

Oxidative NHC Catalysis: An Unconventional Tool for Macrocyclic Oligoesters Synthesis

Marco Bottin,^[a] Graziano Di Carmine,^[a] Olga Bortolini,^[b] Carmela De Risi,^[a] Monica Bertoldo,^[a] Tommaso R. I. Cataldi,^[c] Cosima D. Calvano,^[c] Alessandro Massi,^[a] and Daniele Ragno^{*[a]}

Abstract: The application of N-heterocyclic carbene (NHC) catalysis under highly diluted oxidative condition to the polycondensation of dialdehydes and diols is herein presented as an alternative, atom-economical synthetic route to macrocyclic oligoesters (MCOs). The disclosed protocol paves the way to the straightforward access to MCOs, starting from commercial dialdehydes, avoiding the use of toxic diacyl chlorides, commonly employed in traditional MCOs synthetic processes. The method is totally metal-free, takes place in the green Me-THF solvent and requires the use of a fully recyclable quinone oxidant. The protocol versatility is confirmed by the employment of fossil-based and bio-based

monomers such as 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (BHMF), and isomannide, synthesizing a series of novel and known synthetically relevant macrocyclic oligoesters, fully characterized by NMR and MALDI-TOF MS analysis, with product yields (51–86%) comparable to those obtained by traditional synthetic routes. Finally, to emphasize the synthetic relevance of the target macrocycles, an entropically-driven ring opening polymerization (ED-ROP) key study has been performed, optimizing the organocatalyzed synthesis of poly(2,5-furan-dimethylene 2,5 furandicarboxylate) (PBHMF) with number-average molecular weight up to 8200 g mol⁻¹ and 66% isolated yield.

Introduction

Due to their remarkable qualities and extensive range of uses, from packaging to smart materials, clothing, and electronics, linear polyesters (PEs) are now recognized as one of the major classes of polymers.^[1] Commercial polyesters widely used in our everyday life like poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and poly(butylene succinate) (PBS), are mainly constituted by petrochemical monomers. Main critical issues related to the massive production and consumption of fossil-based polyesters are the depletion of crude oil resources and environmental concerns related to their frequent low levels of biodegradability. In addition, traditional polymer-

ization strategies often require harsh reaction conditions, metal catalysts, with production of undesired by-products that need to be removed from the reaction mixtures. Therefore, in order to solve these issues and provide practical answers, the scientific community has recently driven extensive research on polymers from renewable feedstocks and greener polymerization strategies.^[2]

In this respect, bio-based polyesters, derived from raw biomass represent the future.^[3] As environmentally friendly substitutes for industrial PEs made from terephthalic acid, polyfuranates^[4] attracted the interest of both academia and industry. Indeed, thanks to their advantageous mechanical and barrier qualities, recyclable nature, and integration into a circular economy, poly(ethylene furanoate) (PEF)^[5] and poly(butylene furanoate) (PBF)^[6] will be soon produced on a wide scale.

From the synthetic point of view, common strategies for the production of PEs are the step-growth polymerization of hydroxy acids or diol/diacid pairs,^[7] and the ring-opening polymerization (ROP) of lactones.^[8] Step-growth polymerization is usually carried out in a two-stage bulk process: a condensation reaction leading to a prepolymer that is in turn converted into the final polyester by transesterification, often requiring high temperatures and low pressures to achieve satisfactory molecular weights. Differently, the ring-opening of a lactone, generally promoted by a catalyst/initiator couple, is a chain-growth polyaddition process that requires less severe reaction conditions to obtain high molecular weight products. No volatile by-products have to be removed with improved atom economy, minimization of side reactions and energy consumption.

[a] M. Bottin, Dr. G. Di Carmine, Dr. C. De Risi, Prof. M. Bertoldo, Prof. A. Massi, Dr. D. Ragno
Department of Chemical, Pharmaceutical and Agricultural Sciences
University of Ferrara
Via L. Borsari, 46, 44121 Ferrara (Italy)
E-mail: daniele.ragno@unife.it

[b] Prof. O. Bortolini
Department of Environmental and Prevention Sciences
University of Ferrara
Via L. Borsari, 46, 44121 Ferrara (Italy)

[c] Prof. T. R. I. Cataldi, Prof. C. D. Calvano
Department of Chemistry, Interdepartmental Center SMART
University of Bari
Via Orabona 4, 70126 Bari (Italy)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202301416>

© 2023 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Although several polyesters are still produced on industrial scale by step-growth polycondensation, ROP processes are progressively emerging as valuable alternatives, in particular for the synthesis of renewable polymers.^[9] Monomers employed in ring-opening processes can be small-to-medium size cyclic oligoesters (number of skeletal ring atoms between 3 and 12) or macrocyclic oligoesters (MCOs, 14 skeletal atoms at least). Smaller cycles are very reactive in ROP processes, due to ring strain and the whole process is favoured by enthalpy factors. Differently, the ROP of MCOs proceeds without enthalpy exchange and it is mainly driven by entropy. For this reason, it is commonly called entropy-driven ring opening polymerization (ED-ROP).^[10] Recently ED-ROP strategies have been widely explored, especially in the synthesis of bio-based polyesters, starting from macrocyclic oligoesters derived from renewable resources.^[11]

Currently adopted strategies for MCOs synthesis are cyclodepolymerizations (CDPs),^[12] high dilution and pseudo-high dilution condensation (HDC),^[10,11,13] mediated by chemical or enzymatic species (Figure 1).

The former method, first studied by Carothers and co-workers,^[14] allows the synthesis of MCOs through the depolymerization of the corresponding linear polyester, leading to the preferential formation of cycles if they are continuously removed from the reaction mixture by high vacuum distillation or under high dilution conditions. On the other hand, high dilution condensation (HDC) and pseudo-HDC, originally reported by Brunelle group,^[15] rely on the cyclization of the starting monomers under optimal diluted conditions that, according to the Ziegler–Ruggli principle,^[16] might shift the reaction equilibrium in favour of cyclization rather than polymerization. In this respect, highly efficient enzymatic protocols for the production of MCOs through cyclodepolymerization^[17] and condensation under high dilution conditions^[18] were recently reported. With a focus on the chemical synthesis of MCOs through polycondensation, pioneering works were conducted by Brunelle^[13,15] in the field of terephthalic macrocyclic oligoesters such as cyclic ethylene

terephthalate and cyclic butylene terephthalate; likewise, Muñoz-Guerra^[19] and Morbidelli^[20] groups provided pivotal contributions on the production of furanic MCOs like cyclic ethylene 2,5-furandicarboxylate and cyclic butylene 2,5-furandicarboxylate. It is important to point out that all these works share the same synthetic strategy, which consists in the polycondensation between a diol and a diacid, typically activated as diacyl chloride. Reactions proceed under pseudo-high dilution conditions with sterically unhindered amines as the promoters, affording a mixture of a homologous family of MCOs constituted by cycles of different size. Notably, the drawback of this methodology is the use of overstoichiometric amounts of the amine, also needed to neutralize the HCl released in the reaction; in this respect, the replacement of acyl chlorides with different classes of starting substrates could represent a step-forward, avoiding corrosive and hazardous HCl production and the employment of overstoichiometric neutralizing agents.

