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A Greener Approach to 2,5-Furandicarboxylate Macrocycles and their Entropically Driven Ring Opening Polymerization

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Thermoplastic polyesters (PEs), with their versatile properties, are indispensable in everyday life. However, increasing concerns about the environmental impact of fossil-based polymers have driven research into renewable alternatives. Among bio-based polymers, furan-derived PEs such as poly(ethylene furanoate) (PEF) have garnered significant attention. The synthesis of PEF, as well as other similar 2,5-furandicarboxylic acid (FDCA)-based polymers, is mainly based on bulk polycondensation (PC) that in general requires elevated temperatures and low pressure, making the process energy-intensive and vulnerable to thermo-oxidative degradation. In this view, entropically driven ring opening polymerization (ED-ROP) might represent an interesting potential alternative since it requires milder conditions and is intrinsically more atom economic. From these premises, this work focuses on developing an alternative synthetic strategy to bio-based PEs through ED-ROP of macrocycles derived from FDCA dimethyl ester (FDME). These macrocycles were prepared by reacting FDME with diols via pseudo-high dilution condensation (PHDC) using dibutyltin(IV) oxide as a catalyst and cyclopentyl methyl ether as a recyclable green solvent. Isolation of the pure macrocycles is achieved by simple crystallization from the reaction mixture. Subsequent ROP of pure macrocycles is investigated as a viable route to prepare the related PEs in mild reaction conditions.

1. Introduction

Thermoplastic polyesters (PEs) are widely used in industries such as packaging, textiles, electronics, and smart materials, demonstrating their versatility and importance. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are among the most significant PEs which have become indispensable in our daily life.[1,2] However, their reliance on a fossil-derived monomer, terephthalic acid (TA), has significantly contributed to increase greenhouse gas emissions, plastic pollution, and dependence on nonrenewable resources. To address these challenges the integration of bio-based monomers, particularly those derived from abundant renewable biomass has emerged as a greener approach.[3–10]

In recent years, 2,5-furandicarboxylic acid (FDCA)[11] and its ester, FDCA dimethyl ester (FDME),[12] derived from hemicellulosic materials have been extensively investigated as potential substitutes for petroleum-based monomers. Specifically, FDCA is a versatile bio-based platform chemical with applications that extend beyond polymer production, serving also as a key intermediate in organic synthesis, as well as in the development of metal–organic frameworks (MOFs) and pharmaceuticals.[10] As a result, in 2030, FDCA is foreseen to reach a global market value of roughly USD 811.9 million.[13] This bio-based monomer has proven to be very efficient in replacing fossil-based TA, significantly reducing the environmental footprint of polymer manufacturing and promoting the transition to a sustainable and circular economy.[2,14]

In particular, regarding bio-based PEs, poly(ethylene furanoate) (PEF) is the most investigated material for its potential applications in food packaging and textiles. Compared to PET, amorphous PEF has an eleven times better oxygen permeability, and almost twenty times better carbon dioxide permeability indicating superior barrier properties.[15,16] PEF is currently commercialized via the YXY plant-to plastic process by Avantium.[17,18]

Other furan-based PEs, such as poly(butylene 2,5-furanoate) (PBF), poly(propylene 2,5-furanoate) (PPF), and poly(hexamethylene 2,5-furanoate) (PHF), have also garnered significant interest for their promising properties and potential applications.[19]

The typical procedure to synthesize these FDCA-based PEs, including PEF, is via a two-step bulk polycondensation (PC) method involving an initial esterification step of FDCA (or its derivatives) with a diol, followed by a polyesterification step.[20] Although the first report on PEF synthesis dates back to 1946,[21] only a few studies-most notably Moore and Kelly[22] and, more recently, Gandini et al.,[23] Gruter et al.,[24] and Bikiaris et al.,[25]

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have investigated this synthesis, which has remained largely unchanged. Challenges such as high melting point and poor solubility of FDCA were mitigated by using FDME, which offers numerous advantages, e.g., reduced discoloration during polymerization, greater stability, and easier polymer purification.[19,26–29] However, achieving high molecular weights through PC typically requires elevated temperatures and low pressure, making the process energy-intensive and vulnerable to thermo-oxidative degradation.[30] An alternative methodology to overcome these limitations could be preparing these bio-based PEs via ring opening polymerization (ROP). Unlike PC, ROP operates under milder reaction conditions and, most importantly, displays a high inherent atom economy since no by-products are formed during the polymerization.[31] Compared to smaller cyclic oligoesters incorporating 3–12 skeletal ring atoms—e.g., glycolide, lactide, and ε-caprolactone[32,33]—macrocyclic esters with at least 14 skeletal atoms such as macrolactones and macrocyclic oligoesters (MCOs) rely on the entropically driven ROP (ED-ROP).[34–38] In fact, the polymerization of small rings is an enthalpy-driven process due to the relief of ring strain. In contrast, for large macrocycles, polymerization involves only minor enthalpy changes but leads to increased conformational freedom, making the process entropy-driven (ED-ROP).

A significant advantage of ED-ROP is that it can be used as a closed-loop approach for the recycling of PEs; in fact, PEs at their end-life can be thermally cyclodepolymerized to regenerate their corresponding MCOs that in turn can be used as monomers for novel materials, aligning with circular economy principles (**Scheme 1**).[30]

MCOs can be synthesized through various methods, including cyclization or extraction from their corresponding PEs, although traditional PC generally leads to limited amounts of MCOs (Scheme 1).[37] In this view, high dilution condensation (HDC), pseudo HDC (PHDC), and cyclodepolymerization (CDP) are the most used synthetic approaches (Scheme 1).[30,37–39]

