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Published in:
Sustainability & Green Polymer Chemistry Volume 2

DOI:
[10.1021/bk-2020-1373.ch001](https://doi.org/10.1021/bk-2020-1373.ch001)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

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Citation for published version (APA):

Silvianti, F., Maniar, D., Boetje, L., & Loos, K. (2021). Green Pathways for the Enzymatic Synthesis of Furan-Based Polyesters and Polyamides. In H. N. Cheng, & R. A. Gross (Eds.), *Sustainability & Green Polymer Chemistry Volume 2: Biocatalysis and Biobased Polymers* (Vol. 2, pp. 3-29). (ACS Symposium Series; Vol. 1373). American Chemical Society. <https://doi.org/10.1021/bk-2020-1373.ch001>

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Chapter 1

Green Pathways for the Enzymatic Synthesis of Furan-Based Polyesters and Polyamides

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The attention towards the utilization of sustainable feedstocks for polymer synthesis has grown exponentially in recent years. One of the spotlighted monomers derived from renewable resources is 2,5-furandicarboxylic acid (FDCA), one of the most promising bio-based monomers, due to its resemblance to petroleum-based terephthalic acid. Very interesting synthetic routes using this monomer have been reported in the last two decades. Combining the use of bio-based monomers and non-toxic chemicals via enzymatic polymerizations can lead to a robust and favorable approach towards a greener technology of bio-based polymer production. In this chapter, a brief introduction to FDCA-based monomers and enzymatic polymerizations is given, particularly focusing on furan-based polymers and their polymerization. In addition, an outline of the recent developments in the field of enzymatic polymerizations is discussed.

Introduction

Polymers are macromolecules that consist of many small molecular fragments known as repeating units (1). Allocated by their origin, polymers can be classified as natural or synthetic polymers. Natural polymers can be found in living organisms, for example, lignocellulose, starch, proteins, DNA, and RNA. Synthetic polymers are conventionally produced via the polymerization of simple building blocks and can be tailored to meet specific demands. Driven by the establishment and advancement of common polymerization techniques, the growth of synthetic polymers was prominent in the early twentieth century (2), which led to a significant rise in the consumption of this class of materials.

Polymers are known as ubiquitous and valued materials that play an important role in our daily lives due to their broad range of applications, such as in packaging, coatings, fibers, adhesives, foams, and specialty polymers. However, the massive demand for polymeric materials was accompanied by a

severe environmental problem. The polymer industry is mostly dependent on the fossil feedstock and petroleum-based engineering processes (3, 4). This is of great concern as fossil fuels are limited and are expected to be depleted within a few centuries (5–7). As a consequence, the polymer industry faces rising pressure to develop environmentally friendly and sustainable production processes and materials. To address these challenges, it is necessary to develop sustainable polymer materials. One approach that has attracted considerable research effort is the polymerization of monomers or platform chemicals from renewable resources. Hence, the synthesis and application of high-performance, sustainable polymers have increasingly attracted the attention of scientists. In addition, sustainable polymers have been developed in recent years due to their eco-friendly advantages and abundance in nature.

For a polymer to be sustainable, it should obey the following four criteria (8–11) (illustrated in Figure 1):

- (1) renewable raw materials, catalysts, and solvents are used;
- (2) green synthesis routes that are clean and prevent waste or toxic chemicals exposure to the environment should be used;
- (3) high energy efficiency of the manufacturing process and applications are required;
- (4) polymers should have a low carbon trace, for example, decomposable polymers or polymers that can be recycled or discarded with a low environmental effect.

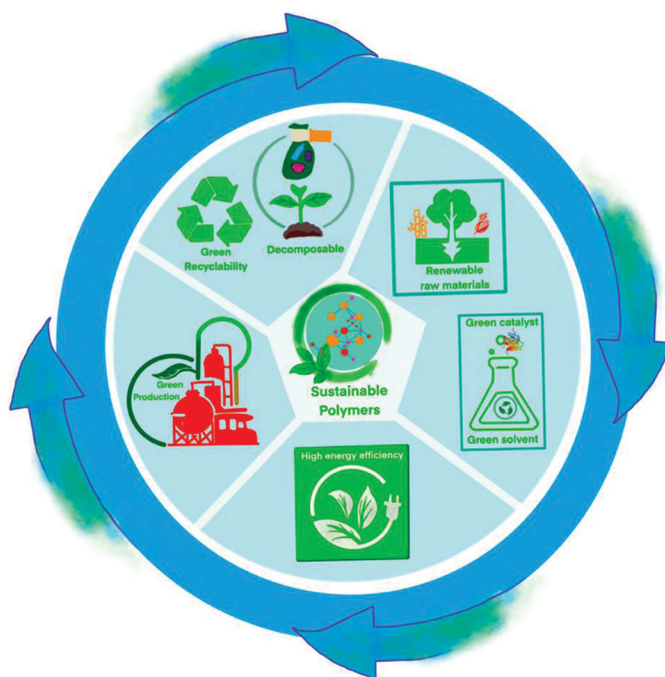


Figure 1. Entangle elements for sustainable polymers.

By utilizing bio-based monomers in enzymatic polymerizations, many requirements of the above-mentioned list can be fulfilled since bio-based monomers, and enzymic catalysts are derived from biomass feedstock, which consists of sustainable materials. Furthermore, the synthesis processes of enzymatic polymerizations are clean and energy-efficient without toxic residuals contaminating the final products and environment (9, 12).

2,5-Furandicarboxylic acid (FDCA) is one of the interesting bio-based furan monomers derived from biomass feedstock for polyesters and polyamides synthesis (13–15). As shown in Scheme 1, FDCA has two dicarboxylic acid groups, that can be used in polycondensation reactions, by esterification it can form dimethyl 2,5-furandicarboxylate (DMFDCA), which is generally used in polymerizations due to the better solubility compared to FDCA. FDCA-based polymers show analogous or even superior thermal and mechanical properties than petrochemical-based polymers, i.e., terephthalic acid (TPA) and isophthalic acid (IPA) based polymers (6, 16, 17). Hence, it is interesting to discover a green approach towards various furan-based polymers and to have the opportunity to explore their potential applications.



Scheme 1. Chemical structure of FDCA and its ester DMFDCA.

Bio-Based Polymers

Recently, there has been growing interest in polymers derived from renewable resources because of their environmentally friendly character and their abundance in nature (8, 17, 18). Many bio-based polymers are commercially available nowadays, i.e., starch, polylactic acid (PLA), poly(butylene succinate) (PBS), polyhydroxybutyrate, polyhydroxyalkanoates (PHAs), poly(ϵ -caprolactone) (PCL), poly(butylene adipate-co-butylene terephthalate) (PBAT), bio-poly(ethylene terephthalate), bio-poly(trimethylene terephthalate) (Bio-PTT), bio-polyamide (Bio-PA), and many others. One can attain polymers from renewable resources by modification of bio-based polymers, via conversion of biomass into monomers along with polymerization or using microorganisms and plants (8, 19).