Given the emerging role of organocatalysis in polymer chemistry,^[21] as part of our ongoing research activities in the field, we wondered if an organocatalyzed general protocol for the selective synthesis of MCOs, avoiding the use of toxic diacyl chlorides, could be developed.

Recently, we described novel general methods for the synthesis of fossil- and bio-based polyesters^[22] (Scheme 1, a) and polyamides^[23] (Scheme 1, b) promoted by N-heterocyclic carbenes (NHCs) under oxidative conditions,^[24] starting from dialdehydes and diols/diamines. The peculiarity of the proposed methodology relies in the activation under mild reaction conditions of readily available dialdehydes, through the generation of highly reactive acyl azolium intermediates, via Breslow intermediate oxidation, in the presence of an external oxidant (Scheme 1). As a prosecution of our studies in the field, in 2022 we described the organocatalyzed synthesis of poly(hydroxymethylfuroate) (PHMF) via ring-opening polymerization of 5-hydroxymethylfurfural-based cyclic oligoesters^[25] (Scheme 1, c). The synthesis of furanic MCOs was promoted by NHCs under highly diluted oxidative conditions, allowing the direct self-condensation of the platform chemical HMF.

According to this scientific background and our previous experience, in the present study we report the unprecedented general synthetic protocol for the polycondensation of dialdehydes and diols promoted by NHCs under highly diluted oxidative conditions as an alternative, atom-economical synthetic route to macrocyclic oligoesters (MCOs) (Scheme 1, d). After the optimization study, the potential of the disclosed protocol has been validated by the polycondensation of common fossil-based and bio-based furanic monomers such as 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (BHMF), and isomannide. The synthesized macrocycles have been fully characterized by NMR and MALDI-TOF MS analyses, in order to gain information on the composition of cycle mixtures. Finally, to emphasize the synthetic relevance of MCOs, an ED-ROP key study was selected, optimizing the organocatalyzed synthesis of poly(2,5-furan-dimethylene 2,5 furandicarboxylate) (PBHMF).

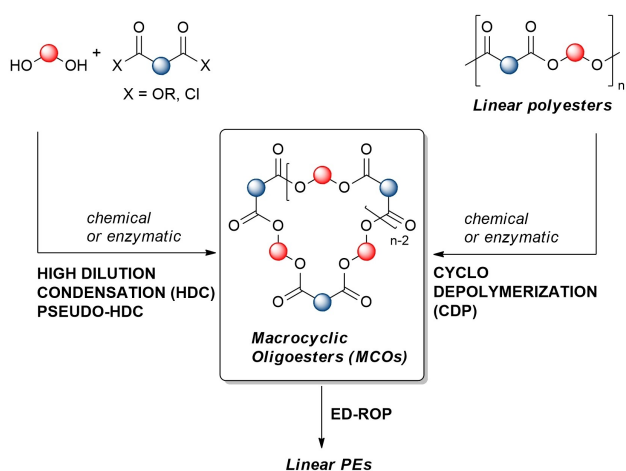
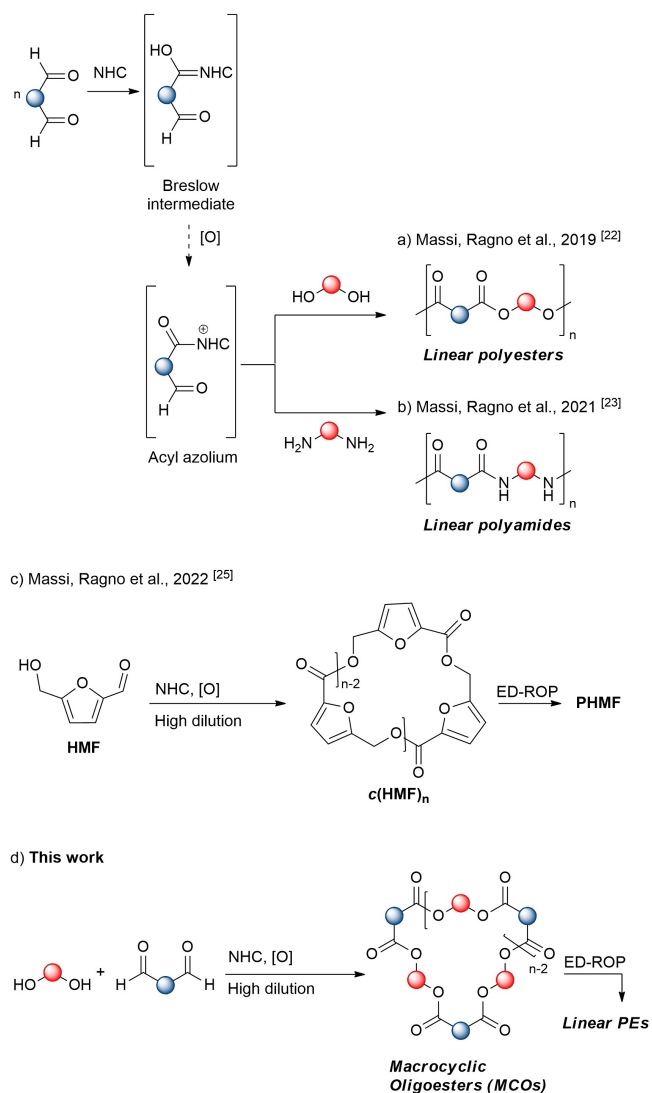


Figure 1. Main strategies for the synthesis of macrocyclic oligoesters (MCOs).



Scheme 1. NHC-catalyzed oxidative strategy to access: (a) linear polyesters; (b) linear polyamides; (c) HMF-derived macrocyclic oligoester $c(\text{HMF})_n$; (d) general macrocyclic oligoesters (MCOs), this work.

Results and Discussion

According to our previous studies,^[22] the polycondensation of ethylene glycol **1a** and terephthalaldehyde **2a** was selected as the benchmark for reaction conditions optimization. Pre-catalysts **A** and **B** were screened in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as base, together with different oxidative systems, solvents and temperatures (Table 1). In order to test the performance of the reaction system, the first experiment was performed at room temperature, in the green solvent 2-methyltetrahydrofuran (Me-THF) under concentrated conditions (0.7 M in Me-THF), using a stoichiometric ratio of diol **1a** and dialdehyde **2a**, pre-catalyst **A**/DBU couple and the Kharasch quinone **5** as oxidant. After 16 h, full conversion of starting material was detected, together with almost quantitative formation of poly(ethylene terephthalate) (PET), which precipitated from the reaction mixture without formation of

Table 1. Screening of reaction conditions for the synthesis of cyclic oligoester **3aa** ($c(\text{ET})_n$).^[a]

Entry	NHCX	Ox. (mol %)	t (h)	Conv. (%) ^[b]	3aa (%) ^[c]	PET (%) ^[d]
1 ^[e]	A	5 (100)	16	> 95	–	82
2	A	5 (100)	16	> 95	34	52
3	A	5 (100)	3	> 95	64	23
4 ^[f]	A	5 (100)	3	> 95	23	49
5 ^[g]	A	5 (100)	3	> 95	26	42
6 ^[h]	A	5 (100)	3	> 95	48	30
7	B	5 (100)	3	> 95	–	54
8	A	Air, 5/6 ^[i]	16	34	11	20
9	A	7 (100)	4	74	33	28
10 ^[j]	A	5 (100)	2	70	18	44
11 ^[j]	A	5 (100)	16	70	11	52
12 ^[j]	B	5 (100)	16	42	10	24