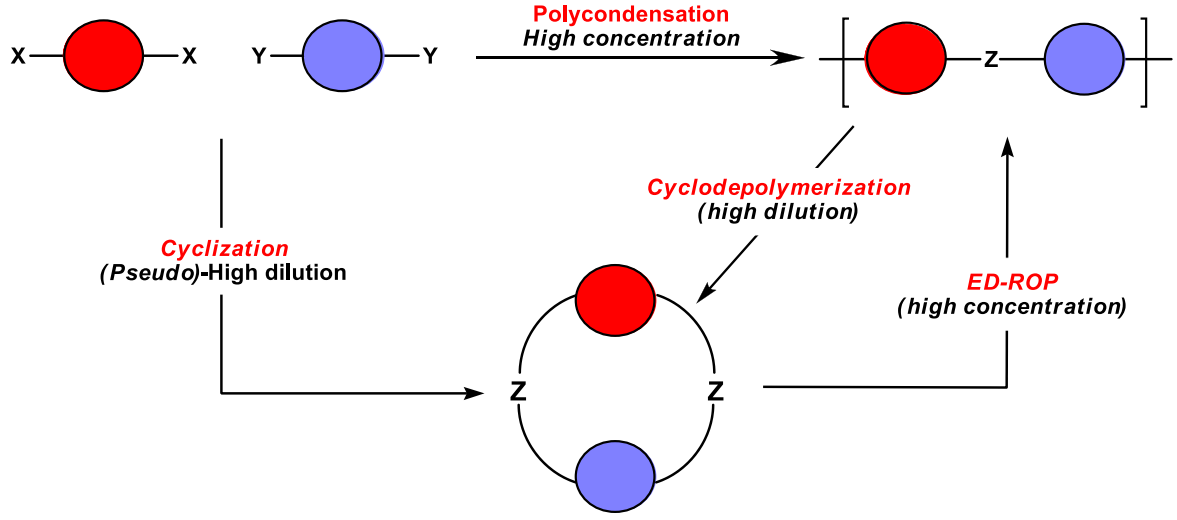
Several examples of bio-based MCOs were reported in the literature, and their ED-ROP was also investigated.[30] Fumaric, succinic, and adipic acids and their esters were among the most studied monomers for the preparation of aliphatic MCOs by reaction with a variety of alkanediols.[40–44] In specific cases, enzymatic cyclization/depolymerization (EC/ED) was also explored with good results mostly using *Candida antarctica* lipase B (CALB).[45–50]

In the case of aromatic cyclic oligoesters, only few examples reported the use of ED-ROP, mostly focusing on MCOs derived from 5-(hydroxymethyl)furfural (HMF) and FDCA. As an example, Ragno and coworkers[51,52] explored the ED-ROP of furan-based MCOs using N-heterocyclic carbene (NHC) catalysts through organocatalytic synthesis. HMF and its derivatives, e.g., 2,5-bis(hydroxymethyl)furan (BHMF) (reacted with dialdehydes) and 2,5-diformylfuran (DFF) (reacted with diols), were all investigated demonstrating the versatility of this approach. The resulting MCOs were isolated in good yields (≈60%) using flash column chromatography. Thus, organocatalyzed ED-ROP was performed leading to PEs with a number-average molecular weight (M_n) of 38 000 that was recently improved via chain extension up to 200 000.[52]

Regarding FDCA-derived MCOs, few studies were recently conducted with the most significant ones summarized in **Table 1**. The so-far reported procedures to MCOs relied on 2,5-furandicarbonyl dichloride and toxic solvents, thus counterbalancing the renewable nature of the furanic bio-based moiety (#1-3; Table 1). Syntheses based on oligomerization (OL) followed by CDP were also investigated. However, these procedures were generally conducted using dichlorobenzene (DCB) as preferred solvent, which is a well-known toxic medium (#4-5; Table 1).[51,53–57] Subsequent ED-ROP of the so-prepared MCOs mixture led to PEF with a M_n value of 30 000.

An interesting alternative procedure used enzymatic catalyst via HDC (#6; Table 1). However, it should be noted that this approach used toluene as solvent and required a reaction time of 7 days.[58]

A common limitation of these studies relies on the fact that ED-ROP was mostly carried out on mixtures of macrocycles that always contain a certain amount of linear oligomers. This affects



Scheme 1. Synthetic approaches to macrocycles and related polymers.

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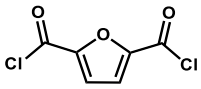
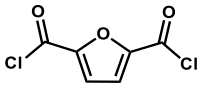
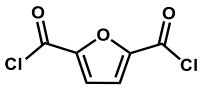
Table 1. FDCA-derived cyclic oligomers and their ED-ROP.

#	FDCA monomer	Diol	Method	MCOs	ED-ROP	M_n	Ref
1		BDO	PHDC	$c(BF)_n$ n = 2-7 not isolated	Mixture of $c(BF)_n$	6000-8000[a]	[53]
2		BDO; EG	PHDC; CDP	$c(BF)_n$ $c(EF)_n$ n = 2-4 isolated HPLC	Mixture of $c(BF)_n$ and $c(EF)_n$	55 000-65 000[b]	[54]
3		BDO; ISOS	PHDC	$c(BF)_n$ $c(IMF)_n$ n = 2-4 isolated flash chromatography	Mixture of $c(BF)_n$ $c(IMF)_n$	39 000-63 000[b]	[55]
4	linOEF	–	OL then CDP	$c(EF)_n$ n = 2-4 isolated by precipitation	Mixture of $c(EF)_n$	–	[56]
5	linOEF	–	OL then CDP	$c(EF)_n$ n = 2-4 isolated by precipitation	Mixture of $c(EF)_n$	30 000[b]	[57]
6	FDME	HDO	PHDC (enzymatic)	$c(HF)_n$ n = 2-4 isolated by precipitation	Mixture of $c(HF)_n$	9100[b]	[58]

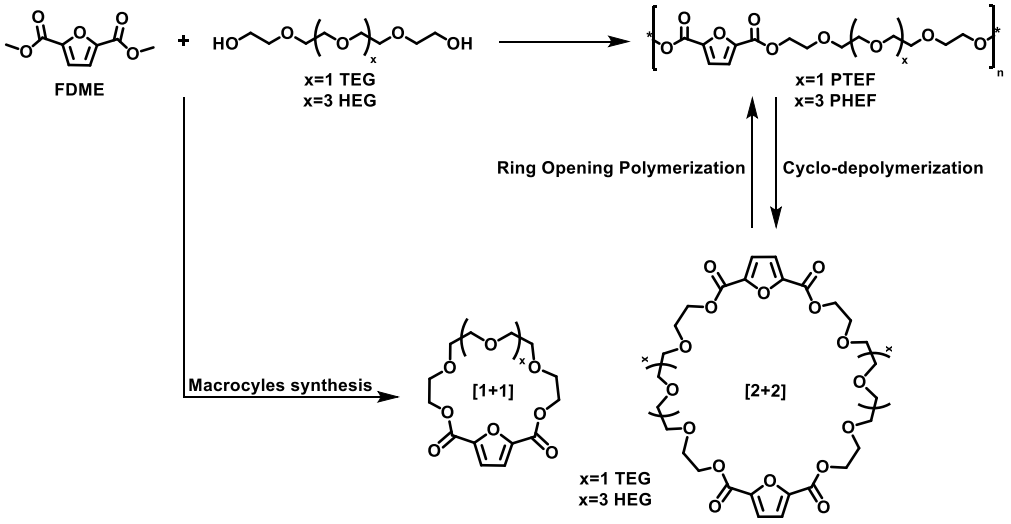
EG = ethylene glycol; BDO = 1,4-butandiol; ISOS = isosorbide; HD = 1,6-hexanediol; $C(EF)_n$ = cyclic ethylene 2,5-furandicarboxylate; $c(BF)_n$ = cyclic butylene 2,5-furandicarboxylate; $c(IMF)_n$ = cyclic isosorbide furandicarboxylate; $c(HF)_n$ = cyclic hexylene 2,5-furandicarboxylate; linOEF = short oligomers of (ethylene furanoate); PHDC = (pseudo)-high dilution condensation; OL = oligomerization; CDP = cyclodepolymerization. [a]Calculated via ^{1}H-NMR analysis. [b]Calculated via gel permeation chromatography (GPC).

the starting material purity, which is required to achieve high molecular weight materials.