Bio-based polymers are polymers made from renewable resources and are considered potential replacements for petroleum-based polymers (20–23). These polymers are classified into many types. For example, based on the availability of raw materials, the bio-based polymers can primarily be divided into three groups containing natural polymers, bio-synthetic polymers, and chemical-synthetic polymers (3, 8, 19, 20, 24, 25). Generally, a natural polymer can be directly used or produced by chemical or physical modification, while a bio-synthetic polymer is formed by synthesizing a polymer using organisms and plants, such as PLA, and a copolymer that is synthesized by direct fermentation of metabolically engineered *Escherichia coli* (26). Hereafter, chemical-synthetic polymers are bio-based polymers created from natural resources derived molecules or by the breakdown of bio-based macromolecules via the arrangement of chemical and biochemical methods (3). For example, polyethylene furanoate (PEF) is a bio-based polymer that classifies as a chemical-synthetic polymer. They can be made by 3 steps: (1) catalytic dehydration of fructose in an alcohol medium to form alkoxy-methylfurfural (RMF); (2) catalytic oxidation using acetic acid to produce furandicarboxylic acid (FDCA); and (3) catalytic transesterification polymerization of bis(hydroxyethyl)-2,5-furandicarboxylate in ethylene glycol (EG) (27).

One of the advantages of utilizing bio-based polymers is the lower emissions of carbon dioxide in contrast to conventional petrol-based polymers. The carbon atoms in bio-based polymers result from the atmospheric carbon dioxide; additionally, their incineration does not release extra carbon dioxide to the atmosphere (21, 28). Furthermore, bio-based polymers can have superior characteristics over traditional polymers, e.g., they are eco-friendly, sustainable, decomposable, and so on (29, 30).

Furan-Based Monomers

Shifting from petro-based feedstock to renewable resources can rectify some environmental problems associated with petrochemical extraction and render a sustainable polymer production. A nearly infinite supply of bio-based monomers can be generated from biomass as an origin of raw materials (31). Biomass is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a “material produced by the growth of microorganisms, plants, or animals” (32). Among the various types of biomass, starch, vegetable oil, cellulose, lignin, and proteins are the most widely used sources to generate diverse building blocks for bio-based polymers. Each type of biomass gives access to different types of building blocks, and some of them are already industrially produced (33), as illustrated in Figure 2.

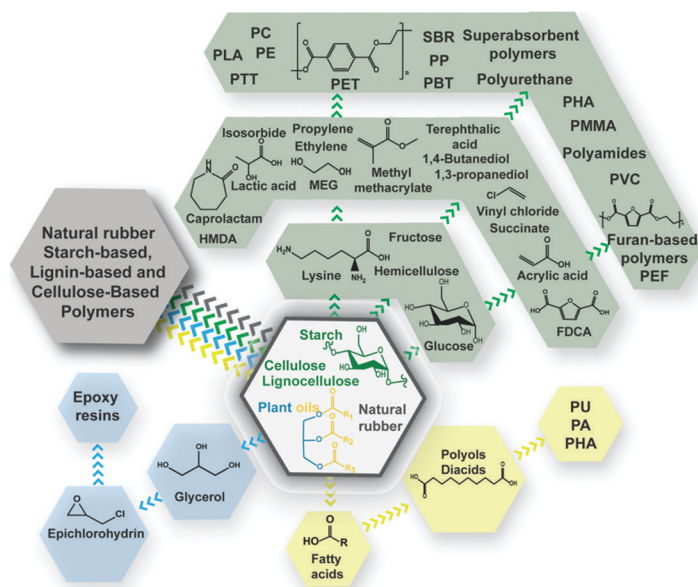
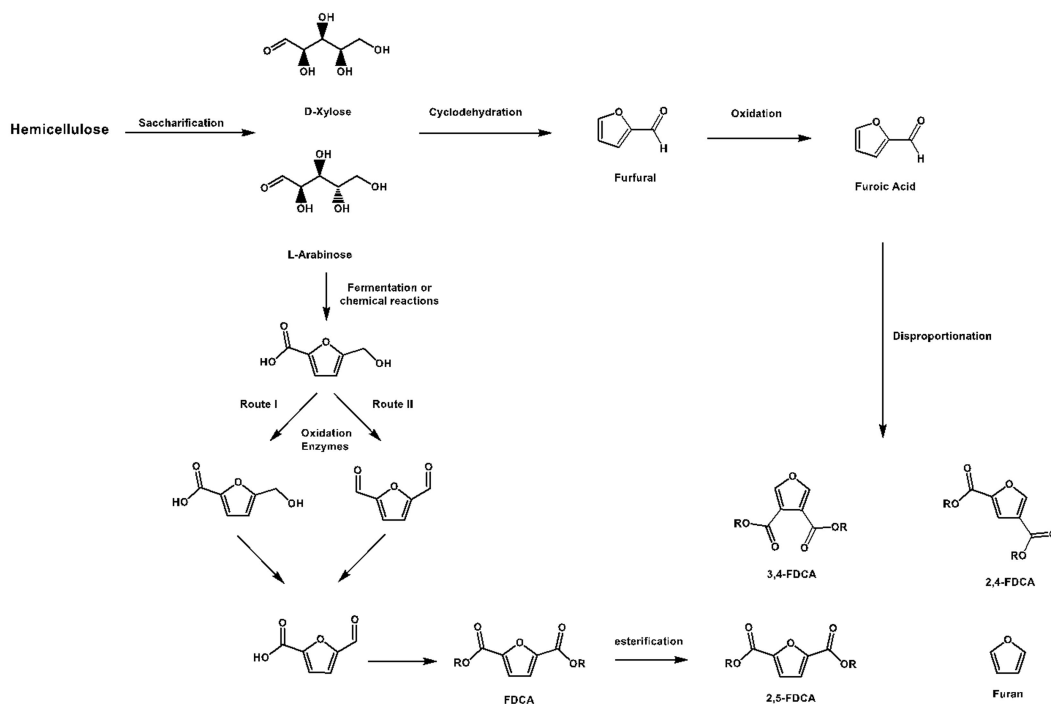


Figure 2. Major conversion pathways from biomass to building blocks and polymers.

Cellulose is one of the main elements of biomass, wood, cotton, and other plant fibers and represents the most abundant organic compound produced by living organisms (34). Hence, cellulose has been the primary raw material of bio-based polymers for nearly the last 150 years (34). The first thermoplastic polymer—celluloid—was developed from cellulose nitrate and nitric acid by Hyatt Manufacturing Company in 1870 and led to the development of an industrial scale of new materials based on cellulose modification (34, 35). 2,5-furandicarboxylic acid (FDCA) is one of the interesting bio-based monomers derived from cellulosic biomass and is used in polyester, polyamide, and poly(ester amide) synthesis (13, 14, 17, 36–38). As already mentioned above, FDCA-based polymers have comparable properties to petrochemical-based polymers, making FDCA valuable as a bio-based monomer (17, 39–42). Within a large variety of renewable building blocks, furan derivatives and furan chemistry occupy a special position in polymer chemistry. The similarity between furan and phenyl rings opens an opportunity for a bio-based alternative for phenyl-based polymers. A whole new chapter in polymer science can be created from furan compounds that are readily prepared from sugars and/or polysaccharides.

