ChCl, while it decreased up to 70% in Gly-ChCl. Hawkins and Handy also noticed that, compared to glycerol, urea's preorganized nature and stronger hydrogen bond can positively influence the catalytic activity of their eutectic solvent, as such for U-ChCl.<sup>45</sup>

As illustrated in Figures 3 and 4, compared to DESs, ILs display better performance as a solvent for enzymatic polymerization. This can be due to the better activity and stability of CALB in ILs since IL-charged cations and anions may interact electrostatically with the lipase in a favorable manner. Specifically, ILs with lower hydrogen-bond basicity contain BF<sub>4</sub>, PF<sub>6</sub>, and NTf<sub>2</sub> anions because of their ability to reduce interference with the internal hydrogen bonds of an

enzyme.<sup>60–62</sup> However, issues may arise regarding the toxicity of ILs, including the fluorinated ILs, even though it reported that it is safe to use ILs at certain concentrations, higher than 1000 mg L<sup>-1</sup>.<sup>63</sup> Therefore it is worth noting to consider an even greener solvent alternative for future studies. However, for enzymatic polymerization in DESs, their constituent components affect the variation of their hydrogen-bond network, hence influencing the enzyme activity's stability, the solvation conformation in the reaction system, and the polarity.<sup>55,56,64,65</sup> It was reported that the enzyme possesses high activity in DESs containing water due to its ability to modify the viscosity and polarity of DESs. Up to 10% of water addition to the enzymatic reaction in DESs effectively enhanced the reaction rate and results, while more than 15% water addition caused a decrease in the yield due to which the competitive hydrolysis occurred.<sup>55,56,64,66–71</sup> Therefore, for enzymatic synthesis of FPEs in DESs, further studies are required to know the preferred DES composition.





**Figure 9.**  $\overline{DP}_n$  and  $\overline{DP}_w$  comparison between the enzymatic and control reactions of the obtained PDOF determined by SEC as a function of the polymerization time in U-ChCl.

**Table 2.** Thermal Properties of the Obtained FPEs Using the One-Step Method

polymers	solvent	DSC <sup>a</sup>			TGA <sup>b</sup>
		$T_g$ (°C)	$T_m$ (°C)	$T_c$ (°C)	$T_{d-max}$ (°C)
PHF	U-ChCl	10	104/119	99	389
	Gly-ChCl	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>
	BMIMPF <sub>6</sub>	8	99/111	90	352
POF	EMIMBF <sub>4</sub>	6	108/116	96	390
	U-ChCl	10	109/123	102	392
	Gly-ChCl	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	389
PDF	BMIMPF <sub>6</sub>	3	110/119	90	348
	EMIMBF <sub>4</sub>	4	110/118	99	382
	U-ChCl	8	95/102	84	395
PDOF	Gly-ChCl	5	83/88	73	397
	BMIMPF <sub>6</sub>	8	92/103	81	362
	EMIMBF <sub>4</sub>	8	88/100	78	393
	U-ChCl	9	68/84/96	72	393
	Gly-ChCl	5	75/82	64	401
EMIMBF <sub>4</sub>	BMIMPF <sub>6</sub>	12	97/102	87	367
	EMIMBF <sub>4</sub>	10	94/101	82	392

<sup>a</sup> $T_g$  = glass transition temperature from the modulated DSC heating scan,  $T_m$  = melting temperature from the second heating scan,  $T_c$  = crystallization temperature from the cooling scan. <sup>b</sup> $T_{d-max}$  = temperature at the maximum rate of decomposition. <sup>c</sup>Not determined.

### 3.3. Influence of the Polycondensation Process

As illustrated in Figure 3, the yield from one-step polymerization was always less than 60%, which could be owing to molecular sieves' inability to absorb the byproduct methanol or water contaminants from the raw material. Therefore, to further study the influence of the polycondensation process on the enzymatic polymerization of furanic-polyesters in ILs and DESs, we performed a two-step polycondensation method of PDF enzymatic synthesis at two different vacuum conditions. First, by applying a vacuum of 600 mmHg after 2 h of the precondensation reaction, methanol as a byproduct could be removed. Second, we also implemented higher vacuum conditions using 30 mmHg in the second step of the polymerization, which allowed the system to eliminate methanol and water more efficiently. As can be seen in Figure

5 and Table S4, we found no significant difference in the yield and molecular weight between the two applied methods, especially for U-ChCl and BMIMPF<sub>6</sub>, while for EMIMBF<sub>4</sub>, we can see a slightly different results.