[a] Conditions: **1a** (0.40 mmol), **2a** (0.40 mmol), **NHCHX** (0.04 mmol), DBU (0.10 mmol), Me-THF (30.0 mL); mol % are referred to reactive functional groups. [b] Detected by ¹H NMR of the crude reaction mixture (durene as internal standard). [c] Isolated yield after flash chromatography. [d] Isolated yield after trituration of the raw reaction mixture with CPME. [e] Me-THF (6.0 mL). [f] Anhydrous DCM as solvent. [g] T = 0 °C. [h] Me-THF (60.0 mL). [i] **5** (5 mol %), **6** (2.5 mol %). [j] **1a** and **2a** (0.4 mmol in 2 mL Me-THF) were added dropwise simultaneously to the reaction mixture over 1 h.

linear oligomers **4aa** and the desired cyclic species **3aa** ($c(\text{ET})_n$, entry 1).

According to the Ziegler–Ruggli principle,^[16] next experiments were carried out at lower concentration of reactants to maximize the rate of intramolecular reactions and favour the formation of cyclic over linear oligomers. Gratifyingly, dilution of the reaction mixture to 0.013 M in Me-THF allowed the synthesis of the target macrocycle **3aa** in 34% isolated yield

after 16 h (entry 2). The reduction of reaction time to 3 h (entry 3) revealed to be crucial for reaction selectivity, reducing PET formation (23 %) and favouring **3 aa** production (64 % yield). This behaviour was rationalized considering that NHCs are efficient ROP catalysts and transesterification agents.^[26] Hence, reaction time control became crucial because prolonged reaction time could cause ring opening of the cyclic species **3 aa** with formation of linear undesired products. Solvent change to dichloromethane and temperature reduction (0 °C) had a negative outcome on reaction selectivity (entries 4 and 5), leading to higher amounts of the undesired linear polymer. Further dilution of the reaction mixture (0.006 M, entry 6) led to modest results without improving the best selectivity achieved under 0.013 M conditions (entry 3). At this stage, the pyrrolidine-based pentafluorophenyl pre-catalyst **B** was screened under the optimal reaction conditions. In our previous contribution,^[22] azolium salt **B** allowed for fine tuning the selectivity in the synthesis of linear versus cross-linked polyglycerols; therefore, we wondered if **B** could play a key role in the preferential formation of cycles **3 aa** as well. Unfortunately, after full starting material conversion (3 h), MCOs **3 aa** were not detected (entry 7). Subsequently, the use of air as the terminal oxidant was evaluated by applying the biomimetic system of electron-transfer mediators (ETMs) developed by Bäckvall^[27] and Sundén^[28] groups (entry 8). This strategy relies on the use of catalytic quinone **5** (5 mol %), which is reduced to the corresponding diol **5'** during acyl azolium formation; reoxidation of **5'** by atmospheric oxygen in the presence of catalytic iron(III) phthalocyanine **6** (2.5 mol %) finally restores the active oxidant **5**. After 16 h only a poor 34 % conversion of starting material was detected, probably due to slow reaction kinetics working with catalytic oxidant, with unsatisfactory selectivity towards MCOs **3 aa**. The last oxidative species screened was phenazine **7**, without substantial improvements in terms of substrate conversion and cycles yield (entry 9). Finally, the pseudo-high dilution protocol developed by Brunelle^[15] and co-workers was considered, in order to enhance intramolecular over intermolecular reactivity. By slowly adding streams of both monomers with the same rate, high dilution levels of reaction intermediates are achieved, allowing the accumulation of higher concentrations of MCOs compared to regular high dilution conditions. Accordingly, **1 a** and **2 a** were simultaneously added dropwise at the same rate to the reaction mixture over 1 h, in order to maintain the reagents equimolarity in the reaction mixture, leading to 70 % monomer conversion after 2 h with poor selectivity (entry 10). Moreover, the effect of reaction time extension to 16 h was negligible on the reaction outcome, without substrate conversion and selectivity increases (entry 11). Finally, as it could be expected, screening of pre-catalyst **B** under the pseudo-high dilution conditions revealed to be inefficient (entry 12). In the light of these results, the best reaction conditions were found in entry 3, with satisfactory **3 aa** isolated yield (64 %), with short reaction time (3 h), employing stoichiometric oxidant **5** and catalytic pre-catalyst **A/DBU** couple. Considering process sustainability, it is important to underline that quantitative recycle of quinone **5** and Me-THF solvent were studied. In details, the reaction mixture was

concentrated to recover Me-THF and the resulting solid residue was triturated with cyclopentyl methyl ether (CPME) allowing removal of the insoluble PET through filtration. After column chromatography of the filtrate, alcohol **5'** was quantitatively re-oxidized to quinone **5** with air in the presence of catalytic phthalocyanine **6** (for details see the Experimental Section).

Once established the best reaction conditions, the scope of the oxidative polycondensation of diols **1** with fossil-based dialdehydes **2 a-b** affording MCOs **3** was studied (Table 2). Of note, MCOs **3** were obtained as a mixture of macrocycles with different size, whose composition was investigated through MALDI-TOF MS analysis (see the Supporting Information). Actually, the use of a mixture of MCOs in place of a pure cycle revealed to be beneficial in several ED-ROP processes due to the lower melting points, lower viscosities, and higher solubilities of the polymerization mixtures.^[10b] As general remark, it is important to emphasize that most of the synthesized macrocycles **3** are key and valuable intermediates for the synthesis of the corresponding high molecular weight polymers or copolymers through ring-opening polymerization processes. Moreover, the reported yields concern macrocycles **3** and linear oligoesters **4** isolated by chromatography, while insoluble polyesters were removed from the reaction mixture by filtration during workup procedures.

As shown in the reaction optimization section, the straightforward access to cyclic ethylene terephthalate (**3 aa**, **c(ET)_n**) was achieved with satisfactory 64 % yield (entry 1). MALDI mass spectrum of **3 aa** exhibited the occurrence of various cyclic oligomers (from $n=2$ to $n=7$) separated by a fixed monomer unit of 192.0 Da (Figure 2). As can be noticed, alongside the protonated species of each oligomer also sodiated and potassiated adducts are observed due to the great affinity of ester residues for both ions. For instance, the oligomer with $n=6$ is observed as a triplet at m/z 1153.261, 1175.243 and 1191.217 referred respectively to $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$ adducts. Analogously, all the synthesized macrocycles have