Generally, FDCA can be obtained from polysaccharides or sugars by biocatalytic oxidation of 5-(hydroxymethyl)furfural (HMF) (6, 9, 41, 43–45). The biocatalytic oxidation route of HMF to

FDCA using HMF oxidase can occur by two routes (44), as can be seen on Scheme 2. The first presented oxidation of the aldehyde group of HMF into the carboxylic acid, followed by forming 5-(hydroxymethyl)furan-2-carboxylic acid (*route I*), the second oxidation yields 5-formylfuran-2-carboxylic acid, and this will ultimately be transformed into FDCA. In the second place (*route II*), the alcohol group of HMF is oxidized to the analogous aldehyde, forming furan-2,5-dicarbaldehyde, followed by additional oxidations similar to route I yielding FDCA. Another alternative route of FDCA derivation was reported by Fu et al. and van Es et al., they presented the synthesis of 2,5-FDCA using a catalytic conversion of furfural into 2,5-FDCA (46, 47). As can be seen in Scheme 2, after furfural oxidation forming furoic acid, dicarboxylic acids (FDCA) and furan unsubstituted compounds are obtained. Interestingly, not only the 2,5-isomer (70%) but also the 2,4-isomer (30%) and to a smaller amount extent the 3,4-isomer (<5%) are formed (47). Polyesters containing the three different isomers of the furandicarboxylic acid groups, i.e., 2,5-, 2,4- or 3,4-FDCA, and a series of industrially applicable aliphatic diols were already reported using titanium(IV) isopropoxide as a catalyst (37, 48, 49). Currently, as one of the promising monomers for polyesters and polyamides, FDCA is commercially produced by several chemical companies.



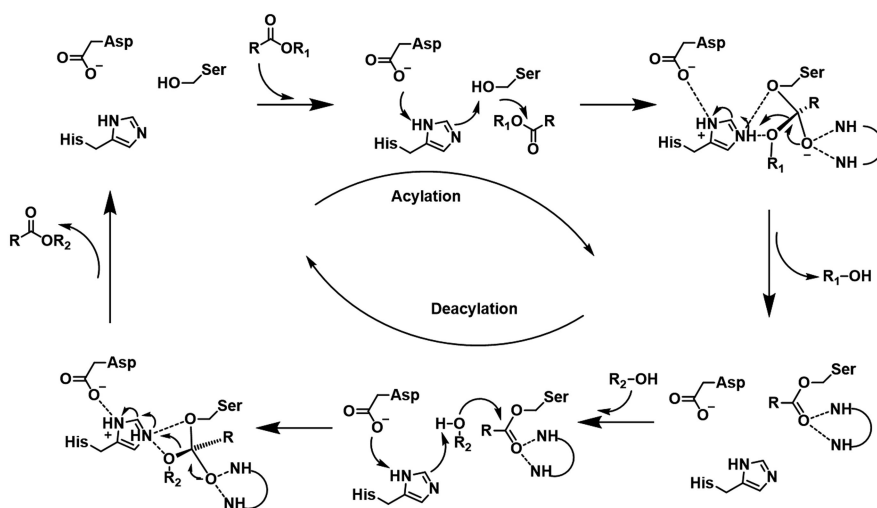
Scheme 2. FDCA derivation routes.

Enzymatic Polymerization

Biocatalytic synthesis of polymeric materials is of interest due to its advantages, e.g., selectivity and considerable environmental impact, etc. Currently, enzymes are already used in the production of food products, i.e., wine, vinegar, cheese, as well as in the manufacturing of products like leather and linen (50, 51). As a catalyst, enzymes are highly efficient, reaction rates can be increased up to 10 billion times than the normal reactions, and enzymes have a high selectivity for specific substrates (50).

Enzymatic polymerization is expressed as an in vitro polymer synthesis (9, 12). Non-toxic enzymes from natural resources can act under mild reaction conditions; hence, enzymatic polymerizations are regarded as an effective technique for developing sustainable polymers and for reducing dependence on fossil fuel resources (9, 52). Recently, many biocatalyzed synthetic routes towards polymers have been explored, including polyesters, polyamides, polylactate, vinyl polymers, etc. (53, 54).

Lipases are popular enzymes in the biocatalytic synthesis of polyesters. Lipases are enzymes that catalyze the hydrolysis reaction of ester bonds in lipids in nature. Water-insoluble long fatty acids from a triglyceride can be hydrolyzed with lipase to form diglycerides, mono-glycerides, and glycerol in aqueous media. As reported by Casas-Godoy et al. (55), a general catalytic reaction cycle of lipases begins with acylation, which involves transferring a proton among the serine, the histidine, and the aspartate residues of the active site of the lipase, resulting in a hydroxyl group activation of the catalytic serine. This serine hydroxyl residue, with consequently enhanced nucleophilicity, reacts with the carbonyl group's substrate. The initial tetrahedral intermediate is produced by a negative charge on the carbonyl group's oxygen. The hole of the oxyanion stabilizes the charge scattering and decreases the state energy of the tetrahedral intermediate by creating no less than two hydrogen-bonds. The next step is deacylation and recovering the active site of the enzyme. In terms of the nucleophile, it depends on the type of reactions; it can be water leading to hydrolysis while an alcohol leads to an alcoholysis reaction. The schematic cycle of lipase catalysis can be seen in Scheme 3.



Scheme 3. General mechanism of Lipases catalysis.

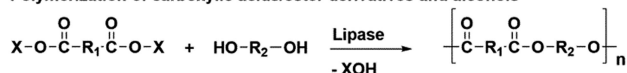
Currently, *Candida antarctica* lipase B (CALB) is a very popular lipase for polyester and polyamide polymerization, because of its high selectivity, wide substrate availability, high thermal stability, and high catalytic performance (9). As mentioned by its name, CALB is isolated from the yeast species *Candida antarctica* and exists in two forms: A and B, entitled as CALA and CALB. The specificity towards substrates of these two forms are different; the A-lipase is working in an unspecified way towards triglycerides and has a low activity regarding simple ester molecules, while the B-lipase by contrast is less working towards big triglycerides but very good towards a wide scope of esters, amides, and thiol molecules (56, 57).

Enzymatic synthesis of polyesters can be performed through three different approaches (Scheme 4): (a) step-growth polycondensation; (b) ring-opening polymerization; (c) an integrating of ring-

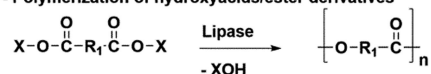
opening polymerization and polycondensation (9). In general polycondensation and ring-opening are the preferred methods.

a) Step-growth polycondensation

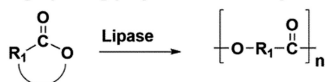
- Polymerization of carboxylic acids/ester derivatives and alcohols



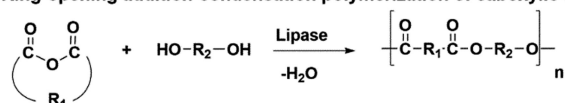
- Polymerization of hydroxyacids/ester derivatives



b) Ring-opening polymerization of cyclic esters



c) Ring-opening addition-condensation polymerization of carboxylic anhydrides



Scheme 4. Main lipase-catalyzed synthesis methods of polyesters.