As shown in Figure 5a, PDF possesses the best result in BMIMPF<sub>6</sub> and almost similar yields of 55 and 54% for the 30 and 600 mmHg methods were achieved, respectively. Moreover, almost similar  $\overline{M}_n$  and  $\overline{M}_w$  were found for both methods as well (see Figure 5b). However, we discovered no significant difference in the yield and  $\overline{M}_n$  than the one-step method, but  $\overline{M}_w$  rose by 12%. For the second IL, EMIMBF<sub>4</sub>, the two-step enzymatic synthesis of PDF resulted in up to 23% decreased  $\overline{M}_n$  and  $\overline{M}_w$  as compared to the one-step method and the yield dropped by 45% (see Tables S1 and S4). As observed during the reaction, EMIMBF<sub>4</sub> turned more viscous after the vacuum was applied to the reaction implying limiting mass transfer in the system and reducing the reactivity.

Also, the two-step enzymatic synthesis of PDF using DESs did not give a better result than the one-step method. Lower  $\overline{M}_n$  and  $\overline{M}_w$  but up to 24% higher yields were achieved in U-ChCl using the 600 and 30 mmHg methods (see Tables S1 and S4). For Gly-ChCl, no different results between the one-step and two-step methods were observed, showing only 4 and 3% yields, respectively. Likewise,  $\overline{M}_n$  and  $\overline{M}_w$  revealed 1600 and 2000 g mol<sup>-1</sup> for the one-step method and 1700 and 2100 g mol<sup>-1</sup> for the two-step method, respectively. These results indicate that water influences the enzyme activity in the same way as outlined above when DESs are employed as solvents. This agrees with several reports mentioned above regarding enzyme activity influenced by water addition.<sup>55,56,64,66–71</sup>

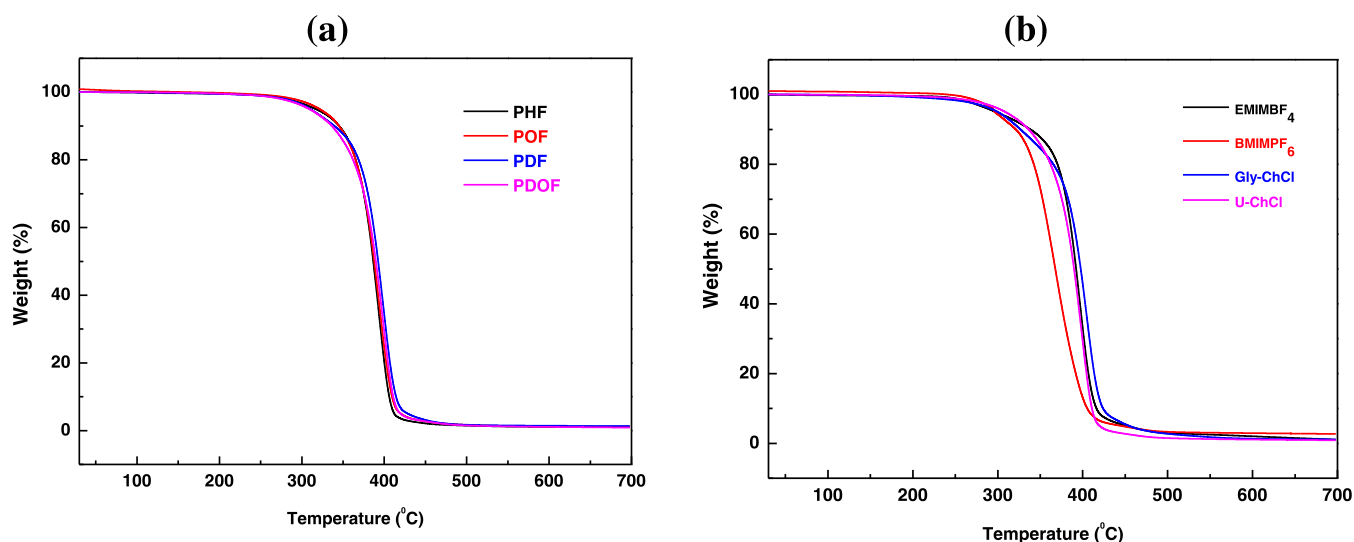
### 3.4. FPE Product Appearance

We observed no coloration on furanic-aliphatic polyesters synthesized both in ILs and DESs (see Figure 6). This result supports our premise that enzymatic polymerization can remarkably prevent coloration in FDCA-based polymer production. The coloration issue was frequently reported in FDCA-based polymers due to the decarboxylation of FDCA at the high-temperature reaction.<sup>6,7,72</sup> We have successfully addressed the coloration issue from the IL residue that was observed in our previous work on the enzymatic synthesis of PEAfS.