From these premises, the present work aims to develop a greener route to FDME-derived MCOs and investigate the subsequent ED-ROP of pure macrocycles (**Scheme 2**). To identify the most effective promoter for MCOs preparation, a preliminary screening on the transesterification of FDME with ethylene glycol monomethyl ether (EGME) was conducted. Afterwards, the best-found promoter was tested for MCOs synthesis with different glycols e.g., tetraethylene glycol (TEG) and hexaethylene glycol (HEG) in PHDC. Finally, the obtained macrocycles were subjected to ED-ROP to evaluate their performance as monomers and assess the properties of the resulting PEs.

2. Results and Discussion

In order to find the best promoter for the cyclization of FDME with the diols selected for this study, namely TEG and HEG, preliminary investigations were conducted on the transesterification of FDME with EGME. The latter glycol was selected as reagent so to avoid the formation of oligomers that could arise in the presence of a diol. Transesterification trials were conducted at reflux temperature for 6 h using cyclopentyl methyl ether (CPME) as green solvent (**Table 2**). Conversion of FDME and reaction selectivity towards either the bis(2-methoxyethyl) furan-2,5-dicarboxylate **1** and 2-(2-methoxyethyl) 5-methyl furan-2,5-dicarboxylate **2** were evaluated by gas chromatography-mass spectrometry (GC-MS).



Scheme 2. Overview of bio-based FDME derived MCOs and polymers investigated in this work.

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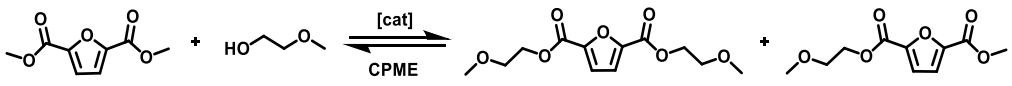
Table 2. Catalyst screening for the transesterification reaction between FDME and EGME.



FDME EGME 1 2

#	Base/acid [0.5 eq. mol]	Conv. [%]	Selectivity [%]	
			1	2
1	K_2CO_3	79	45	55
2	TBD	84	38	62
3	DBU	79	45	55
4	DABCO	16	0	100
5	Bu_2SnO	89	59	41
6	$Bi(OTf)_3$	29	90	10

Reaction conditions: FDME (1.08 mmol) and EGME (2.17 mmol) were dissolved in CPME (5.0 mL), and the promoter (0.5 eq. mol) was added to the solution. The reaction mixture was left under stirring for 6 h at reflux temperature. Conversion and selectivity were determined via GC-MS.

For this screening, basic (#1-4; Table 2) and acidic (#5-6; Table 2) promoters were tested. Bases such as potassium carbonate (K_2CO_3), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) led to high substrate conversions (79–84%) while exhibiting moderate selectivity toward the desired product **1** (#1-3, Table 2). K_2CO_3 and DBU turned out to be the best bases with an evaluated yield of ≈35% of **1**. Among the acid promoters, dibutyltin(IV) oxide (Bu_2SnO) was the most efficient one, achieving the highest conversion rate of 89% with good selectivity toward the symmetrical compound **1** (#5; Table 2). In contrast, bismuth(III) trifluoromethanesulfonate ($Bi(OTf)_3$), although demonstrating the highest selectivity for the wanted molecule, showed only moderate conversion (#6; Table 2).

Considering these results, Bu_2SnO was selected as the most effective promoter for the synthesis of MCOs.

2.1. Macrocycle Synthesis

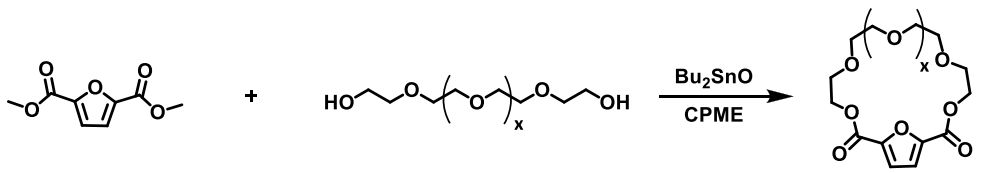
PHDC was selected as an alternative procedure to common cyclization reactions as this methodology avoids the use of an excess of solvent making the process greener. In a typical reaction, a solution of Bu_2SnO in CPME was heated at the reflux temperature in a three-necked flask equipped with a Dean–Stark apparatus. FDME (5.43 mmol) and the selected glycol were dissolved in CPME and transferred to a dropping funnel. The monomer mixture was then added dropwise under nitrogen flow, and once the addition was finished, the solution was left reacting overnight. The final monomer concentration was calculated to be 5.0 g L^{-1}.

After cooling, CPME was distilled off under vacuum and recycled in subsequent trials. High-resolution mass spectrometry (HR-MS) analyses of the crude reaction mixture (Figure S5 and S6, Supporting Information) confirmed the formation of several macrocycles with [1 + 1] and [2 + 2] being the ones formed in larger amounts (**Scheme 3**).

In preliminary trials, purification was conducted by column chromatography leading to the recovery of the smallest macrocycle obtainable with TEG and HEG, namely FDE-18-crown-6 and FDE-24-crown-8, respectively. However, subsequent attempts led to the discovery of a simpler purification technique. In fact, it was possible to isolate both MCOs by precipitation after the addition of hot ethyl acetate to the dried reaction mixture. FDE-18-crown-6 and FDE-24-crown-8 were both recovered as white crystals in ≈30% yield. Characterization of these macrocycles confirmed the proposed structures, and HR-MS analyses proved the purity of these compounds.

Both cyclization reactions were then tested on a larger scale at higher concentration (9.0 g L^{-1} instead of 5.0 g L^{-1}; see #2 and #4; **Table 3**). In these trials, FDE-18-crown-6 and FDE-24-crown-8 were recovered with similar isolated yields using the same purification technique.