a) Hydrolysis



b) Esterification



c) Transesterification

- Alcoholysis



- Acidolysis



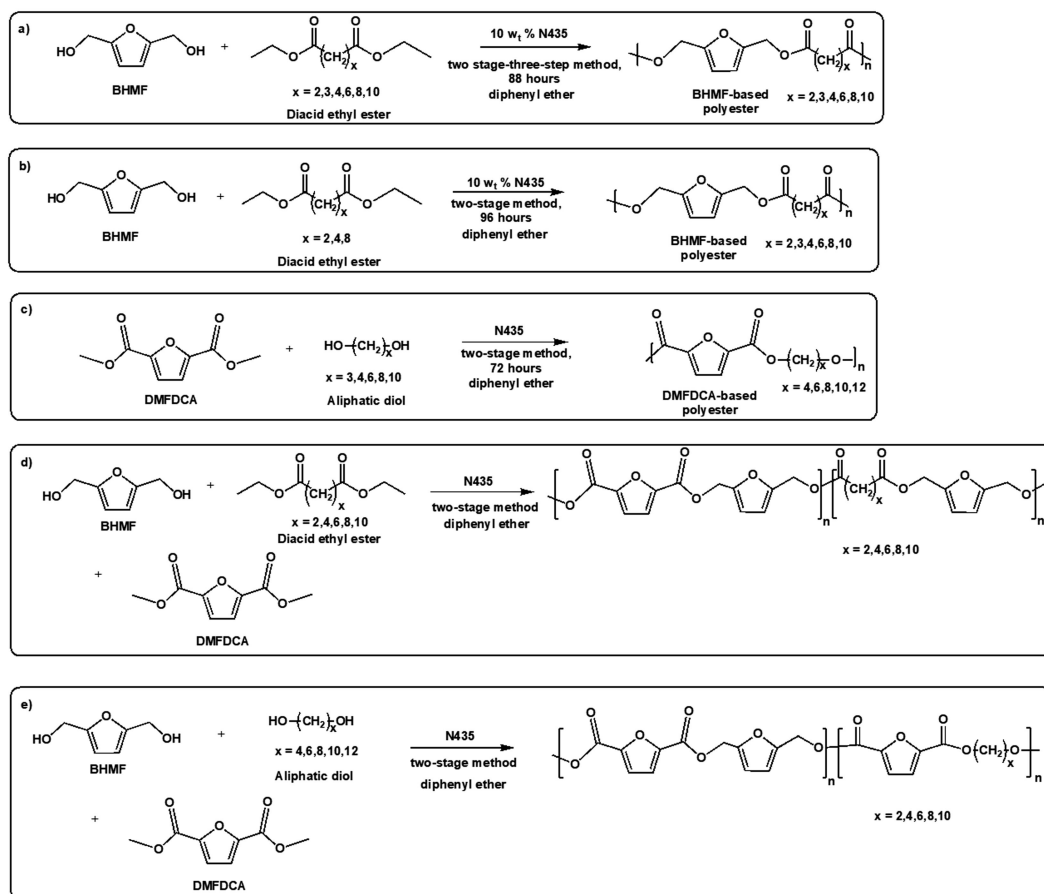
c) Interesterification



Scheme 5. Basic elemental modes lipase-catalyzed reaction on polyesters synthesis.

Lipases can have high catalytic reaction rates when the reactions are performed in nonpolar organic solvents, depending on the solvent hydrophobicity (9, 58–62). Recently, some solvents, which are generally claimed as “green,” for example, ionic liquids (ILs), deep eutectic solvents (DESs), hydrofluorocarbon solvents (HFCs), and supercritical carbon dioxide (scCO₂), were also utilized as a medium for enzymatic polymerization. Some publications reported the enzymatic synthesis of polymers in green solvents, i.e., ring-opening polymerization of ε-caprolactone (PCL) using Novozyme-435 lipase, this reaction was successfully conducted in a hydrophobic ILs, namely 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆), which successfully produced PCL in 85% monomer conversion with a high number-average molecular weight (*M_n*) of 5942

g mol⁻¹ (58). While polylactide was obtained via a CALB-catalyzed ring-opening polymerization of l-lactide in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), achieving M_n 55000 g mol⁻¹ (56). Furthermore, based on the literature review, lipases can catalyze the ring-opening polymerization of caprolactone in DESs (59, 60) which are considered to be green and can be simply arranged from low-cost renewable raw materials (61–63).



Scheme 6. Lipase-catalyzed polymerizations of furan-based polyesters.

Furan-Based Polyesters

One of the most popular 100% bio-based polyesters, poly(ethylene furanoate) (PEF), has been produced and commercialized by Avantium (NL). This polymer is synthesized via the copolymerization of FDCA with monoethylene glycol (MEG). Since both monomers can be derived from initial biomass material, and the obtained PEF is 100% recyclable, PEF is regarded as a bio-based analog to polyethylene terephthalate (PET) (64). In the late 1970s, Moore and Kelly (65, 66) started their studies in the synthesis of furanic-aromatic polyesters. Consisting of furanic and benzenic or furanic rings only in their backbone, this family of furan polyesters became attractive due to their improved mechanical and thermal properties and/or their liquid crystalline properties. For instance, Gandini et al. (67, 68) reported the synthesis of poly(1,4-phenylbismethylene 2,5-furandicarboxylate) (PHBMF), poly(2,5-furandimethylene 2,5-furandicarboxylate) (PBHMF), and poly(1,4-phenylene 2,5-furandicarboxylate) (PHQF). All described polyesters presented high

thermal stability, especially PHQF with a very high decomposition temperature of almost 490 °C. PHQF was revealed to have high crystallinity and no thermal transition appeared below 400 °C, indicating that the melting temperature (T_m) was above its degradation temperature.

Currently, PET is the most produced polyester and is considered as the fourth largest produced polymer in the world, up to 70% of polymers fiber production (2). The total European plastics demand in the packaging market in 2018 reached the highest account at 39.9% per 51.2 million tons, which is predominantly composed of PE, PP, and PET (69). Therefore, it is demanding to develop bio-based alternatives such as PEF.

Table 1. Comparison of Furan-Based Polyesters Obtained by Enzymatic Polymerization of BHMF and Diacid Ethyl Ester (C_x , PE-BHMF-ac); DMFDCA and Aliphatic Diols (C_x , PE-DMFDCA-ol); BHMF, Diacid Ethyl Ester, and DMFDCA (C_x , PE-BHMF-DMFDCA-ac); BHMF, Aliphatic Diols, and DMFDCA (C_x , PE-BHMF-DMFDCA-ol)

Polymer	T_g^a (°C)	T_m^a (°C)	T_d-max^b (°C)	M_n^c (g/mol)	M_w^c (g/mol)	X_c^d (%)	Ref.
C ₄ , PE-BHMF-ac	-19	-	300/446	2200	3400	43	80
	-15	-	268	2800	25400	16	82
C ₄ , PE-DMFDCA-ol	36	169	396	1200	1700	42	79
C ₄ , PE-BHMF-DMFDCA-ac	-8 ^e	-	240 ^e	8900 ^e	16850 ^e	-	81
	-	-	-	1800 ^f	4100 ^f	-	81
C ₄ , PE-BHMF-DMFDCA-ol	15 ^g	142 ^g	370 ^g	1975 ^g	2820 ^g	-	81
	-	118 ^h	370 ^h	1400 ^h	1500 ^h	-	81
C ₆ , PE-BHMF-ac	-38	51/66	319/453	2400	3300	55	80
C ₆ , PE-DMFDCA-ol	16	140	397	2500	3800	37	79
C ₆ , PE-BHMF-DMFDCA-ac	-16 ^e	57 ^{e,i}	250/310/460 ^e	5400 ^e	9300 ^e	-	81
	-	-	-	-	-	-	-
C ₆ , PE-BHMF-DMFDCA-ol	12 ^g	120 ^g	390 ^g	5600 ^g	18000 ^g	-	81
	-0.7 ^h	108 ^h	380 ^h	1620 ^h	2110 ^h	-	-
C ₈ , PE-BHMF-ac	-29	69/79	327/452	2200	3600	55	80
	-22	81	291/443	3000	20400	19	82
C ₈ , PE-DMFDCA-ol	6	141	399	3300	4800	26	79
C ₈ , PE-BHMF-DMFDCA-ac	-19 ^e	62 ^{e,i}	250/310/450 ^e	6350 ^e	11650 ^e	-	81
C ₈ , PE-BHMF-DMFDCA-ol	2 ^g	123 ^g	390 ^g	16050 ^g	35350 ^g	-	81
	7 ^h	88 ^h	390 ^h	3100 ^h	5650 ^h	-	81
C ₁₀ , PE-BHMF-ac	-8	80/85	332/452	2200	3900	65	80
C ₁₀ , PE-DMFDCA-ol	-5	106	402	23700	48700	21	79
C ₁₀ , PE-BHMF-DMFDCA-ac	-19 ^e	79 ^e	280/320/460 ^e	2500 ^e	3450 ^e	-	81
	-	-	-	670 ^f	1800 ^f	-	81
C ₁₀ , PE-BHMF-DMFDCA-ol	6 ^g	90 ^{g,i}	390 ^g	13900 ^g	28650 ^g	-	81
	-	92 ^h	390 ^h	1500 ^h	1600 ^h	-	81