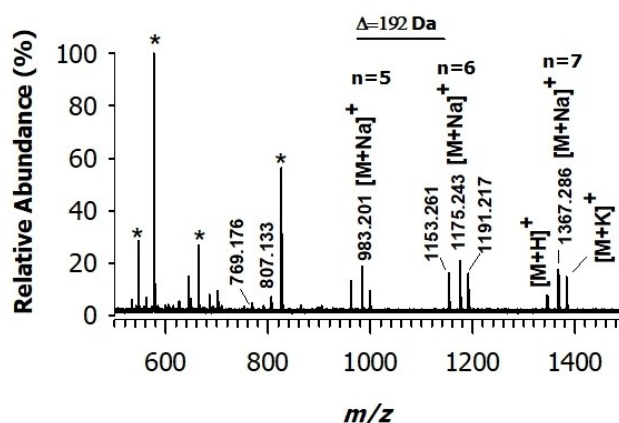
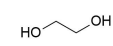
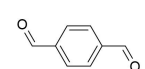
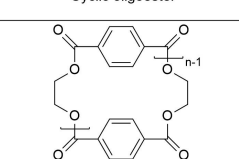
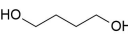
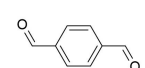
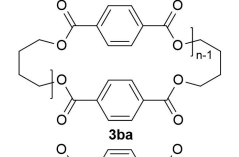
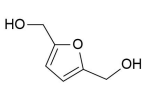

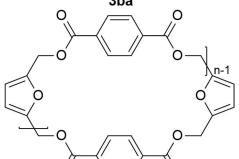
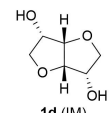

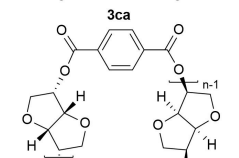
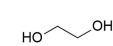
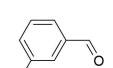
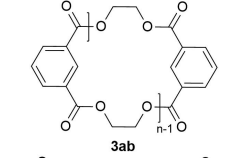
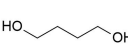
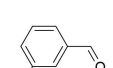
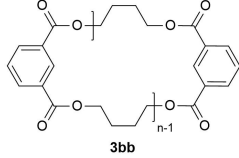
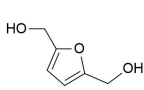
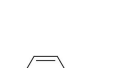
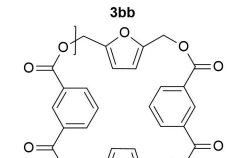
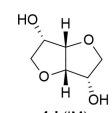

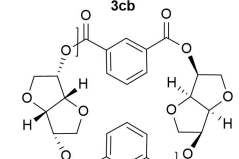


Figure 2. Zoom of MALDI-TOF mass spectrum (500–1500 m/z) in positive reflector ion mode of compound **3 aa**, **c(ET)_n**. Peaks marked with an asterisk are referred to the dithranol matrix-related ions. For full spectra see the Supporting Information.

Table 2. Scope of the oxidative polycondensation of diols **1** and fossil-based dialdehydes **2 a–b** for the synthesis of cyclic oligoesters **3**.^[a]

Entry	Diol	Dialdehyde	Cyclic oligoester	Cyclic oligoester acronym	Yield (%) ^[b]	Cyclic oligoester composition ^[c]	Linear oligoester Yield (%) ^[b]
1	 1a	 2a	 3aa	c(ET)_n	64	n = 2 - 7	-
2	 1b	 2a	 3ba	c(BT)_n	53	n = 2 - 9	-
3	 1c (BHMDF)	 2a	 3ca	c(BHMT)_n	51	n = 2 - 6	-
4	 1d (IM)	 2a	 3da	c(IT)_n	54	n = 2 - 3	4da (25)
5	 1a	 2b	 3ab	c(EI)_n	86	n = 2 - 11	4ab (6)
6	 1b	 2b	 3bb	c(BI)_n	51	n = 2 - 10	4bb (30)
7	 1c (BHMDF)	 2b	 3cb	c(BHM)_n	63	n = 2 - 7	-
8	 1d (IM)	 2b	 3db	c(II)_n	54	n = 2	4db (27)

[a] **1** (0.40 mmol), **2** (0.40 mmol), **A** (0.04 mmol), DBU (0.10 mmol), **5** (0.80 mmol), Me-THF (30.0 mL); mol % are referred to reactive functional groups. [b] Isolated yield after flash chromatography. [c] Detected by MALDI-TOF MS analysis.

been characterized and the relevant MALDI spectra are reported in the Supporting Information.

Notably, **c(ET)_n** were efficiently employed by MacKnight^[29] and Burch^[30] for the synthesis of high performance PET composites. Next, cyclic butylene terephthalate (**3ba**, **c(BT)_n**) was prepared with 53 % yield (entry 2, *n* = 2 to 9). Initially synthesized by Brunelle and co-workers through sterically unhindered amine promotion,^[13,15] **c(BT)_n** has been efficiently employed for high molecular **PBT**^[31] and **PBT** copolymers^[19b,32] production. The scope of reaction was next extended to bio-based diols. First, 2,5-bis(hydroxymethyl)furan (BHMf) **1c**,^[33] a HMF-derived diol commonly employed in the production of polyesters and polyurethanes,^[34] was reacted with terephthalaldehyde **2a**, affording the novel macrocycle **3ca** (**c(BHMT)_n**) with 51 % yield as a mixture of different size macrocycles from dimers to hexamers (entry 3). Isomannide (IM), a bio-based bicyclic diol belonging to the isohexide family, was then condensed with **2a**, allowing the straightforward synthesis of previously undisclosed **3da** (**c(IT)_n**) (*n* = 2, 3) with 54 % yield, together with linear oligoester **4da** which was isolated with 25 % yield (entry 4). In this respect, isomannide was selected over its widely studied isomer isosorbide,^[35] because the latter showed enhanced preference for linear products.^[19c] Next, cyclic isophthalate oligomers were readily obtained by the optimized protocol starting from diols **1a-d** and isomeric isophthalaldehyde **2b**. Coupling of ethylene glycol (EG)

1a with **2b** afforded, for the first time, the corresponding macrocycle **3ab** (**c(EI)_n**) with almost quantitative yield (86 %, *n* = 2 to 11, entry 5), together with traces of the corresponding linear oligomer **4ab** (6 %). Switch to butanediol **1b** led to the production of **3bb** (**c(BI)_n**) (51 % yield, *n* = 2 to 10, entry 6), a valuable macrocycle recently employed by Muñoz-Guerra and co-workers in the synthesis of poly(butylene 2,5-furandicarboxylate-co-isophthalate) copolyesters.^[36] In addition, linear oligoester **4bb** was isolated as by-product with 30 % yield. Finally, the employment of BHMf and IM afforded respectively the unprecedented macrocycles **3cb** (**c(BHMI)_n**) (63 %, *n* = 2 to 7, entry 7) and **3db** (**c(II)_n**) (54 %, *n* = 2, entry 8) together with the corresponding linear species **4db** (27 %).