Avoiding column chromatography for purification, combined with the possibility to recycle the reaction media, represents an improved greener approach to the related bio-based



FDME x=1 TEG x=3 HEG x=1 FDE-18-crown-6 x=3 FDE-24-crown-8

Scheme 3. Macrocycles synthesis via PHDC.

Table 3. Macrocycles synthesis via PHDC.

#	FDME [g]	Diol [eq. mol]	Conc. [g/L]	Temp. [°C]	Time [h]	Yield [%][a)]
1	1.0	TEG (1.0)	5.0	Reflux	18	**FDE-18-Crown-6** 25
2	5.0	TEG (1.0)	9.0	Reflux	18	**FDE-18-Crown-6** 26
3	1.0	HEG (1.0)	5.0	Reflux	18	**FDE-24-Crown-8** 33
4	5.0	HEG (1.0)	9.0	Reflux	18	**FDE-24-Crown-8** 33

All reaction were conducted using Bu_2SnO as promoter (2.72 mmol, 0.50 eq. mol). [a)]The macrocycles were isolated as pure via precipitation in hot ethyl acetate.

macrocycles. These aspects not only minimize waste but also reduce the environmental impact of the process, making it an effective alternative to conventional methods.

2.2. FDME-Derived PEs by PC and ED-ROP

2.2.1. PTEF and PHEF Synthesis via PC

Before subjecting the pure macrocycles to ED-ROP (**Scheme 4**, Equation 1), the related PEs, e.g., poly(tetraethylene 2,5-furandicarboxylate) (PTEF) and poly(hexaethylene 2,5-furandicarboxylate) (PHEF), were prepared through conventional PC (Scheme 4, Equation 2).

The polymerizations were carried out using an adapted two-stage procedure.[59] In this approach, FDME and the diol in 1.0:2.0 mol ratio were first heated from 150 °C to 170 °C under nitrogen atmosphere in the presence of the selected catalyst, titanium(IV) butoxide (TBT, 0.0012 eq. mol). Thus, an additional mole equivalent of FDME was added to ensure complete glycol consumption, and the temperature was increased to 230 °C under vacuum (**Table 4**). The so-formed PTEF and PHEF were purified by dissolving the final products in chloroform and then precipitating the polymers in an excess of cold methanol. PTEF and PHEF were collected by centrifugation and dried in an oven at 40 °C.

The low yields of the isolated PEs can be ascribed to the challenges associated with the recovery of the polymers. In fact, the polymers obtained were viscous liquids; thus, their isolation through precipitation in cold methanol was quite difficult. This might have led to material loss and thus to the indicated moderate yield.

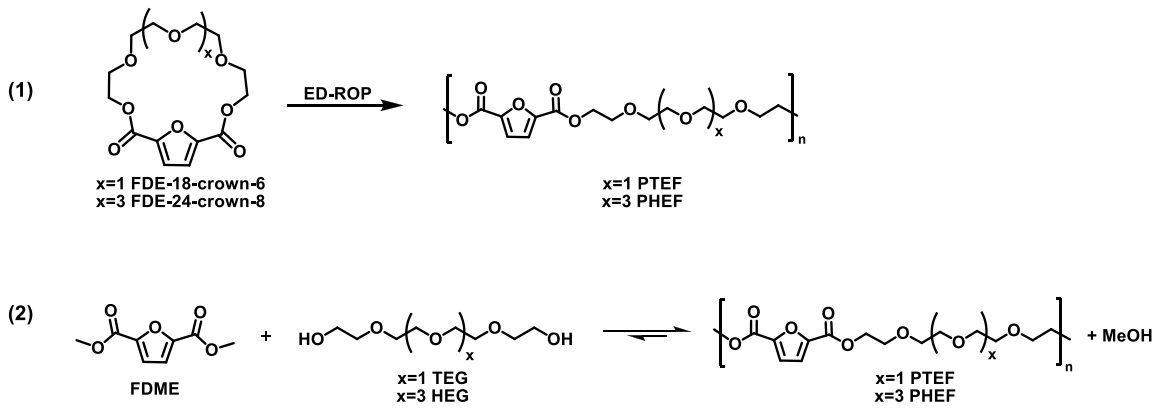
Intrinsic viscosity measurements were then conducted using an Ubbelohde-type viscometer. The viscosity-average molecular weight (M_v) of PTEF and PHEF were calculated using the Mark–Houwink equation using the K and α parameters for PET.[60] M_v values were higher than 27 000 and 40 000 for PTEF and PHEF, respectively.

The DSC thermograms revealed, as expected, sub-ambient glass transition values[61] (T_g) of −7 and −17 °C for PTEF and PHEF, respectively, due to the high mobility and flexibility of oxyethylene subunits. These results are in accordance with the DMTA analysis, displaying in the tan δ trace maximum at −6.6 and −16.9 °C, respectively. The TGA analysis showed that PHEF displayed superior thermal stability than PTEF with a decomposition temperature at 5% weigh loss ($T_{d5\%}$) of 265 °C (PTEF: 197 °C) while the maximum decomposition temperature (T_d) reached 401 °C (#2, Table 4). These values indicate that both the new polymers synthesized here possess a balance between flexibility and thermal resistance.

The XRD patterns for those polymers showed that they have an amorphous nature, displaying a broad halo peak between 2θ 15° and 30° (Figure S25 and S27, Supporting Information).

2.2.2. PTEF and PHEF Synthesis via ED-ROP

$Bi(OTf)_3$ was chosen as the catalyst for ED-ROP based on a previously published procedure reporting ROP of ε-caprolactone and α-methylene-γ-butyrolactone among other small size cyclic lactones.[62,63] Unlike conventional metal catalysts, which often require higher temperatures for activation and may lead to degradation of sensitive monomers or products, $Bi(OTf)_3$ offers milder reaction conditions, preventing the thermal degradation of the macrocycles previously synthesized. The ability of $Bi(OTf)_3$ to operate under such conditions highlights its suitability for the controlled polymerization of sensitive bio-based monomers.



Scheme 4. Synthesis of linear PEs via ED-ROP (top). Synthesis of linear PEs via PC (bottom).

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Table 4. Preparation of linear PTEF and PHEF via bulk PC.

#	PE	Yield [%]	[η] [dL/g]	M_v [Da]	T_g [°C]	$T_{d5\%}$ [°C]	T_d [°C]
1	**PTEF**	34	0.49	27 540	−7	197	380
2	**PHEF**	48	0.63	40 050	−17	265	401

Table 5. Synthesis of PTEF via ED-ROP.