In the synthesis of furanic-aliphatic polyester, we have successfully separated the ILs and obtained a high purity product. This can be explained by the properties of the furanic-aliphatic polyesters, which have a low polarity and are structurally symmetric from the ester functional groups. Hence, the polyesters can be straightforwardly trapped by nonpolar solvents in the purification stage. Moreover, the amide group of PEAfS has been observed to form hydrogen-bonded complexes with ILs.<sup>73,74</sup> As a consequence, PEAf production requires multiple purifying steps.<sup>17</sup>

### 3.5. Kinetics Study

To better understand enzymatic polymerization in ILs and DESs, we investigated the enzymatic polymerization kinetics of the one-step method by <sup>1</sup>H NMR and SEC (see Figures 7 and 8) and the kinetics of control reactions (see Figure S2) by <sup>1</sup>H NMR. As illustrated in Figures 3 and 4, we discovered that enzymatic polymerization of PDF produced high molecular weights and yields in all media. Therefore, in this study, we focus on performing the kinetic analysis to PDF enzymatic synthesis. As shown in Figure 7, PDF was already produced



**Figure 10.** (a) Representative TGA traces of the obtained furanic-aliphatic polyesters synthesized in U-ChCl. (b) Representative TGA traces of the obtained PDOF synthesized in both ILs and DESs.

within 30 minutes of the reaction, except for the reaction in Gly-ChCl. The PDF formation can be verified by the signal appearance at 4.28 ppm, which belongs to the methoxy group of the oligoesters. On the other hand, the control showed the appearance of the oligoester methoxy peak slightly only for reaction in BMIMPF<sub>6</sub> and U-ChCl; it appeared after 2 and 1 h, respectively (see Figure S2). Moreover, the decrease of the methoxy group signal from DMFDCA at 3.9 ppm implies that DMFDCA was already transformed into oligoester. This result is in agreement with our previous finding, in which oligoester and oligoamide were detected after 2 h of the reaction using the enzyme.<sup>75,76</sup> Additionally, when we compare the two ILs, the higher signal intensity of the oligoesters methoxy group was detected for the reaction in BMIMPF<sub>6</sub> (see Figure 7). This suggests that BMIMPF<sub>6</sub> is a more suitable solvent than EMIMBF<sub>4</sub>. However, for polymerization in Gly-ChCl (see Figure S11c), the methoxyl group signal of the oligoester only appeared after 6 h and not significantly improved after 72 h. This indicated that the polymerization occurred slowly in this reaction system. This supports our hypothesis that glycerol can form a barrier that reduces enzyme activity. Hence, the polymer was not effectively propagated despite the longer reaction time.<sup>57,58</sup>

From the SEC analysis (see Figure 8), it can be seen that polymerizations of PDF using ILs show a significant increase of  $\overline{DP}_w$  from 2 to 9 h of the reaction time and a subsequent decrease of  $\overline{DP}_w$  after 10 h, while the  $\overline{DP}_n$  stays relatively the same after 10 h. This insignificant decrease in DP might be due to ester hydrolysis, temporarily dominating the reaction equilibrium. However, upon further increase of the polymerization time to 72 h, the ester linkage formation is prevalent again. On the other hand, as we proceeded under vacuum reactions, which did not significantly increase the results, we assume that the high viscosity of ILs during 47 h results in an instability of mass transfer or in reduced enzyme reactivity in the system. Further experiments must be undertaken to fully understand this behavior of the system. For the reaction in U-ChCl, the DP shows a declining path up to 6 h of the reaction time, followed by a steady increase up to 72 h. In contrast, the reaction in Gly-ChCl showed a sharp increase in the first 6 h of the reaction time, then subsequently decreased after 9 h, and