^a Glass transition and melting temperature measured from the second heating scan of differential scanning calorimetry (DSC). ^b temperature at a maximum rate of decomposition measured by thermogravimetric analysis (TGA). ^c M_n and M_w were determined by size-exclusion chromatography (SEC). ^d X_c = degree of crystallinity, calculated from wide-angle X-ray diffraction (WAXD) profile. ^e feed ratio of DMFDCA, BHMF, diacid ethyl ester = 12.5 %: 50 %: 37.5 %. ^f feed ratio of DMFDCA, BHMF, diacid ethyl ester = 50 %: 25 %: 25 %. ^g feed ratio of DMFDCA, BHMF, aliphatic diol = 50 %: 12.5 %: 37.5 %. ^h feed ratio of DMFDCA, BHMF, aliphatic diol = 50 %: 25 %: 25 %. ⁱ Measured from the first DSC heating scan.

Several synthetic routes towards PEF have been developed with polycondensation, and polytransesterification is mainly conducted using conventional two-stage melt-processes utilizing catalyst and reduced pressure (48, 64, 70, 71). However, speaking of eco-friendly polymer

production, we have to consider not only the bio-based polymer itself but also the need to manage the whole production process. Enzymatic polymerizations offer the best solution to overcome the limitations of the conventional methods. They have been proven to be a robust route for polymer production in a sustainable manner with mild reaction conditions, mainly in view of temperature and the use of renewable non-toxic enzyme catalyst (9, 36, 52).

In terms of polymerization methods, several studies revealed useful method guidelines to achieve high molecular weight polyesters, which is necessary for high-performance properties. During the polymerization, four reactions may occur, namely: hydrolysis, esterification, transesterification (alcoholysis and acidolysis), and interesterification (Scheme 5). These reactions are all reversible; hence, it is crucial to maintain the right reaction conditions to obtain high molecular weight polymers. Generally, side reactions and monomer evaporation will lead to a stoichiometric disproportion of reactants; therefore, it is essential to keep a reaction system in balance. Limiting temperature and vacuum during the first stage of polymerization can prevent the evaporation of volatile monomers (72), and the side products, such as water or alcohol, can be removed by vacuum mostly during the second stage of the polymerization (48, 72, 73). Besides vacuum, molecular sieve also can be used to remove side products via adsorption (72). The molecular weight can also be improved by properly increasing the polymerization temperature, extending the time of polymerization, and using the exact amount of catalyst. Based on several studies, the molecular weight of the polymer product via enzymatic polymerization can be significantly influenced by the applied polymerization method, compared to polymerization in bulk, the enzymatic polymerization in the presence of a preferred solvent can be the best method to achieve high molecular weight polymers (74–77). This phenomenon is explained by a lower viscosity of the reaction system, which decreases diffusion constrictions among polymer chain reactants, monomers, and oligomers, while in bulk, the reaction media has a higher viscosity, thereby reducing the diffusion of the reactants (74, 77, 78).

We performed a series of enzymatic polymerizations towards furanic-aliphatic polyesters (79–81). The first study of furan-based polyesters was utilizing 2,5-Bis(hydroxymethyl)furan (BHMF) and several diacid ester (see Scheme 6a) (80), we found that methylene units of dicarboxylic acid significantly influence the thermal stability and crystallinity of the products, both increasing in line with the number of methylene units assembled into the polyesters chain. The recent study by Pellis et al. reports the enzymatic polyester synthesis utilizing BHMF (82). They used three different ester derivatives as co-monomer (see Scheme 6b). The results of thermal stability and M_n were shown to be in accordance with our previous study (80), despite the higher weight average molecular weight (M_w) achieved. A further study was published in 2015 in which we performed an enzymic reaction using DMFDCA and aliphatic diols in order to investigate the effect of diol structures (see Scheme 6c) (79). Besides, to produce high molecular weight polymers, the optimization of reaction conditions such as varied temperature and pressures were studied. Furthermore, recently we reported the enzymatic synthesis of furan-based copolyesters by applying polycondensation methods on DMFDCA and BHMF as the main precursors (see Scheme 6d-e) (81). In this study, we focused on using different furan monomers and changing the incorporated aliphatic chains from diols to diacid ethyl esters. A significant difference in the degree of polymerization (DP) was observed, and it becomes lower when diacid ethyl esters are used (see Figure 3). Besides, the thermal stability and crystallinity were also affected, furan-based copolyesters from diacid ethyl esters were less thermally stable, and some were detected as amorphous materials as can be seen in Figure 4. In Table 1, a comparison of several properties of these polymers is listed.

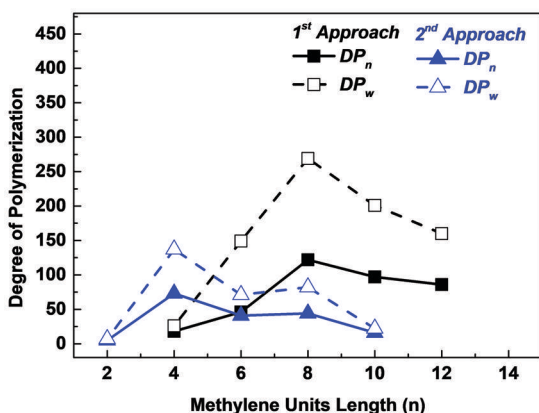


Figure 3. Comparison of degree of polymerization of the furan-based copolyesters using first approach obtained from feed ratio of DMFDCA, BHMF, and aliphatic diols = 50%: 12.5%: 37.5% and from the second approach the feed ratio of DMFDCA, BHMF and diacid ethyl esters = 12.5%: 50%: 37.5%. Reproduced with permission from reference (81). Copyright 2019 John Wiley & Sons.