#	FDE-18-crown-6 [g]	$Bi(OTf)_3$ [%mol]	T [°C]	t [h]	Conv. [%]	Yield [%]	[η] [dL/g]	M_v [Da]
1	0.50	0.05	130	3	57	–	–	–
2	0.50	0.05	130	6	76	–	–	–
3	0.50[a)]	0.05	150-160	6	100	20	0.58	36 000
4	0.50[a)]	0.10	150-160	6	100	20	0.32	14 931
5	2.00[a)]	0.05	150-160	6	85	50	0.35	16 943

Reaction conditions: FDE-18-crown-6 (1.0 eq. mol.) and $Bi(OTf)_3$ (0.05% eq. mol.) Conversion determined via ^{1}H-NMR spectroscopy evaluating the relative integration of the corresponding peaks in the cyclic and polymeric structure (Figure 1). [a)]The reaction mixture was left under stirring for 5 h at 150 °C, and the temperature was increased to 160 °C for 1 h.

It is noteworthy that this is the first time that macrocycles derived from FDME and TEG were investigated via ED-ROP. Thus, it was decided to start by optimizing the reaction conditions of FDE-18-crown-6 ED-ROP, e.g., the reaction temperature, time, and catalyst load (**Table 5**). Results collected showed that at the lower temperature of 130 °C (#1 and #2, Table 5), conversions were modest, and the polymer could not be isolated. A similar result was achieved when the reaction time was extended from 3 to 6 h, even if an increase in FDE-18-crown-6 conversion from 57 to 76% was noted (#1 vs. #2, Table 5).

However, when the polymerization temperature was increased to 150–160 °C (1#3-4, Table 5), complete MCOs conversion was achieved after 6 h, as demonstrated by the disappearance of the singlet at 7.31 ppm in the ^{1}H-NMR spectrum, corresponding to the furanic protons in the macrocycle (see **Figure 1** as an example). The polymer was then purified by dissolution in chloroform and precipitation in cold methanol (overall yield of 20%). The recovered PTEF had an intrinsic viscosity of 0.58 dL g^{-1} and an M_v of 36 000 Da (#3, Table 5). Notably, increasing the catalyst loading to 0.10% mol. (#4, Table 5) resulted in a lower monomer conversion and did not improve the isolated yield. However, it did lead to a decrease in both polymer's intrinsic viscosity and M_v. As comparison, data collected in the previous trial (#3, Table 5) are encouraging, as they support the minimization of catalyst amount in line with green chemistry principles.

In a scale-up reaction, increasing the amount to 2.0 g of FDE-18-crown-6 under identical conditions, the resulting polymer was isolated in significantly higher yields (50%; #5, Table 5), although

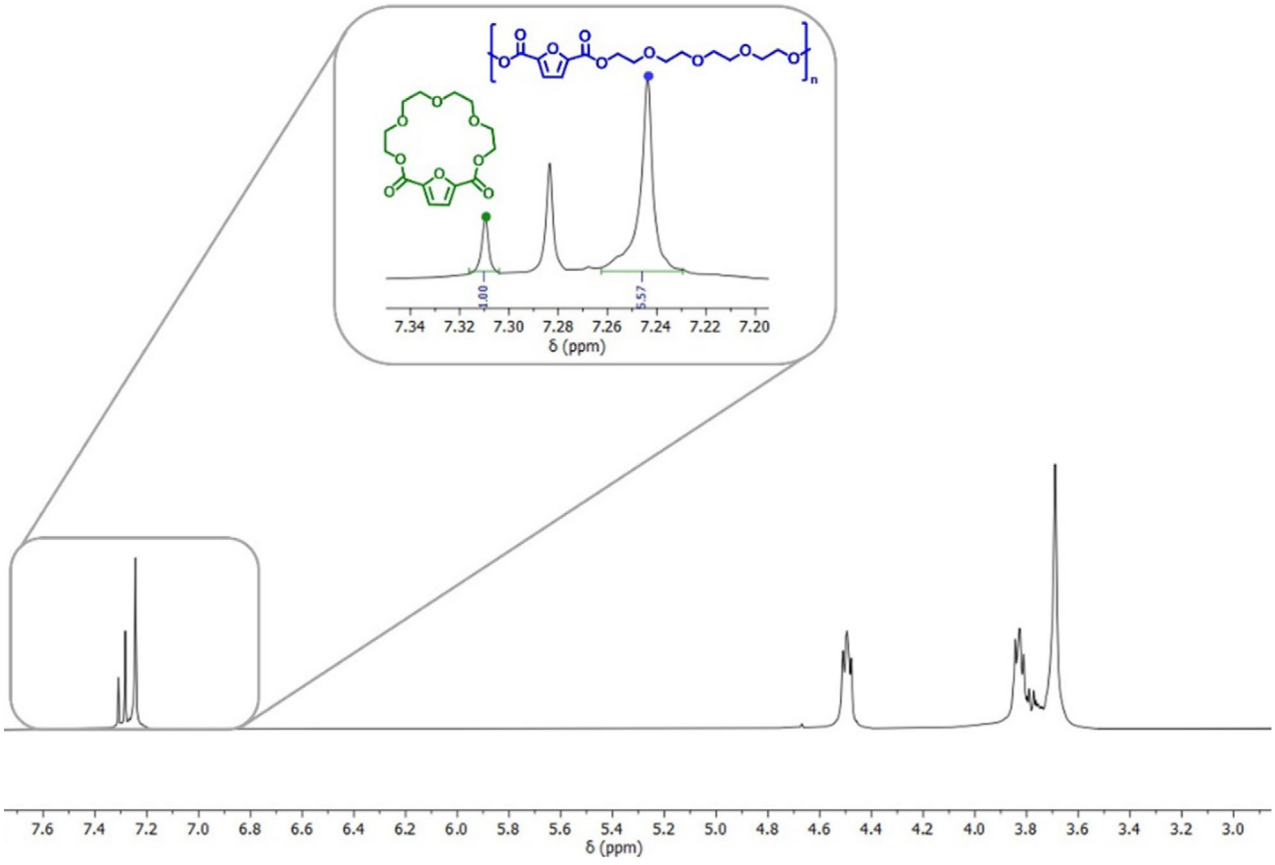

Figure 1. ^{1}H-NMR spectra of the reaction mixture of PTEF synthesis via ED-ROP (#5, Table 5).

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a slight reduction in the intrinsic viscosity and M_v was observed, likely due to chain transfer reactions that occurred at higher monomer concentrations. The ^{1}H-NMR spectrum of PTEF (Figure S7, Supporting Information) displayed the expected signals relative to furanic and aliphatic protons, without any evidence of peaks arising from cyclic monomers. The FTIR spectrum (Figure S12, Supporting Information) evidenced a series of characteristic bands such as ester (1714 and 1270 cm^{-1}) and ether (1106 cm^{-1}) functions.