The scope of the oxidative polycondensation was also extended to the bio-based dialdehyde **2c** (Table 3), confirming the versatility of the novel synthetic protocol, which allows satisfactory substrate variability, paving the way to the production of novel MCOs. In this regard, cellulose-derived dialdehyde **2c** (DFF) was selected as model bio-based substrate, in light of the emerging role of furan-based polymers.^[37] Coupling of DFF with diol **1a** under the optimized conditions afforded the furanic macrocycle **3ac** (**c(EF)_n**), only as dimer (*n* = 2), with 64 % yield (entry 1). Pivotal work from Morbidelli group^[20b] clearly highlights the synthetic relevance of this macrocycle, used as key intermediate in the synthesis of bottle-grade polyethylene furanoate (PEF), an innovative alternative to PET with attractive mechanical and barrier properties.^[5d] Cyclic ethylene 2,5-furandicarboxylate **3ac** was also synthesized and reacted in a subsequent ROP process by Muñoz-Guerra group, for the efficient production of high molecular weight PEF.^[19a] Substitution of ethylene glycol with butanediol **1b** afforded

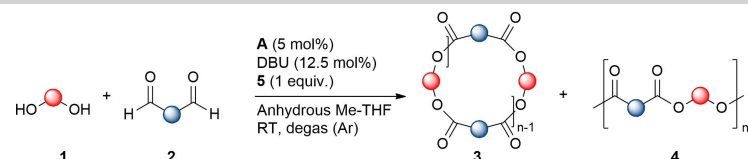
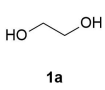
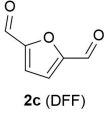
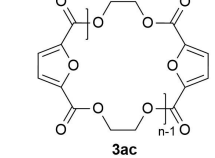
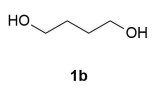
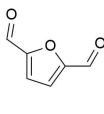
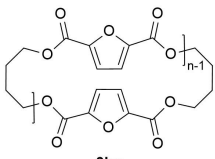
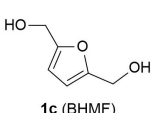
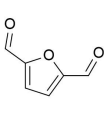
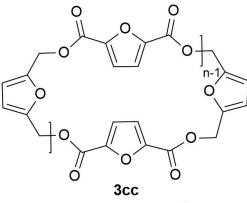
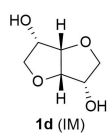
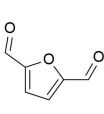
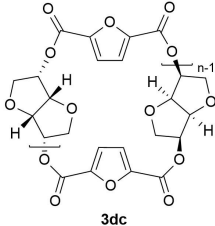
cyclic butylene 2,5-furandicarboxylate (**3bc**, **c(BF)_n**) with 62 % yield as a mixture ranging from dimers to nonamers (entry 2), together with traces (5 %) of the corresponding linear counterpart **4bc**. Notably, **c(BF)_n** was recently employed in ROP processes for the synthesis of polybutylene furanoate (PBF)^[19a,20a] and copolyesters with isomannide,^[19c] terephthalate,^[19b] isophthalate^[36] and succinate^[18a] units. At this stage of the study, the unprecedented fully furan-based macrocycle **3cc** (**c(BHMF)_n**) was prepared, starting from HMF-derived monomers BHMf and DFF (54 % yield, *n* = 2 to 6, entry 3). This macrocycle represents a valuable key intermediate for the synthesis of poly(2,5-furan-dimethylene 2,5 furandicarboxylate) (PBHMf),^[38] a promising polyester derived from cellulose. Finally, isomannide **1a** was condensed with furanic dialdehyde **2c** (entry 4) leading to **3dc** (**c(IF)_n**) (58 % yield, *n* = 2 to 3) and linear oligoester **4dc** (25 % yield). The scientific relevance of this macrocycle was confirmed by its recent employment in ring opening processes for the synthesis of isomannide-containing poly(butylene 2,5-furandicarboxylate) copolyesters.^[19c]

As proof of concept, at this stage of the study, we focused our attention on **3cc**, an unprecedented synthesized macrocyclic ester, which could serve as key intermediate for the synthesis of **PBHMf**. This fully bio-based polyester was first synthesized by Gandini and co-workers in 2011,^[38] through interfacial polycondensation reaction between BHMf and 2,5-furandicarboxylic dichloride and later, in 2019, by our group through NHC oxidative catalysis starting from dialdehyde **2c** (DFF) and the same diol.^[22] Thus, we wondered if the same polymer could be obtained via ring opening polymerization process of **3cc** (**c(BHMF)_n**), in an organocatalytic fashion. In this direction, the thermal stability of **c(BHMF)_n** was evaluated through thermal gravimetric analysis (TGA), in order to find the suitable working temperature range for the ED-ROP process. TGA analysis showed the degradation in nitrogen atmosphere to start at 201 °C (see the Supporting Information), thus suggesting a temperature of 170–180 °C as maximum for conducting the polymerization.

Inspired by our recent work on poly(hydroxymethylfuroate) (**PHMF**) production,^[25] different conditions were screened for the entropy-driven ring opening polymerization process (ED-ROP) (Table 4). Hence, triazabicyclodecene (TBD)/*n*-octanol^[21,25] was employed as catalyst/initiator couple, together with commercial antioxidants Irganox 1010 and Irgafos 126, in order to suppress undesired oxidative radical degradation processes.^[39] Reactions were performed under Ar atmosphere in bulk at 160 °C, according to **c(BHMF)_n** TGA data, previous observations on thermal stability of HMF-derived macrocyclic species,^[25] and to the well-known thermal instability of the furanic methylene groups under acidic and/or oxidative conditions resulting in polymer discoloration and resinification.^[40]

First, reaction was performed with 0.5 mol% of TBD and 0.5 mol% of *n*-octanol, affording, after 5 h, 60 % conversion of starting **c(BHMF)_n** and production of a black polymer which was insoluble in all the main organic solvents commonly used for polymers solubilization (entry 1). According to literature, blackening of furanic polymers is often related to undesired radical processes, leading to highly cross-linked structure.^[40] In order to

Table 3. Scope of the oxidative polycondensation of diols **1** and the bio-based dialdehyde **2c** for the synthesis of cyclic oligoesters **3**.^[a]

Entry	Diol	Dialdehyde	Cyclic oligoester	Cyclic oligoester acronym	Yield (%) ^[b]	Cyclic oligoester composition ^[c]	Linear oligoester Yield (%) ^[b]
							
1	 1a	 2c (DFF)	 3ac	c(EF)_n	64	n = 2	-
2	 1b	 2c (DFF)	 3bc	c(BF)_n	62	n = 2 - 9	4bc (5)
3	 1c (BHMF)	 2c (DFF)	 3cc	c(BHMF)_n	54	n = 2 - 6	-
4	 1d (IM)	 2c (DFF)	 3dc	c(IF)_n	58	n = 2 - 3	4dc (25)

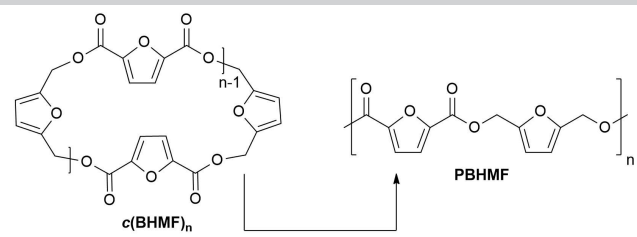
[a] **1** (0.40 mmol), **2** (0.40 mmol), **A** (0.04 mmol), DBU (0.10 mmol), **5** (0.80 mmol), Me-THF (30.0 mL); mol % are referred to reactive functional groups. [b] Isolated yield after flash chromatography. [c] Detected by MALDI-TOF MS analysis.