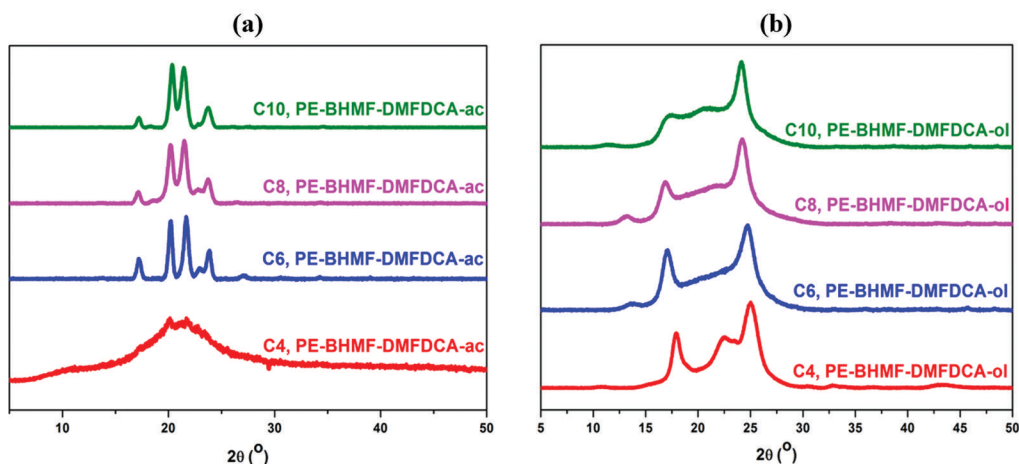


Figure 4. Comparison of Wide-Angle X-Ray Diffraction (WAXD) spectra of the furan-based polyesters from (a) DMFDCA, BHMF, diacid ethyl esters with the feed ratio 12.5%: 50%: 37.5% and (b) DMFDCA, BHMF, aliphatic diol with the feed ratio of 50%: 12.5%: 37.5%. Reproduced with permission from ref. (81). Copyright 2019 John Wiley & Sons.

Furan-Based Polyamides and Poly(ester amides)s

Besides polyester, polyamides are an important family of polymers as they typically exhibit high thermal stability, enhanced mechanical performance, impact strength, and abrasion resistance. Polyamides are generally used as fibers and films for consumer goods, the automotive industry, and electronics. All these appealing characteristics certainly have encouraged studies on furanic polyamides (83–86). FDCA-based polyamides display rather high glass transition temperature (T_g) values and good mechanical performance. The first synthesis of FDCA-based polyamides dates back to 1961 when Hopff and Krieger (87, 88) found that heating of a hexamethylene diammonium FDCA salt resulted in a strong decarboxylation and no discrete polymers were obtained from their attempts. Subsequently, Heertjes and Kok (89) reported that the decarboxylation of FDCA occurred at about 195 °C. They reported polymerization of FDCA, dimethyl 2,5-furandicarboxylate

(DMFDCA), or 2,5-furandicarboxyl dichloride (FDCDCL) with C4, C6, and C8 linear aliphatic diamines and obtained clear, fragile, and light-yellow to brown color FDCA-based polyamides. The T_m of PA-4F, PA-6F, and PA-8F were reported to be 250, 175, and 125 °C, respectively. In contrast, Grosshardt et al (83) reported several amorphous FDCA-based polyamides (PA-6F, PA-8F, PA-10F, and PA-12F) with a T_g ranging from 70 to 110 °C, obtained from the melt-polycondensation using Sn- or Ti-derived catalysts. The companies Avantium and Solvay reported an enhanced method to create higher molecular weight FDCA-based polyamides in two patents (84, 85). Here, Gruter et al. proposed a two-stage polymerization strategy to prevent the occurrence of N-methylation of the poly(amides). In the first stage of the proposed polymerization, DMFDCA and diamines are oligomerized; afterward, the polyamide oligomers are combined by a bifunctional linker.

Poly(ester amide)s are interesting materials as they generally display both characteristics of both polyesters and polyamides. Polyesters freely degrade within hydrolysis of the ester linkage; they are more flexible, and, in general, show better solubility in organic solvents. Due to their hydrogen bonding, polyamides show higher thermal and mechanical robustness. With this combination of features, poly(ester amide)s are mainly suggested for functions that oblige good thermo-mechanical properties, in line with biocompatibility and biodegradation, for example, they would be of high interest for biomedical purposes or as high-performance polymers with lower environmental impact. Surprisingly, compared to the furan-based polyesters and polyamides, recent literature dealing with furan poly(ester amide)s is scarce. Abid et al. (38, 90) developed several furan poly(ester amide)s via bulk polycondensation. They found that the obtained poly(ester amide)s are amorphous polymers, and the increase of the amide fraction is increasing the T_g and decreasing the degradation rate. In a more recent paper, they published the synthesis of sulfonated furanic poly(ester amide)s by coupled simultaneous polyesterification and polyamidation of difuranic diesters and dimethyl 5-sodiosulfoisophthalate (91). Rastogi and Noordover et al. (92) have successfully synthesized novel poly(ester amide)s containing 2,5-furandicarboxylic acid moieties and compared them to the terephthalic acid and isophthalic acid analogs. In a more recent publication, they reported the synthesis of FDCA-based cross-linked poly(ester amide)s via the polymerization of 2,5-bis(4,5-dihydrooxazol-2-yl)furan (2,5-FDCAox) with sebacic acid (93). In addition, the importance of this furan polymer family was also highlighted in a patent on the preparation of biodegradable furan poly(ester amide)s (94). Specifically on FDCA-based poly(ester amide)s, Robert et al. (95) successfully produced it using Titanium(IV) isopropoxide (TIS) as catalyst by melt polycondensation in three stages, i.e. transesterification of DMFDCA to bis(hydroxydecamethylene)-2,5-furan dicarboxylate (BHDF), polyesterification and polycondensation of the co-monomers of BHDF, amido diol and DMFDCA to create poly(ester amide).

As lipases can catalyze the creation of amide bonds, their use as biocatalysts for the in vitro synthesis of polyamides and poly(ester amide)s is clearly attractive. Yet, the lipase-catalyzed polymerization of polyamides has not been studied extensively due to the high T_m and poor solubility of polyamides (9). At temperatures above the T_m of the polyamides, the catalytic activity of lipases decreases significantly because of the protein deactivation and denaturation. In addition, many polyamides can only be dissolved in destructive solvents (concentrated H₂SO₄, formic acid, and trifluoroacetic acid), in which lipases lose their activity.

Nevertheless, some polyamides and oligoamides have been synthesized via an enzymatic pathway (96, 97). In analogy to polyesters, the basic modes of elemental reactions during the polyamide syntheses consist of direct amidation and transamidation (aminolysis) (Scheme 7). The application of vacuum is still necessary for the enzymatic syntheses of polyamides. However, a higher

water amount can be tolerated due to the higher reaction equilibrium constant (hundreds of times larger than for polyesters) (98). Hence, the applied vacuum in the lipase-catalyzed synthesis of polyamides is relatively high in comparison to the polyester analogs (100 to 2 mmHg). Besides that, molecular sieves are also used merged with a vacuum step (99–101).

a) Amidation

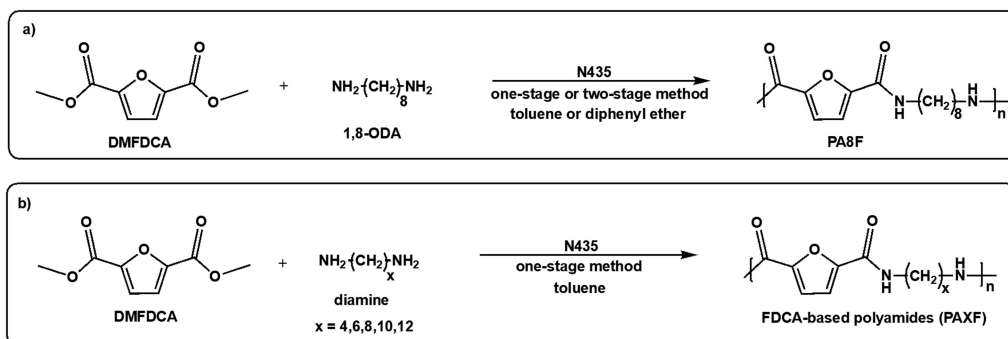


b) Transamidation
Aminolysis



Scheme 7. Basic elemental modes of lipase-catalyzed reactions in polyamide synthesis.