DSC and DMTA analyses of this polymer revealed a T_g of −8 °C, typical of polymers that incorporate flexible ether moieties. The polymer demonstrated excellent thermal stability, with a $T_{d5\%}$ of 265 °C and T_d of 366 °C, highlighting its suitability for applications requiring moderate thermal resilience.

The optimal conditions for PTEF synthesis were applied to the ED-ROP of FDE-24-crown-8 (**Table 6**).

The polymerization of FDE-24-crown-8 using $Bi(OTf)_3$ as a catalyst achieved quantitative MCOs conversion comparable to the ED-ROP of FDE-18-crown-6 (compared trials #1, Table 6 and #3, Table 5). The absence of cyclic monomer in the final product was confirmed by ^{1}H-NMR spectroscopy e.g., only one singlet was present in the region of 7.25 ppm attributed to the furanic H_3 and H_4 protons of PHEF (Figure S8, Supporting Information). Once again, the yield varied significantly, increasing from 30 to 61% when scaling up the reaction from 0.50 g to 2.00 g (#2, Table 6). The resulting polymer exhibited an intrinsic viscosity of 0.31 dL/g and a M_v of 13 899. The thermal characterization revealed a lower T_g (−18 °C) than that of PTEF due to the longer polyoxyethylene subunits and high thermal stability, with $T_{d5\%}$ and T_d of 313 °C and 384 °C, respectively. These results suggest that the polymer possesses a balance of flexibility and thermal resilience, making it suitable for applications requiring elasticity under moderate thermal conditions. Also, in this case, the XRD patterns showed that these two polymers are amorphous as confirmed by the presence of halo peaks between 2θ 15° and 30° (Figure S26 and S28, Supporting Information).

Table 7 summarizes the properties of PTEF and PHEF synthesized via ED-ROP compared to those of their counterparts prepared by PC route. Although both methods yielded polymers with the same chemical structure, their different synthetic methodologies influenced the resulting material properties. A key difference between the two approaches is the reaction temperature. ED-ROP operates under comparatively milder conditions (150–160 °C), while the PC method required significantly higher temperatures (up to 230 °C under vacuum). This difference is due to the polymerization mechanism, ED-ROP takes advantage of the entropic gain associated with ring opening—which requires less thermal energy—while PC is a step-growth reaction that relies on elevated temperatures to drive the equilibrium towards polymer formation. Catalyst choice further differentiates the two methods, as ED-ROP utilizes $Bi(OTf)_3$, a Lewis acid catalyst that is effective under mild conditions and has low toxicity. In contrast, the PC method uses TBT a conventional more toxic catalyst.

Table 6. Synthesis of linear PHEF via ED-ROP.

#	FDE-24-crown-8 [g]	$Bi(OTf)_3$ [%mol]	T [°C]	t [h]	Conv. [%]	Yield [%]	[η] [dL/g]	M_v
1	0.50	0.05	150-160	6	100	30	0.30	13 489
2	2.00	0.05	150-160	6	99	61	0.31	13 899

Reaction conditions: FDE-24-crown-8 (1.0 eq. mol.) and $Bi(OTf)_3$ (0.05% eq. mol.) The reaction mixture was left under stirring for 5 h at 150 °C, and the temperature was increased to 160 °C for 1 h. Conversion determined via ^{1}H-NMR spectroscopy.

Table 7. Comparison between the polymers properties synthesized via ED-ROP and conventional PC.

Polymer	Yield [%]	[η] [dL/g]	M_v [Da]	T_g [°C]	$T_{d5\%}$ [°C]	T_d [°C]
PTEF via ED-ROP	20	0.58	36 000	−8	265	366
PTEF via PC	34	0.49	27 542	−7	197	380
PHEF via ED-ROP	30	0.30	13 489	−18	313	384
PHEF via PC	48	0.63	40 049	−17	265	401

3. Conclusion

In this study, we successfully developed a greener route for the synthesis of FDME-derived MCOs and investigated their potential in ED-ROP for PEs production. A preliminary catalyst screening allowed to identify Bu_2SnO as the most effective catalytic system, which was subsequently applied to the synthesis of MCOs using TEG and HEG as diols via PHDC. The resulting macrocycles—FDE-18-crown-6 and FDE-24-crown-8—were synthetized in moderate yields and efficiently recovered as white crystals using an alternative greener purification technique, eliminating the need for column chromatography and reducing solvent waste.

PTEF synthesized via ED-ROP exhibited higher intrinsic viscosities and M_v than those produced by PC route. Thermal analyses revealed enhanced thermal stability, with initial decomposition temperatures of 265 °C and a T_d value of 366 °C, quite similar to the polymer achieved via PC. In the case of PHEF, the polymer prepared via PC exhibited a higher molecular weight compared to the one achieved via ED-ROP, despite thermal analyses showing similar degradation temperatures.

Although PTEF and especially PHEF require further optimization to match the performance of PEs like PEF, their competitive thermal stability poses them as promising candidates for applications requiring flexibility and high-temperature resistance. Additionally, their relatively low glass transition temperatures of −8 °C for PTEF and −18 °C for PHEF indicate flexibility at room temperature, making them suitable for applications requiring a balance between flexibility and thermal resistance.

4. Experimental Section

Materials

All reagents and solvents were purchased from Sigma-Merk. Dimethyl furan-2,5-dicarboxylate (FDME, 99.9%) was acquired from

Sarchem Laboratories or prepared following our previously published procedures.[12,64]

Characterization

^{1}H- and ^{13}C-NMR spectra of the synthesized materials were recorded with Bruker 300 and 400 MHz spectrometers. Acetone-d_6 was used to dissolve the MCOs samples and $CDCl_3$ to dissolve the polymer ones.

HR–MS spectra were acquired by means of a Bruker compact QTOF with a mass resolution of 30.000 in positive polarity mode. The mass calibration was conducted using a sodium formate cluster's solution, and the data were processed in HPC mode. The acquisition was conducted in full scan mode in the range 50 to 500 m z^{-1}, with a 4.0 L min^{-1} at 180 °C of source dry gas. The ion formula of each compound was calculated with the Smart formula tool within the Bruker software platform by using a 4 mDa of mass confidence and considering the isotopic pattern ratio.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained using a PARAGON 1000 Perkin-Elmer FTIR spectrometer equipped with a single-horizontal Golden Gate ATR cell, recorded within the range of 500–4000 cm^{-1} at a resolution of 8 cm^{-1}.

Differential scanning calorimetry (DSC) was carried out in a Netzsch Caliris 300 equipment, and the thermograms were recorded following a heating rate of 5 °C min^{-1} and cooling of 50 °C min^{-1} under a nitrogen flow of 40 mL min^{-1} in a temperature range from −40 °C to 120 °C.