suppress this competitive reaction pathway, catalyst and initiator loadings were increased (1 mol%, entry 2), leading to a black polymer (12 mol% yield) which resulted to be partially soluble in a solution of CDCl₃:TFA = 1:1, suitable for NMR analysis and NMR number-average molecular weight calculation ($M_n = 3200 \text{ g mol}^{-1}$). The structure of **PBHMf** was confirmed by NMR spectroscopy (see the Supporting Information), while the M_n values reported in Table 4 were obtained from the integral ratios of peaks corresponding to the repeating (furan-2-yl)methylene and terminal hydroxymethyl groups (5.35 and 4.57 ppm, respectively). Gratifyingly, further catalyst/initiator increase (2% mol, entry 3) was responsible for the production of **PBHMf** as a brownish solid, fully soluble in CDCl₃:TFA = 1:1, with substantial yield (66%) and M_n improvements (8200 g mol^{-1}). Finally, increase of TBD/*n*-octanol to 5 mol% (entry 4) led to good yield (74%) with a lower value of chain length ($M_n = 4100 \text{ g mol}^{-1}$); this result well agrees with a polymerization process occurring by ring opening polymerization under almost living conditions. Indeed, by assuming the yield as monomer conversion, based on the increased amount of the initiator from entry 3 to entry 4

the expected M_n for entry 4 would be 3700 Da, thus a value reasonably closed to the observed one. Hence, conditions of entry 3 were selected as the most performing, achieving the production of **PBHMf** for the first time via ED-RDP process, starting from macrocycles **3cc** (**c(BHMF)_n**), with satisfactory levels of yield and chain length, higher than those obtained by Gandini (60% yield, $M_n = 3880 \text{ g mol}^{-1}$) and comparable to those achieved later by our group (78% yield, $M_n = 7800 \text{ g mol}^{-1}$) through step-growth polycondensations.

Conclusions

In summary, we have described the unprecedented synthesis of macrocyclic oligoesters (MCOs) starting from diols and dialdehydes, mediated by an N-heterocyclic carbene (NHC) catalyst under high dilution oxidative conditions. The disclosed method allows straightforward access to MCOs starting from commercial dialdehydes, without the need of previous substrate activations, thus avoiding the use of toxic acyl chlorides. From the

Table 4. Optimization study for the synthesis of PBHMF through organocatalyzed ED-ROP of $c(\text{BHMF})_n$ 3 cc.^[a]


Entry	TBD:n-octanol (mol %)	Conv ^[b] (%)	Yield ^[c] (%)	M _n ^[d] (g/mol)	Color
1	0.5:0.5	60	–	–	Black
2	1:1	71	12	3200	Black
3	2:2	75	66	8200	Brownish
4	5:5	88	74	4100	Brownish

[a] $c(\text{BHMF})_n$ (100 mg, 0.4 mmol of repeating units), Irganox 1010 (0.1% w/w), Irgafos 126 (0.3% w/w), Ar atmosphere, T=160°C, 5 h. [b] Calculated from recovered $c(\text{BHMF})_n$. [c] Isolated yield. [d] Determined by ¹H NMR (CDCl₃:TFA = 1:1).

sustainability point of view, the process is totally metal-free, takes place in the green (recyclable) Me-THF solvent and the use of stoichiometric amounts of a quinone oxidant is well tolerated thanks to its quantitative recovery and recycle. Macrocycle structures were confirmed by NMR and cycles size were elucidated by MALDI-TOF MS analysis. The versatility of the disclosed protocol was confirmed by the employment of fossil-based and bio-based monomers, affording the corresponding macrocycles with good yields (51–86%) and short reaction time (3 h). Taking in mind that driving reaction selectivity towards the formation of cyclic species represents a very challenging task, the results achieved in this work can be considered more than satisfactory; indeed, the disclosed protocol proved to be effective for the production of a series of novel and known synthetically relevant macrocyclic oligoesters, with product yields and selectivities comparable to those observed in the traditional synthetic routes for MCOs production, starting from diacyl chlorides. At the same time, it is important to highlight the relevance of the reported synthetic targets which is well documented by the growing number of processes involving their use as starting monomers in entropically driven ring-opening polymerizations. Finally, in order to prove their synthetic suitability, an organocatalytic ED-ROP study promoted by TBD was conducted, affording poly(2,5-furan-dimethylene 2,5 furandicarboxylate) (PBHMF) with number-average molecular weight up to 8200 g mol⁻¹ and 66% isolated yield.

Experimental Section

General experimental procedures used in this study are listed and described in the Supporting Information.

General procedure for the synthesis of cyclic oligoesters 3

A mixture of diol 1 (0.4 mmol), aldehyde 2 (0.4 mmol), oxidant 5 (328 mg, 0.8 mmol) and pre-catalyst A (9 mg, 0.04 mmol) in anhydrous Me-THF (30.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, DBU was added (15 μL, 0.10 mmol), and the reaction was stirred at room temperature for 3 h. The mixture was concentrated and the resulting residue triturated with fresh portions of CPME (3 × 10 mL), centrifugated and finally filtered. The polymeric precipitate was separated from the reaction mixture while the organic solution was eluted from a column of silica gel with a suitable elution system to give, in order of elution, alcohol 5', macrocyclic oligoesters 3 and linear oligomers 4 (see the Supporting Information for details).

Procedure for oxidant 5 recycle

The quantitative recycle of diquinone 5 was conducted stirring the isolated 5' (295 mg, 0.72 mmol) with iron(II) phthalocyanine 6 (11 mg, 0.08 mmol) in Me-THF (8 mL) under air atmosphere (1 atm, balloon) for 16 h. Filtration over celite and concentration under reduced pressure afforded diquinone 5 as a red amorphous solid (260 mg, 88%).

General procedure for the synthesis of PBHMF

$c(\text{BHMF})_n$ (100 mg, 0.4 mmol of repeating units) was dissolved in CPME (5 mL) in a reaction flask. Then, a mixture containing the required amounts of TBD, n-octanol and antioxidants Irganox 1010 and Irgafos 126 (according to Table 4) in CPME was added to MCOs solution and stirred for 30 min. After solvent removal under reduced pressure, the reaction flask was connected to a glass oven (Büchi GKR-50) and dried under vacuum for 30 min. Finally, the reaction mixture was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times to remove residual oxygen, then heated at T=160°C under mechanical rotation for the 5 h at atmospheric pressure. After cooling, the resulting product was triturated with CPME (10 mL). The soluble fraction contained unreacted cycles while the precipitate corresponded to PBHMF which was then analyzed by NMR (see the Supporting Information for characterization details).

Acknowledgements

We gratefully acknowledge the University of Ferrara (fondi FAR) and Italian Minister of University and Research (project PRIN 2022) for financial support. Thanks are also given to Paolo Formaglio for NMR experiments.

Conflict of Interests

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.