We recently reported various enzymatic pathways towards aliphatic and semi-aromatic polyamides or oligoamides (99, 102–105), including FDCA-based furanic aliphatic polyamides (106). We successfully investigated the enzymatic synthesis of FDCA-based polyamides by focusing on synthesizing poly(octamethylene furanamide) (PA8F) (106) (see Scheme 8a). In this study, the obtained PA8F shows a comparable crystalline structure and thermal stability to poly(octamethylene terephthalamide), which is known as petroleum-based polyamide. We optimized the reaction conditions and found that using 20 wt% of N435 gave the highest yields and M_n on both methods of one stage and two stage. To continue our study on the one-stage method of enzymatic polymerization, we performed the enzymatic synthesis of FDCA-based polyamides by using several bio-based aliphatic diamines with different chain lengths (see Scheme 8b) (107). The enzymatic polymerization kinetics was studied using DMFDCA and 1,8-ODA as the precursors. This study highlighted that the phase separation of FDCA-based oligoamides/polyamides happened in the early stages of reaction and followed to a subsequent enzymatic solid-state polymerization. Furthermore, enzymatic polymerization time could be shortened from 72 ~ 24 hours, which means enzymatic polymerization can be comparable to conventional methods based on the reaction time and the resulting molecular weights (107).

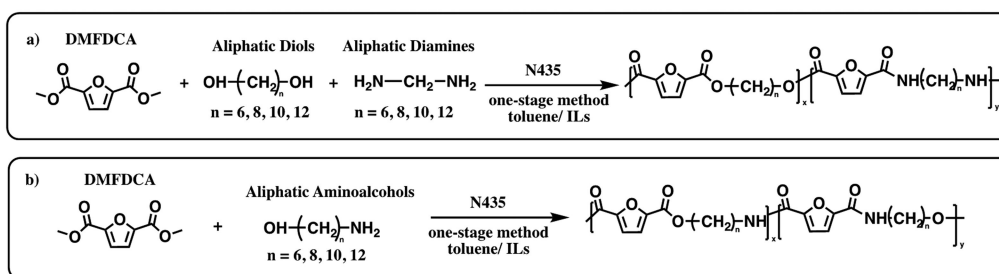


Scheme 8. Lipase-catalyzed polymerization of FDCA-based polyamides.

To the best of our knowledge, despite the extensive studies on enzymatic synthesis of furan polyesters and polyamides, similar studies on furan poly(ester amide)s are very limited up to now, especially on FDCA-based poly(ester amide)s. So far, as we mentioned above, Abid et al. have reported several studies on the synthesis of furan-based poly(ester amide)s utilizing $\text{Zn}(\text{AcO})_2$ as

catalyst (38, 90, 91), Noordover et al. utilized triphenyl phosphite as a catalyst for the poly(ester amide)s synthesis (93), and Robert et al. reported FDCA-based poly(ester amide)s using TIS as catalyst (95).

Recently, we successfully performed an enzymatic polymerization of FDCA-based poly(ester amide)s using two different approaches and reaction media, including ILs, i.e., [BMIM]PF₆ and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF₄) (see Scheme 9) (108). The purpose of using ILs is to improve the sustainability of the whole synthetic process. ILs are reported as green solvents due to their potential of low volatility and low toxicity (109–111), besides they have outstanding catalytic activity and tunabilities (112–114). According to this study, the first novel FDCA-based poly(ester amide)s reported via enzymatic polymerization using N435, achieved high M_n up to 13000 g mol⁻¹ for poly(dodecamethylene furanoate-co-dodecamethylene furanamide) (PEAF12) and high T_m of 92 °C, while the T_{d-max} of this semicrystalline material presented at 395 °C is comparable to PEF, which is around 389 °C (108, 115), see Table 2. Furthermore, we also revealed in this study, the selectivity of CALB towards the substrate, even though characteristically the reactivity of aminoalcohols are more reactive than their diols. On the first approach, using aliphatic diols and aliphatic diamines as substrates successfully obtained the higher molecular weight than the second one using aliphatic aminoalcohols. However, in general, CALB have the same preference towards ester and amide formation.



Scheme 9. Lipase-catalyzed synthesis of FDCA-based poly(ester amide)s from a) DMFDCA, aliphatic diols, and aliphatic diamines and b) DMFDCA and aliphatic aminoalcohols.

Table 2. Comparison of the Thermal Properties of PEF and PEAF12

Polymer	T_g (°C)	T_m (°C)	T_{d-max} (°C)	Ref.
PEF	80.7/88	210/213.8/230	398/567.5	(3, 115)
PEAF12	25	92	395	(108)

ILs and DESs as Alternative Green Reaction Medium

Solvent is one of the important parts in enzymatic polymerization as mentioned above, a preferred solvent can enhance the catalytic activity of lipases and tends to keep a good equilibrium reaction which is related to high molecular polymer product. Improvement and implementation of sustainable solvent media have been a trending topic in the last two decades. ILs are considered to be “green solvents” mostly due to the benefit of their nonvolatile properties as compared to the volatile organic compounds (VOCs) in traditional industrial solvents. Using ILs would avoid the emission of VOCs, a primary source of environmental contamination (116–118). Moreover, they have very

worthy properties as reaction media, due to their high recyclability, low toxicity, low volatility, being less-flammable, and unique solubility for organic and inorganic materials (109–112, 117, 119, 120). In addition, ILs are suitable for enzymatic reactions, as they can stabilize lipases (121, 122). However, for several reasons, ILs are not always considered as “green,” specifically, they can cause water contamination as commonly used chemicals. Furthermore, some ILs syntheses and purifications employed toxic chemicals, yet they can be aimed to be eco-friendly with large possible profits for sustainable chemical (123, 124).

ILs are generally defined as salts with a melting temperature below 100 °C, developed from conventional high-temperature melted salts (116, 117, 120, 122, 125–127). They are liquids that consist of a mixture of salts ionic species, an anion, and a cation. Although both individual species have extremely high melting points, their proper incorporation leads to the creation of a liquid phase that has a lower melting point temperature. This occurs due to an asymmetrical size between the anion and cation, which lean to decrease the lattice energy of salts crystalline form (121, 122). Standard ILs are created from organic cations, for example, 1,3-dialkylimidazolium, tetraalkylammonium, paired with various anions that have a strongly delocalized negative charge (e.g., BF_4 , PF_6 , NO_3 , MeOSO_3 , bis((trifluoromethyl)sulfonyl)imide, or NTf_2) (118, 122). The physical properties of ILs (e.g., density, viscosity, melting points, and polarity) can be easily tuned by the appropriate selection of anions and/or cations (112, 118, 121) – see Figure 5.

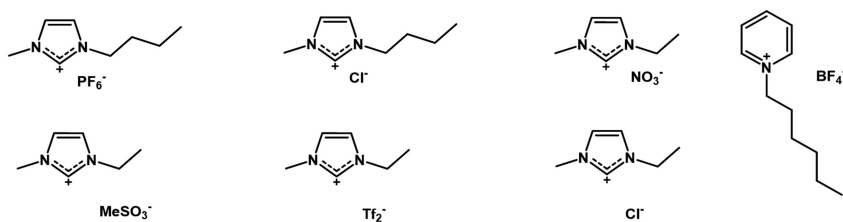


Figure 5. Examples of ILs involving of simple salts.