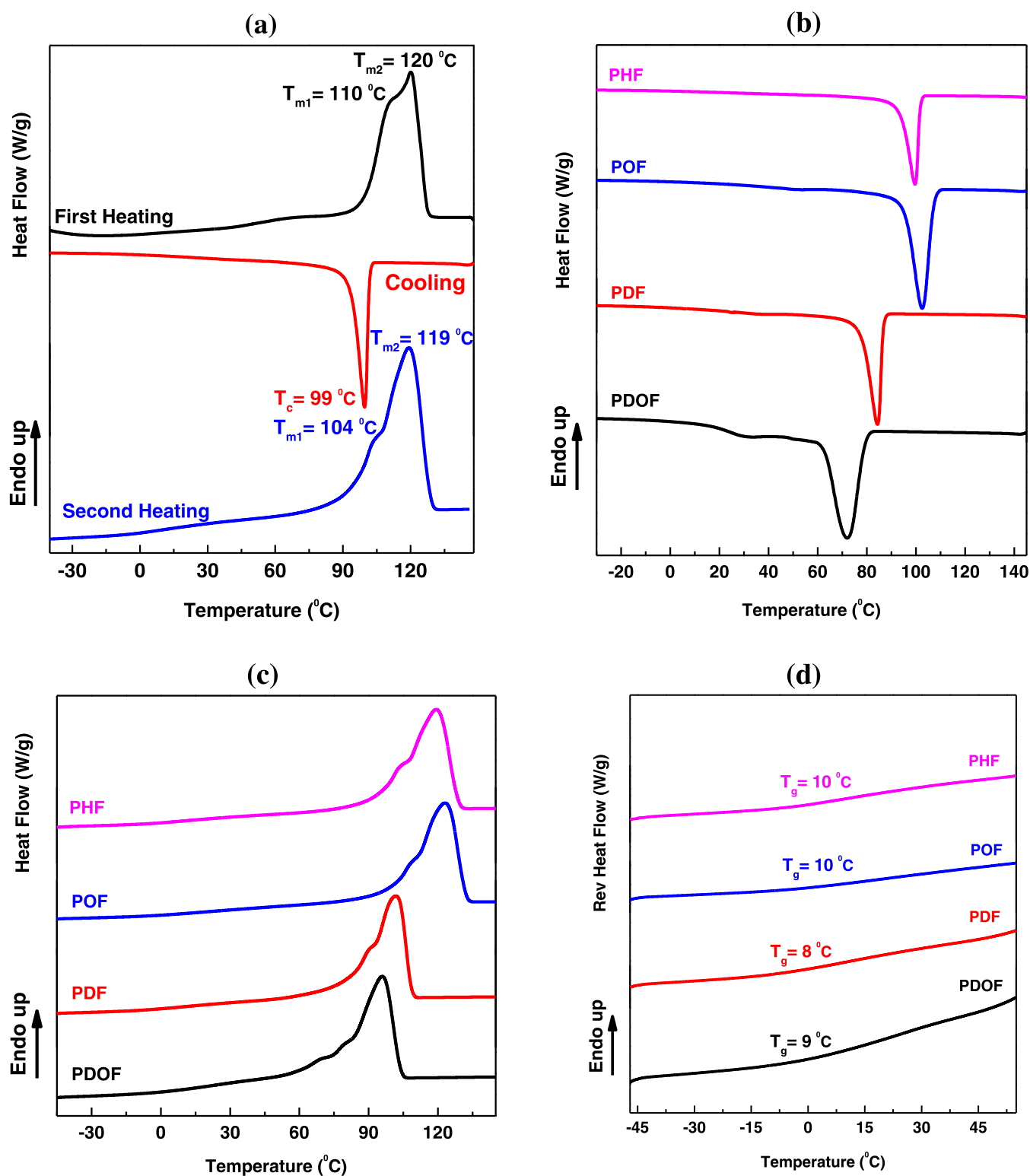
slightly increased again in the last 72 h. As expected, this sudden decrease can be explained by the glycerol barrier formation on the enzyme. As the reaction proceeds, sufficient agitation may be achieved during the polymerization; hence, we see a slight increase in the DP after 24 h. Based on this result, we can conclude that the enzymatic reaction using Gly-ChCl occurred effectively in a short time, up to 6 h.

Interestingly, the control reaction in U-ChCl gives comparable results to its enzyme-catalyzed polymerization, resulting PDOF with  $\overline{M}_w$  up to 2.5 kg mol<sup>-1</sup> and a yield of 43% (see Table S2). However, if we compare the control to the enzyme-catalyzed reaction (see Figure 9), a steady increase in DP was observed after 50 h in the enzyme-catalyzed polymerization. This suggests that, despite the U-ChCl catalysis, enzyme activity has a specific influence to determine the final polymerization results. Therefore, it can be concluded that enzymes play the main role in catalyzing and stabilizing the polymerization reaction. In addition, we found that  $\overline{M}_n$  and  $\overline{M}_w$  increase up to 24 and 29%, respectively, when the enzyme is used as a catalyst in the polymerization using U-ChCl.