Keywords: Macrocycles · N-heterocyclic carbene · Oligoesters · Organocatalysis · Ring-opening polymerization

- [1] a) D. V. Rosato, *Plastic Product Material and Process Selection Handbook*, Elsevier, New York, **2004**; b) J. E. McIntyre, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, **2004**, pp. 1–28.
- [2] Selected recent reviews: a) C. Maraveas, *Polymer* **2020**, *12*, 1127; b) S. Walker and R. Rothman, *J. Cleaner Prod.* **2020**, *261*, 121158; c) A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi, *New Biotechnol.* **2021**, *60*, 146–158; d) R. L. Quirino, K. Monroe, C. H. Fleischer, E. Biswasa, M. R. Kessler, *Polym. Int.* **2021**, *70*, 167–80; e) N. Lee, Y. T. Kim, J. Lee, *Polymer* **2021**, *13*, 364.
- [3] a) I. Alastair, A. N. Martin, *J. Cleaner Prod.* **2013**, *45*, 38–49; b) C. Vilela, A. F. Sousa, A. C. Fonseca, A. C. Serra, J. F. J. Coelho, C. S. R. Freire, A. J. D. Silvestre, *Polym. Chem.* **2014**, *5*, 3119–3141; c) K. M. Zia, A. Noreen, M. Zuber, S. Tabasum, M. Mujahid, *Int. J. Biol. Macromol.* **2016**, *82*, 1028–1040; d) S. Lambert, M. Wagner, *Chem. Soc. Rev.* **2017**, *46*, 6855–6871; e) A. Ganidni, T. M. Lacerda, *Macromol. Mater. Eng.* **2022**, *307*, 2100902.
- [4] a) A. Gandini, D. Coelho, M. Gomes, B. Reis, A. Silvestre, *J. Mater. Chem.* **2009**, *19*, 8656–8664; b) A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G.-J. M. Gruter, J. F. J. Coelho, A. J. D. Silvestre, *Polym. Chem.* **2015**, *6*, 5961–5983; c) B. Y. Karlinskii, V. P. Ananikov, *Chem. Soc. Rev.* **2023**, *52*, 836–862.
- [5] a) A. J. J. E. Eerhart, A. P. C. Faaij, M. K. Patel, *Energy Environ. Sci.* **2012**, *5*, 6407–6422; b) D. S. Van Es, F. van der Klis, R. J. I. Knoop, K. Molenveld, L. Sijtsma, J. Van Haveren, *Other Polyesters from Biomass Derived Monomers, in Bio-Based Plastics: Materials and Applications*, ed. Kabasci, John Wiley & Sons Inc., Hoboken, NJ, USA, **2013**, pp. 241–274; c) K. Hwang, W. Jeon, S. Youn Lee, M. Kim, Y. Park, *Chem. Eng. J.* **2020**, *390*, 124636; d) X. Fei, J. Wang, J. Zhu, X. Wang, X. Liu, *ACS Sustainable Chem. Eng.* **2020**, *8*, 23, 8471–8485.
- [6] J. Zhu, J. Cai, W. Xie, P. Chen, M. Gazzano, M. Scandola, R. A. Gross, *Macromolecules* **2013**, *46*, 796–804.
- [7] a) A. Fradet, M. Tessier, in *Synthetic Methods in Step-Growth Polymers* (Eds.: M. E. Rogers, T. E. Long), Wiley, New York, **2003**, pp. 17–34; b) H. Kricheldorf, *Polycondensation: History and New Results*, Springer Berlin Heidelberg, **2013**.
- [8] a) A. Duda, A. Kowalski, in *Handbook of Ring-Opening Polymerization*, **2009**, pp. 1–51; b) L. E. Elizalde, G. de los Santos-Villarreal, J. L. Santiago-García, M. Aguilar-Vega, in *Handbook of Polymer Synthesis, Characterization and Processing* (Eds.: E. Saldívar-Guerra, E. Vivaldo-Lima), Wiley, New York, **2013**, pp. 41–63.
- [9] a) I. van der Meulen, E. Gubbels, S. Huijser, R. Sablong, C. E. Koning, A. Heise, R. Duchateau, *Macromolecules* **2011**, *44*, 11, 4301–4305; b) G. L. Gregory, E. M. López-Vidal, A. Buchard, *Chem. Commun.* **2017**, *53*, 2198–2217; c) L. Al-Shok, D. M. Haddleton, F. Adams, *Progress in Catalytic Ring-Opening Polymerization of Biobased Lactones in Advances in Polymer Science*, Springer, Berlin, Heidelberg, **2022**, pp. 1–71.
- [10] a) S. Strandman, J. E. Gautrot, X. X. Zhu, *Polym. Chem.* **2011**, *2*, 791–799; b) P. Hodge, *Chem. Rev.* **2014**, *114*, 2278–2312.
- [11] A. Martínez de Ilarduya, S. Muñoz Guerra, *Polym. Chem.* **2020**, *11*, 4850–4860.
- [12] P. Hodge, *React. Funct. Polym.* **2014**, *80*, 21–32.
- [13] D. J. Brunelle, *J. Polym. Sci. Part A* **2008**, *46*, 1151–1164.
- [14] E. W. Spanagel, W. H. Carothers, *J. Am. Chem. Soc.* **1935**, *57*, 929–934.
- [15] D. J. Brunelle, J. E. Bradt, J. Serth-Guzzo, T. Takekoshi, T. L. Evans, E. J. Pearce, P. R. Wilson, *Macromolecules* **1998**, *31*, 4782–4790.
- [16] a) P. Ruggli, *Justus Liebigs Ann. Chem.* **1912**, *392*, 92; **1913**, *399*, 174; **1916**, *412*, 1; b) L. Ruzicka, M. Stoll, H. Schinz, *Helv. Chim. Acta* **1926**, *9*, 249; c) K. Ziegler, H. Eberle, H. Ohlinger, *Justus Liebigs Ann. Chem.* **1933**, *504*, 94; d) K. Ziegler, in *Methoden der Organischen Chemie 4th ed.* (Eds.: H. J. Houben, T. Weyl), Thieme, Stuttgart, **1955**; Vol. 4/II, pp. 729–822; e) L. Rossa, F. Vögtle, *Top. Curr. Chem.* **1983**, *113*, 1–86.
- [17] a) Y. Osanai, K. Tushima, S. Matsumura, *Green Chem.* **2003**, *5*, 567–570; b) I. Flores, A. Martínez de Ilarduya, H. Sardón, A. J. Müller, S. Muñoz-Guerra, *ACS Appl. Polym. Mater.* **2019**, *1*, 321–325.
- [18] a) J. C. Morales-Huerta, C. B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra, *Polym. Chem.* **2017**, *8*, 748–760; b) A. Kundys, E. Bialecka-Florjanczyk, A. Fabiszewska, J. Malajowicz, *J. Polym. Environ.* **2018**, *26*, 396–407.
- [19] a) J. C. Morales-Huerta, A. Martínez De Ilarduya, S. Muñoz-Guerra, *Polymer* **2016**, *87*, 148–158; b) J. C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra, *ACS Sustainable Chem. Eng.* **2016**, *4*, 4965–4973; c) J. C. Morales-Huerta, A. Martínez De Ilarduya, S. León, S. Muñoz-Guerra, *Macromolecules* **2018**, *51*, 3340–3350.
- [20] a) D. Pfister, G. Storti, F. Tancini, L. I. Costa, M. Morbidelli, *Macromol. Chem. Phys.* **2015**, *216*, 2141–2146; b) J. G. Rosenboom, D. K. Hohl, P. Fleckenstein, G. Storti, M. Morbidelli, *Nat. Commun.* **2018**, *9*, 2701; c) P. Fleckenstein, J.-G. Rosenboom, G. Storti, M. Morbidelli, *Macromol. React. Eng.* **2018**, *12*, 1800018.
- [21] a) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2010**, *43*, 2093–2107; b) A. P. Dove, *ACS Macro Lett.* **2012**, *1*, 1409–1412; c) W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle, D. Taton, *Prog. Polym. Sci.* **2016**, *56*, 64–115; d) X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, *Chem. Rev.* **2018**, *118*, 839–885; e) A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long, H. Sardon, *Prog. Polym. Sci.* **2019**, *90*, 164–210.
- [22] D. Ragno, G. Di Carmine, A. Brandolese, O. Bortolini, P. P. Giovannini, G. Fantin, M. Bertoldo, A. Massi, *Chem. Eur. J.* **2019**, *25*, 14701–14710.
- [23] D. Ragno, A. Brandolese, G. Di Carmine, S. Buoso, G. Belletti, C. Leonardi, O. Bortolini, M. Bertoldo, A. Massi, *Chem. Eur. J.* **2021**, *27*, 1839–1848.
- [24] Selected reviews on oxidative NHC-catalysis: a) C. E. I. Knappe, A. Imami, A. J. Von Wangelin, *ChemCatChem* **2012**, *4*, 937–941; b) S. De Sarkar, A. Biswas, R. C. Samanta, A. Studer, *Chem. Eur. J.* **2013**, *19*, 4664–4678; c) J. Mahatthananchai, J. W. Bode, *Acc. Chem. Res.* **2014**, *47*, 696–707; d) M. H. Wang, K. A. Scheidt, *Angew. Chem. Int. Ed.* **2016**, *55*, 14912–14922, (*Angew. Chem.* **2016**, *128*, 15134–15145); e) C. De Risi, A. Brandolese, G. Di Carmine, D. Ragno, A. Massi, O. Bortolini, *Chem. Eur. J.* **2023**, *29*, e202202467.
- [25] D. Ragno, G. Di Carmine, M. Vannini, O. Bortolini, D. Perrone, S. Buoso, M. Bertoldo, A. Massi, *Polym. Chem.* **2022**, *13*, 1350–1358.
- [26] a) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org. Lett.* **2002**, *4*, 21, 3587–3590; b) L. Guo, D. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 18072–18074; c) N. E. Kamber, W. Jeong, S. Gonzalez, J. L. Hedrick, R. Waymouth, *Macromolecules* **2009**, *42*, 1634–1639; d) C. A. Smith, M. R. Narouz, P. A. Lummis, I. Singh, A. Nazemi, C.-H. Li, C. M. Crudden, *Chem. Rev.* **2019**, *119*, 4986–5056; e) L. Wang, G. A. Nelson, J. Toland, J. D. Holbrey, *ACS Sustainable Chem. Eng.* **2020**, *8*, 35, 13362–13368; f) M. S. Zaky, A. Wirocius, O. Coulembier, G. Guichard, D. Taton, *ACS Macro Lett.* **2022**, *11*, 1148–1155.
- [27] J. Piera, J.-E. Bäckvall, *Angew. Chem. Int. Ed.* **2008**, *47*, 3506–3523; *Angew. Chem.* **2008**, *120*, 3558–3576.
- [28] A. Axelsson, A. Antoine-Michard, H. Sundén, *Green Chem.* **2017**, *19*, 2477–2481.
- [29] J. H. Youk, R. P. Kambour, W. J. MacKnight, *Macromolecules* **2000**, *33*, 3594–3599.
- [30] R. Burch, S. R. Lustig, M. Spinu, *Macromolecules* **2000**, *33*, 5053–5064.
- [31] J. Pinaud, R. Tang, O. Gimello, J.-J. Robin, *J. Polym. Sci. Part A* **2017**, *55*, 1611–1619.
- [32] a) M. P. F. Pepels, F. van der Sanden, E. Gubbels, R. Duchateau, *Macromolecules* **2016**, *49*, 4441–4451; b) W. Wang, F. Wu, H. Lu, X. Li, X. Yang, Y. Tu, *ACS Appl. Polym. Mater.* **2019**, *1*, 2313–2321.
- [33] a) Y. Jiang, A. J. Woortman, G. O. Alberda van Ekenstein, D. M. Petrovic, K. Loos, *Biomacromolecules* **2014**, *15*, 2482–2493; b) M. Chatterjee, T. Ishizaka, H. Kawanami, *Green Chem.* **2014**, *16*, 4734–4739; c) W. Hao, W. Li, X. Tang, X. Zeng, Y. Sun, S. Liu, L. Lin, *Green Chem.* **2016**, *18*, 1080–1088.
- [34] a) C. Zeng, H. Seino, J. Ren, K. Hatanaka, N. Yoshie, *Macromolecules* **2013**, *46*, 1794–1802; b) Y. Jiang, A. J. Woortman, G. O. Alberda van Ekenstein, D. M. Petrovic, K. Loos, *Biomacromolecules* **2014**, *15*, 2482–2493; c) C. Post, D. Maniar, V. S. D. Voet, R. Folkersma, K. Loos, *ACS Omega* **2023**, DOI: 10.1021/acsomega.2c07629.
- [35] a) M. Rose, R. Palkovits, *ChemSusChem* **2012**, *5*, 167–176; b) C. Dusseigne, T. Delaunay, V. Wiat, H. Wyart, I. Suisse, M. Sauthier, *Green Chem.* **2017**, *19*, 5332–5344; c) D. Ragno, C. Leonardi, G. Di Carmine, O. Bortolini, A. Brandolese, C. De Risi, A. Massi, *ACS Sustainable Chem. Eng.* **2021**, *9*, 8295–8305; d) D. Ragno, C. De Risi, A. Massi, G. di Carmine, S. Toldo, C. Leonardi, O. Bortolini, *Eur. J. Org. Chem.* **2022**, e202200482.
- [36] J. C. Morales-Huerta, A. Martínez De Ilarduya, S. Muñoz-Guerra, *Polymer* **2018**, *10*, 483.