Another sustainable alternative solvent developed from ILs, called DESs, is emerging recently. Same way to ILs, they consist of a combination of compounds, hydrogen-bond donors and acceptors. DESs are generally obtained by combining two elements, namely, hydrogen-bond acceptor (HBA) and hydrogen-bond donor (HBD), which can be related with each other via hydrogen-bond interactions (61, 128–132). Due to this formation of intermolecular hydrogen-bonds, forming asymmetrical ions with low lattice energy, making DESs generally have a much lower melting point than the individual elements (120, 128, 132). Therefore, as like ILs, it is possible to perform reactions in DESs with a temperature below 100 °C. Moreover, comparing to VOCs, DESs are not measured as volatile and flammable, making them “green solvents.” Currently, the most preferred DESs are created by choline chloride (ChCl), carboxylic acids, and other hydrogen-bond donors, i.e., glycerol, urea, succinic acid, and citric acid (128–130, 133, 134). These are known as cheap chemicals. Therefore, DESs possess advantages of low-cost reaction media compared to ILs. This is valuable since the low production cost was mainly considered for commercial manufacturing. In addition, a mixture of ChCl and glycerol is the most used DESs and is non-toxic, because both individual chemicals are commonly used as food additives (135–138). Some structures of the chemical that can be used to form DESs are shown in Figure 6.

Based on the literature, several applications of DESs have been reported, i.e., separation processes (120, 139, 140), carbon dioxide adsorption (141, 142), biomass processing (129, 131, 143), electrochemical processes (132), bio-catalysis (59, 144), polymerization reaction (62, 128,

145), and so on. Related to our interest, some papers reported good catalytic activity of enzymes in DESs, including enzymatic polymerization with a lipase (60, 144, 146–148). It was discovered that CALB effectively produces polymers by ring-opening polymerization of caprolactone using DESs (60). Lipase-catalyzed polymerization of furan-based polyester(amide)s using ILs have been successfully produced in our group, as explained above (see Scheme 9). This shows that alternative green solvents can be a good medium for the enzymatic polymerization of furan-based polymers.

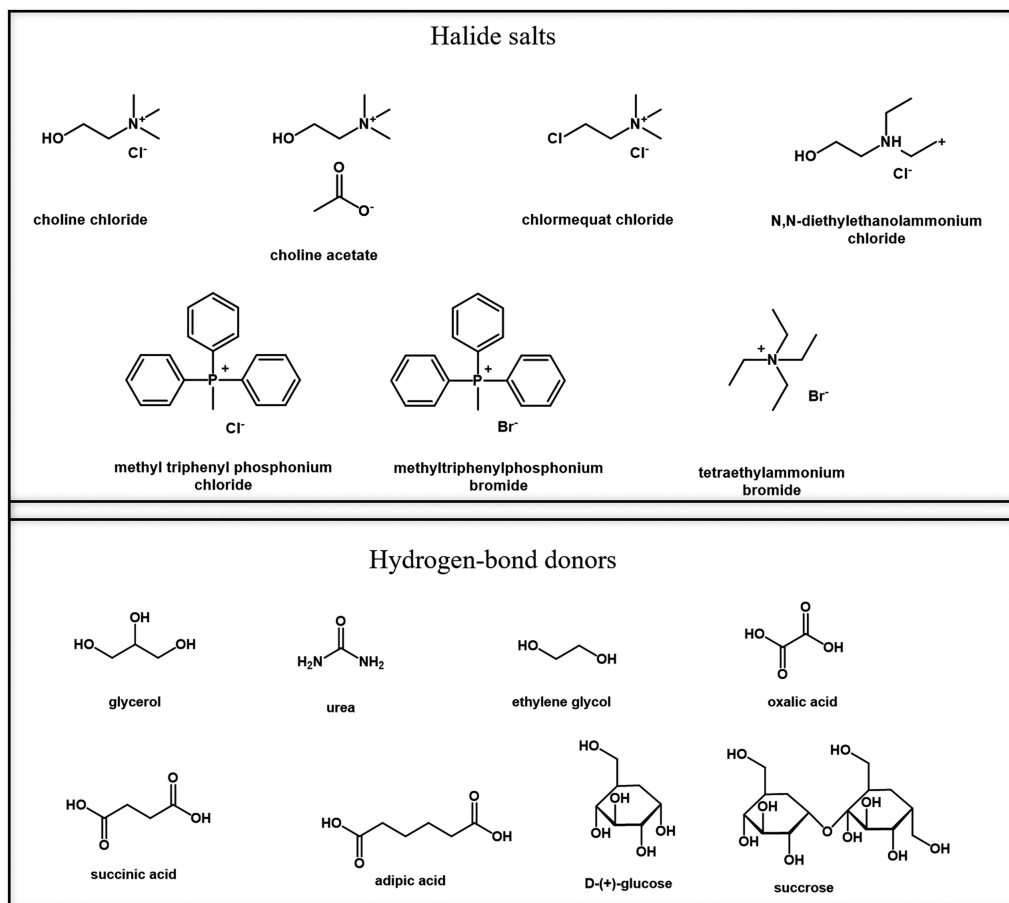


Figure 6. Structures of some halide salts and hydrogen-bond donors used in the formation of DESs.

Conclusion

The enzymatic polymerization of furan-based polymers is highlighted as a favorable green technology towards sustainable polymers. Based on several articles, enzymatic polymerization is recognized to be a robust green technique for the production of bio-based polyesters and polyamides, especially for FDCA-based polyesters, that are considered as an alternative for petroleum-based PET.

The enzymatic polymerization of furanic polyesters and polyamides was extensively reported in the past few years. In terms of the synthetic methods, decades of research have provided a useful guide about which parameters are affecting the enzymatic reaction systems for polyester or polyamides synthesis, even broadened to poly(ester amide)s. The effect of polymerization conditions such as the polymerization parameters including solvents, oligomeration time, vacuum, catalyst

dosage, and the usage of several co-monomers was investigated in regard to reaction optimization to achieved high molecular weight materials.

The core significance of this method as a green process obviously offers a solution to issues in furan-based polymers synthesis in general. However, in specific terms, for sustainable polymer production, it is essential that the entire procedure be “green,” from the starting materials, synthetic process, disposal, and energy consumption. Hence, future studies should focus on a green method of the whole process in enzymatic polymerization, for instance, by using green media such as ILs and DESs. As presented, several combinations of molecules can be chosen to form ILs or DESs. Choosing the appropriate medium is essential because it can affect the yields and especially the molecular weight of polymers. On the other hand, besides pursuing the optimization of the green synthetic process, economic considerations should be taken into account for the competitive scale up in the manufacturing industry, for example, by focusing on low-priced chemicals and performing the synthetic process at low energy consumption.

Currently, the development of enzymatic polycondensations of FDCA-based polymers using several ILs and DESs is conducted in our group to accomplish this goal of greener enzymatic polymerization routes.

Acknowledgments

Fitrilia Silvianti gratefully acknowledges the financial support from the Industrial Human Resource Development Agency of the Ministry of Industry of the Republic of Indonesia (BPSDMI, Kemenperin) and Politeknik ATK Yogyakarta.

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