### 3.6. Crystallinity and Thermal Analysis of the Obtained Furanic-Aliphatic Polyesters

The thermal stability of furanic-aliphatic polyesters was studied by TGA under a nitrogen atmosphere. The values of their thermal transitions and degradation temperatures are summarized in Tables 2 and S5. As shown in Figure 10a, regardless of the diol chain length, a similar degradation profile was observed for polyesters synthesized in U-ChCl. The obtained polyesters typically show a one-step degradation pattern and decompose at a temperature around 390 °C. The representative thermal degradation features of PDOF synthesized in all media are depicted in Figure 10b. PDOF obtained from enzymatic polymerization in all media possesses comparable thermal stability.

As shown in Tables 2 and S5, all obtained polyesters' profiles are similar and represented by the DSC curves of PHF obtained from U-ChCl, depicted in Figure 11a. The endothermic peak is very broad, which indicates multiple melting points around 110 °C ( $T_{m1}$ ) and 120 °C ( $T_{m2}$ ), as observed in the first heating cycle. Similarly, this multiple  $T_m$



**Figure 11.** DSC curves of FPEs from the enzymatic polymerization conducted in U-ChCl using the one-step method: (a) PHF heating and the cooling scan profile, (b) cooling scan profile of FPEs, (c) second heating scan profile of FPEs, (d)  $T_g$  appearance from the modulated DSC heating scan of FPEs.

appeared at 104 and 119  $^{\circ}\text{C}$  in the second heating scan. In the cooling curve, we observe a crystallization temperature ( $T_c$ ) at 99  $^{\circ}\text{C}$ . All furanic-aliphatic polyesters synthesized in U-ChCl possess a  $T_m$  of between 68 and 123  $^{\circ}\text{C}$  and a  $T_c$  of between 64 and 102  $^{\circ}\text{C}$  (see Figure 11b,c). A similar thermal transition profile was also observed for the furanic-aliphatic polyesters

synthesized in Gly-ChCl and ILs, summarized in Table 2. The glass transition temperature ( $T_g$ ) was determined from the modulated DSC heating scan. The  $T_g$  of the obtained furanic-aliphatic polyesters was observed at values ranging from 3 to 12  $^{\circ}\text{C}$  (see Figure 11d and Table 2). The  $T_m$  and  $T_g$  of all obtained FPEs show a decreasing trend with an increase in the

chain length of the diol units. This result was in agreement with our previous studies and can be explained due to the increase in chain flexibility and a reduction in the density of hydrogen bonds and  $\pi$ - $\pi$  stacking.<sup>17,76</sup> All synthesized furanic-aliphatic polyesters are found as semi-crystalline materials and can be recrystallized upon cooling from the melt.

In agreement with the DSC results, the wide-angle X-ray diffraction (WAXD) spectra confirmed that the obtained furanic-aliphatic polyesters possess a semi-crystalline structure. As shown in Figure S9a, all of the obtained PDOF exhibits a similar pattern with one strong diffraction peak at 24.12° and two weak signals at 17.8 and 9.92°. These results match our previous work on furanic-aliphatic polyesters produced by a two-stage method in an organic solvent, diphenyl ether.<sup>43</sup> The WAXD spectra of all furanic-aliphatic polyesters synthesized in U-ChCl are shown in Figure S9b. They have similar diffraction peaks at round 24.12–25.10°, 16.76–17.85°, and 9.92–13.76°.

### 3.7. Greener Product Purification

Chloroform, which usually becomes a preferred solvent in the purification of polyesters, is considered a harmful chemical. Hence, to address this issue, we tested a greener purification method on PDF synthesized in BMIMPF<sub>6</sub> and U-ChCl. Due to their low solubility in organic solvents, separation of ILs and DESs typically can be executed by a simple extraction process.