- [37] a) R. Bielski, G. Gryniewicz, *Green Chem.* **2021**, *23*, 7458–7487; b) N. Li, M. Zong, *ACS Catal.* **2022**, *12*, 10080–10114; c) C. P. Woroch, I. W. Cox, M. W. Kanan, *J. Am. Chem. Soc.* **2023**, *145*, 697–705.
- [38] M. Gomes, A. Gandini, A. J. D. Silvestre, B. Reis, *J. Polym. Sci. Part A* **2011**, *49*, 3759–3768.
- [39] N. Grassie, G. Scott, *Polymer Degradation and Stabilisation*, Cambridge University Press, Cambridge, UK, **1985**, p. 125.
- [40] a) A. Gandini, *Biopolymers - New Materials for Sustainable Films and Coatings* (ed. D. Plackett), John Wiley & Sons, Ltd, Chichester, UK, **2011**, ch. 9, pp. 179–209; b) A. Gandini, M. N. Belgacem, in *Monomers, Polymers and Composites from Renewable Resources* (eds. M. N. Belgacem, A. Gandini), Elsevier, Amsterdam, NL, **2008**, pp. 115–152; c) A. Gandini, M. N. Belgacem, *Prog. Polym. Sci.* **1997**, *22*, 1203–1379; d) A. Gandini, *Polymer Chemistry, in Advances in Polymer Science*, Springer, Berlin, Heidelberg, **1977**, vol. 25, pp. 47–96.

Manuscript received: May 3, 2023

Accepted manuscript online: May 30, 2023

Version of record online: July 6, 2023