Intrinsic viscosity measurements were carried out on an Ubbelohde type viscometer maintained at 25 °C using a 1:1 mixture of phenol/1,1,2,2-tetrachloroethane (TCE) (w/w). Samples were dissolved in the solvent mixture (0.1 g per 20 mL), and the intrinsic viscosity was determined by the ratio of specific viscosity and sample solution concentration following the equation (Equation (1)), where $[\eta]$ represents the intrinsic viscosity, η_{sp} represents the specific viscosity, C represents the solution concentration, and t_0 and t_1 correspond to the solvent mixture elution time of the solvent mixture and PE solution, respectively.

$$[\eta](dL\,g^{-1}) = \frac{\eta_{sp}}{C} \tag{1}$$

where $\eta_{sp} = \frac{t_1 - t_0}{t_0}$

The viscosity-average molecular weight (M_v) of PTEF and PHEF was calculated by the Mark–Houwink equation using the K and α parameters for PET (Equation (2)).

$$[\eta] = 4.68 \times 10^{-4} \cdot M_v^{0.68} \tag{2}$$

Thermogravimetric analyses (TGA) were carried out with a Setaram SETSYS Evolution 1750 analyzer equipped with an alumina plate and type S sensor. Thermograms were recorded under a nitrogen flow of 20 mL min^{-1} and heated at a constant rate of 10 °C min^{-1} from 20 to 800 °C. Thermal decomposition temperatures were taken at the onset of significant weight loss (5%) ($T_{d5\%}$) and at maximum decomposition temperatures from the heated samples (T_d).

X-ray diffraction (XRD) analyses were carried out using the Philips X'pert MPD instrument operating with CuKα radiation ($\lambda = 1.5405980$ Å) at 40 kV and 45 mA. Samples were scanned in the 2υ range of 5 to 60°, with a step size of 0.1050422° and time per step of 200 s.

Dynamic mechanical thermal analyses (DMTA) of a small amount of powder samples, dispersed in a foldable stainless-steel sheet with a rectangular shape (30.0 × 7.5 mm^2), acquired from Materials Pocket of Triton Technology, were performed with a Tritec 2000 DMTA Triton equipment operating in the bending (single cantilever) mode. Tests were performed at 1 and 10 Hz, and the temperature varied from 100 to 200 °C, at 2 °C min^{-1}.

Transesterification Studies

FDME (0.20 g, 1.08 mmol, 1.00 eq. mol.) and EGME (0.17 g, 2.17 mmol, 2.00 eq. mol.) were dissolved in CPME (5.0 mL), and the promoter (0.54 mmol, 0.5 eq. mol) was added to the solution. The reaction mixture was left under stirring for 6 h at reflux temperature. After the reaction completion, the mixture was cooled to room temperature, the solvent was evaporated under vacuum, and the crude was analyzed via ^{1}H-NMR and GC-MS.

Macrocycles Synthesis—Reaction Setup

The reaction was conducted in a three-necked round-bottom flask equipped with a Dean–Stark apparatus. The Dean–Stark apparatus was positioned on the middle neck and was topped with a water condenser. A dropping funnel containing the monomer mixture was sealed with a lid and inserted into the second neck, while the third neck was equipped with an outlet for nitrogen flow (**Figure 2**).

Synthesis of FDE-18-Crown-6 via PHDC

FDME (1.00 g, 5.43 mmol, 1.00 eq. mol.) and TEG (1.05 g, 5.43 mmol, 1.00 mol eq.) were dissolved in CPME (70 mL) at room temperature under vigorous stirring. Once complete dissolution was achieved, the solution was transferred to the dropping funnel. Bu_2SnO (0.68 g, 2.72 mmol, 0.50 eq. mol.) and CPME (120 mL) were introduced into the flask and heated to the reflux temperature under stirring. Upon reaching the desired temperature, a nitrogen flow was initiated, and the monomer mixture was added dropwise via the dropping funnel over a period of 5 h. Following the complete addition of the monomers, the dropping funnel was removed and replaced with a lid. The reaction was allowed to proceed overnight under the same conditions. Afterwards, the reaction mixture was cooled to room temperature, and CPME was removed under vacuum and recovered for subsequent reactions. The pure [1 + 1] MCO, namely FDE-18-crown-6, was

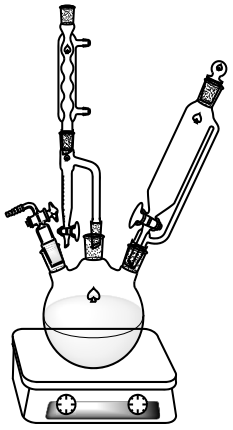

Figure 2. PHDC reaction setup.

recovered as a white crystal after precipitation in hot ethyl acetate (20 mL) and analyzed via ^{1}H-, ^{13}C-NMR, and HR-MS.

^{1}H-NMR (400 MHz, Acetone-d_6), δ ppm: 7.38 (s, 2 H); 4.43-4.41 (m, 4 H); 3.82-3.80 (m, 4 H); 3.73-3.71 (m, 4 H); 3.67-3.64 (m, 4 H).

^{13}C-NMR (100 MHz, Acetone-d_6), δ ppm: 157.7; 146.5; 118.6; 70.7; 70.0; 68.3; 65.0.

HRMS: m/z $[M + NH_4]^+$ calc. for: 332.1340; found: 332.1336.

Synthesis of FDE-24-Crown-8 via PHDC

FDME (1.00 g, 5.43 mmol, 1.00 eq. mol.) and HEG (1.53 g, 5.43 mmol, 1.00 mol eq.) were dissolved in CPME (70 mL) at room temperature under vigorous stirring. Once complete dissolution was achieved, the solution was transferred to the dropping funnel. Bu_2SnO (0.68 g, 2.72 mmol, 0.50 eq. mol.) and CPME (120 mL) were introduced into the flask and heated to the reflux temperature under stirring. Upon reaching the desired temperature, a nitrogen flow was initiated, and the monomer mixture was added dropwise via the dropping funnel over a period of 5 h. Following the complete addition of the monomers, the dropping funnel was removed and replaced with a lid. The reaction was allowed to proceed overnight under the same conditions. Afterwards, the reaction mixture was cooled to room temperature, and CPME was removed under vacuum and recovered for subsequent reactions. The pure [1 + 1] MCO, namely FDE-24-crown-8, was recovered as a white crystal after precipitation in hot ethyl acetate (20 mL) and analyzed via ^{1}H-, ^{13}C-NMR and HR-MS.