The recovery procedure of BMIMPF<sub>6</sub>, a hydrophobic ILs, was conducted as follows: methanol was directly added to the crude reaction mixture, followed by standard filtration to separate the enzyme and molecular sieve from the solution. After that, the solution was cooled to -20 °C for 1–2 h resulting in a precipitated PDF product. PDF precipitates are then collected and separated from the liquid phase containing methanol and BMIMPF<sub>6</sub>. As shown in Figure S7, the <sup>1</sup>H NMR product shows relatively high purity, free from BMIMPF<sub>6</sub>. Using a rotary evaporator, we then separated the remaining nonvolatile BMIMPF<sub>6</sub> from volatile methanol, resulting in a pure solvent that can be reused.

When the reaction was complete, the PDF product was discovered detached from the U-ChCl. As a result, the PDF can be easily separated from the U-ChCl following the reaction. Nevertheless, we discovered that some enzyme beads remained attached to the product. To obtain a pure product, a suitable solvent must be used; instead of chloroform, we can use DCM, which is less harmful than chloroform. Additionally, we used the extraction method to perform the U-ChCl recovery procedure. The crude reaction mixture was added with a saturated salt solution (as the aqueous phase) and DCM (as the organic phase). Subsequently, a solution with an upper organic phase containing PDF and a lower aqueous phase containing U-ChCl was obtained and separated using a separation funnel. Then, a pure PDF product could be obtained by evaporating the DCM using a rotary evaporator (see Figure S7). The isolated DCM can be reused for another purification.

## 4. CONCLUSIONS

This work demonstrates a successful synthesis of bio-based furanic-aliphatic polyesters via enzymatic polymerization in green solvents, i.e., ILs and DESs, with a yield of up to 56%. We found that the reaction in tested ILs, BMIMPF<sub>6</sub> and EMIMBF<sub>4</sub>, resulted in polymers with a comparable degree of polymerization ( $\overline{DP}_w$ ) using a one-step enzymatic polymerization. These results show that both ILs are suitable for

CALB-catalyzed synthesis of furanic-aliphatic polyesters. For the reaction in DESs, U-ChCl displayed a steady performance for 72 h, while Gly-ChCl showed better performance in a shorter reaction time (6 h). This can be explained by the enzyme instability in the Gly-ChCl reaction system, glycerol possibly trapped to the enzyme active site. Consequently, glycerol can compete with the esters as a cosubstrate or change the initial composition of the eutectic mixtures. In our system, sufficient agitation during the reaction can prevent these problems and significantly improve the reaction condition. Furthermore, we found that FPE polymerization in ILs shows better results compared to that in DESs. The hydrogen-bond network of DESs, which depends on the eutectic mixture composition, can affect their physical–chemical properties. Therefore, this will have a significant effect on enzyme activity. All of the obtained FPEs are semi-crystalline materials and thermally stable with a decomposition temperature of around 390 °C.  $T_m$  and  $T_g$  of all obtained FPEs are between 82 and 123 °C and 3 and 12 °C, respectively. On the other hand, we found no significant improvement in the yield and molecular weight of PDFs when a two-step enzymatic polymerization was applied. Finally, we demonstrate the recyclability of both ILs and DESs via a simple extraction method in the purification step. This highlights that we successfully enhanced the sustainability of the whole process for furanic-aliphatic polyester production and complied with the requirements for sustainable polymers.

In future research, we will focus on greener methods to purify the products. While to optimize enzymatic polymerization in DESs, future work should investigate the composition of DESs and the water content in the reaction. In addition, a two-step polymerization method using vacuum and various temperatures will be taken into account to discover the best condition for enzyme catalysis in ILs and DESs to elevate the yield and molecular weight of a product. Since it is essential to scale up this system for the manufacturing industry, a higher yield relative to above 60% and higher molecular weights are preferable, and this will be the focus of future studies.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acspolymersau.2c00035>.

Characterization data, data analysis results and table of molecular weights, and dispersities and yield can be found in the supporting information (PDF)

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CRedit: **Fitrilia Silvianti** conceptualization (equal), data curation (lead), formal analysis (lead), investigation (lead), methodology (lead), visualization (lead), writing-original draft (lead), writing-review & editing (equal); **Dina Maniar** conceptualization (supporting), methodology (equal), project administration (supporting), supervision (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Laura Boetje** investigation (supporting), writing-review & editing (supporting); **Albert Jan Jacob Woortman** methodology (supporting), writing-review & editing (supporting); **Jur van Dijken** methodology (supporting), writing-review & editing (supporting); **Katja Loos** conceptualization (equal), funding acquisition (lead), methodology (equal), project administration (lead), resources (lead), supervision (lead), writing-original draft (equal), writing-review & editing (equal).

### Notes

The authors declare no competing financial interest.

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