^{1}H-NMR (400 MHz, Acetone-d_6), δ ppm: 7.38 (s, 2 H); 4.52-4.50 (m, 4 H); 3.83-3.81 (m, 4 H); 3.65-3.63 (m, 4 H); 3.60-3.56 (m, 4 H); 3.52-3.50 (m, 4 H); 3.45-3.42 (m,4 H).

^{13}C-NMR (100 MHz, Acetone-d_6), δ ppm: 157.6; 146.9; 118.7; 70.9; 70.5; 70.4; 70.3; 68.5; 64.4.

HRMS: m/z $[M + NH_4]^+$ calc. for: 420.1864; found: 420.1861.

Synthesis of FDE-18-Crown-6 via PHDC—Large Scale

FDME (5.00 g, 27.15 mmol, 1.00 eq. mol.) and TEG (5.27 g, 27.15 mmol, 1.00 mol eq.) were dissolved in CPME (210 mL) under vigorous stirring at room temperature. Once complete dissolution was achieved, the solution was transferred to the dropping funnel. Bu_2SnO (3.38 g, 13.58 mmol, 0.50 eq. mol.) and CPME (360 mL) were introduced into the flask and heated to the reflux temperature. Upon reaching the desired temperature, a nitrogen flow was initiated, and the monomer mixture was added dropwise via the dropping funnel over a period of 5 h. Following the complete addition of the monomers, the dropping funnel was removed and replaced with a lid. The reaction was allowed to proceed overnight under the same conditions. Afterwards, the reaction mixture was cooled to room temperature, and CPME was removed under vacuum and recovered for subsequent reactions. The crude product was recovered as a white crystal after precipitation in hot ethyl acetate (20 mL).

Synthesis of FDE-24-Crown-8 via PHDC—Large Scale

FDME (5.00 g, 27.15 mmol, 1.00 eq. mol.) and HEG (7.63 g, 27.15 mmol, 1.00 mol eq.) were dissolved in CPME (210 mL) under vigorous stirring at room temperature. Once complete dissolution was achieved, the solution was transferred to the dropping funnel. Bu_2SnO (3.38 g, 13.58 mmol, 0.50 eq. mol.) and CPME (360 mL) were introduced into the flask and heated to the reflux temperature. Upon reaching the desired temperature, a nitrogen flow was initiated, and the monomer mixture was added dropwise via the dropping funnel over a period of 5 h. Following the complete addition of the monomers, the dropping funnel was removed and replaced with a lid. The reaction was allowed to proceed overnight under the same conditions. After the reaction mixture was cooled to room temperature, CPME was removed under vacuum and recovered for subsequent reactions. The crude product was recovered as a white crystal after precipitation in hot ethyl acetate (20 mL).

Polymers Synthesis: Synthesis of PTEF and PHEF via PC Route

PC trials were performed by adapting a two-step procedure previously reported in the literature.[52]

In the first step, FDME (1.00 g, 5.43 mmol, 1.00 eq. mol.) and TEG (2.11 g, 10.86 mmol, 2.00 eq. mol.) were mixed in a two-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a trap linked to the vacuum system. The flask was immerged into an oil bath and the mixture, under stirring, was heated under a nitrogen atmosphere until the melting of the reagents. The catalyst titanium(IV) tert-butoxide (TBT) (2.22 mg, 6.5×10^{-3} mmol, 0.0012 eq. mol.) was then added into the flask, and the mixture was stirred over a period of 3.5 h and then maintained at 170 °C for 1 h.

In the second stage, the reaction mixture was cooled to 150 °C, and an additional quantity of FDME (1.10 g, 6.00 mmol, 1.10 eq. mol.) was added. The mixture was then progressively heated to 170 °C during the course of 3 h under vacuum. Finally, the temperature increased to 210 °C and gradually raised to 230 °C over a period of 2 h. After cooling down, the mixture was then dissolved in chloroform, and the polymer was precipitated by adding the solution into an excess of cold methanol, followed by centrifugation and drying in an oven at 40 °C.

^{1}H-NMR (300 MHz, $CDCl_3$), δ ppm: 7.24 (s, 2 H); 4.51-4.46 (m, 4 H); 3.83-3.80 (m, 4 H); 3.67 (m, 8 H).

^{13}C-NMR (75.47 MHz, $CDCl_3$), δ ppm 157.9; 146.7; 118.7; 70.6; 68.9; 64.5.

The same procedure was used to prepare PHEF: FDME (1.00 g, 5.43 mmol, 1.00 eq. mol.), HEG (3.07 g, 10.86 mmol, 2.00 eq. mol.).

^{1}H-NMR (300 MHz, $CDCl_3$), δ ppm:7.24 (s, 2 H); 4.50-4.47 (m, 4 H); 3.83-3.79 (m, 4 H); 3.69-3.62 (m, 16 H).

^{13}C-NMR (75.47 MHz, $CDCl_3$), δ ppm 157.9; 146.7; 118.7; 70.64-70.55; 68.9; 64.5.

Synthesis of PTEF and PHEF via ED-ROP Route

PTEF and PHEF were synthesized with the same procedure. In a round bottom flask equipped with a water condenser, FDE-18-crown-6 (0.50 g, 1.59 mmol, 1.00 eq. mol.) or FDE-24-crown-8 (0.50 g, 1.24 mmol, 1.00 eq. mol.) were inserted, and upon reaching the melting temperature, $Bi(OTf)_3$ (0.52 mg, 7.95×10^{-4} mmol, 5.0×10^{-4} eq. mol. and 0.41 mg, 6.20×10^{-4} mmol, 5.0×10^{-4} eq. mol. for FDE-18-crown-6 and FDE-24-crown-8 respectively) was added. The solution was left under stirring for 5 h at 150 °C under nitrogen atmosphere and increased to 160 °C for 1 h.

Analyses of PTEF:

^{1}H-NMR (300 MHz, $CDCl_3$), δ ppm: 7.23 (s, 2 H); 4.50-4.47 (m, 4 H); 3.85-3.80 (m, 4 H); 3.68 (m, 8 H). ^{13}C-NMR (75.47 MHz, $CDCl_3$), δ ppm 157.9; 146.7; 118.7; 70.6; 68.9; 64.5.

Analyses of PHEF:

^{1}H-NMR (300 MHz, $CDCl_3$), δ ppm: 7.24 (s, 2 H); 4.50-4.47 (m, 4 H); 3.84-3.81 (m, 4 H); 3.70-3.63 (m, 16 H).

^{13}C-NMR (75.47 MHz, $CDCl_3$), δ ppm: 157.9; 146.7; 118.7; 70.64-70.55; 68.9; 64.5.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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