

Polymerization | Hot Paper |

Oxidative NHC-Catalysis as Organocatalytic Platform for the Synthesis of Polyester Oligomers by Step-Growth Polymerization

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In memory of Professor Cinzia Chiappe.

Abstract: The application of *N*-heterocyclic carbene (NHC) catalysis to the polycondensation of diols and dialdehydes under oxidative conditions is herein presented for the synthesis of polyesters using fossil-based (ethylene glycol, phthalaldehydes) and bio-based (furan derivatives, glycerol, isosorbide) monomers. The catalytic dimethyl triazolium/1,8-diazabicyclo[5.4.0]undec-7-ene couple and stoichiometric quinone oxidant afforded polyester oligomers with a number-average molecular weight (M_n) in the range of 1.5–

7.8 kg mol⁻¹ as determined by NMR analysis. The synthesis of a higher molecular weight polyester (polyethylene terephthalate, PET) by an NHC-promoted two-step procedure via oligoester intermediates is also illustrated together with the catalyst-controlled preparation of cross-linked or linear polyesters derived from the trifunctional glycerol. The thermal properties (TGA and DSC analyses) of the synthesized oligoesters are also reported.

Introduction

In recent years, organocatalytic polymerization strategies have been demonstrated to effectively complement metal-catalyzed approaches for the synthesis of macromolecular materials with the advantage of avoiding metal contamination, which could be unfavorable for applications in the electronic and biomedical fields.^[1] Whereas organocatalytic chain-growth polymerizations have been investigated in depth,^[2] the application of organocatalysts for the synthesis of polyesters (PEs), polyurethanes (PUs), and polycarbonates (PCs) by step-growth polymerization is more limited in spite of the potential benefits associated with this technique, including modularity and compatibility with functionalized monomers to access a wide range of polymers for diversified applications.^[3] Polyester materials are used extensively in clothing, food packaging, biomedical, and electronic devices, accounting for nearly 18% of the world plastic production.^[4] Main strategies for the synthesis of polyesters include the ring-opening polymerization (ROP) of cyclic esters (chain-growth process), the self-polycondensation

of hydroxy acids, and the step-growth polymerization of diols and diacids and their derivatives (Figure 1).^[5]

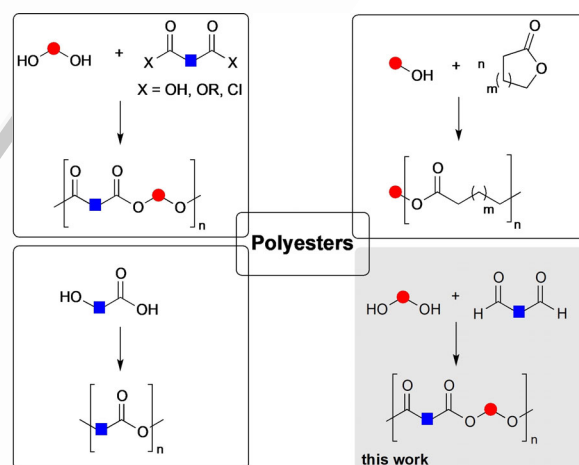


Figure 1. Main strategies for the synthesis of polyesters and the proposed approach.

Although ROP allows for an accurate control of dispersity and molecular weight, the polycondensation of diols and activated carboxylic derivatives still represents the preferred synthetic route for industry.^[4,5] In this area of research, Brønsted base and Brønsted acid organocatalysts have been established as practical, greener alternatives to antimony-based catalysts in a number of studies.^[3,6] Lewis base organocatalysts, namely *N*-heterocyclic carbenes (NHCs),^[7] have also been tested in step-growth polymerization to polyesters, but in a single investiga-

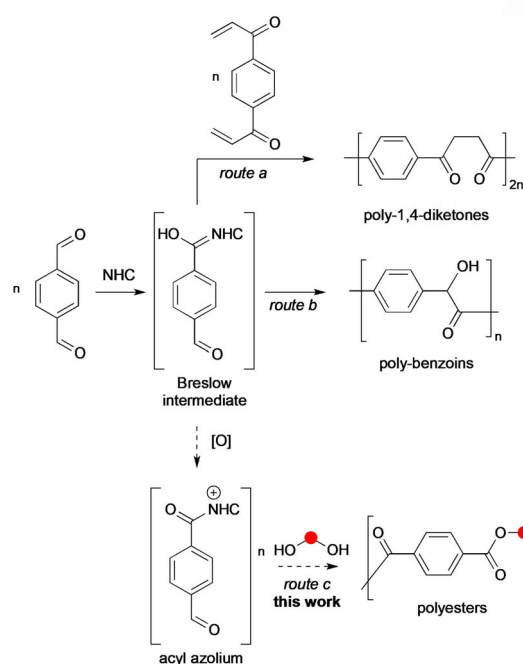
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tion dealing with the poly-condensation of ethyl glycolate and the synthesis of polyethylene terephthalate (PET) by a two-step strategy.^[8]

The peculiar stereoelectronic features of NHCs make these molecules a special class of organocatalysts with three major attributes: ambiphilicity (σ -basicity and π -acidity), moderate nucleophilicity, and strong basicity.^[7] In polymer chemistry, all types of catalytic activation modes by NHCs are conveniently exploited for the preparation of polymers from diverse monomers such as lactones, anhydrides, carbonates, epoxides, lactams, siloxanes, acrylates, and aldehydes.^[9] In this latter case, the ambiphilic character of NHCs accounted for the polybenzoin condensation of terephthalaldehyde^[10] and the iterative Stetter reaction of dialdehydes and enones affording polymeric 1,4-diketones (Scheme 1, routes a,b).^[11] This umpolung (polarity



Scheme 1. NHC umpolung (Routes a, b) and oxidative (Route c) catalysis in polymer chemistry.

reversal) chemistry relies on the formation of the nucleophilic Breslow intermediate as the key catalytic species,^[7] oxidative protocols, however, have recently enriched the toolbox of NHC-based strategies through formation of acyl azolium intermediates to perform a number of normal polarity transformations including the direct aldehyde-to-ester conversion.^[12]

Hence, we present herein the unprecedented polycondensation of dialdehydes and diols promoted by NHCs under oxidative conditions as an alternative, atom-economical synthetic route to polyesters by using the step-growth polymerization technique (Figure 1; Scheme 1, Route c).

The combination of environmental concerns and depletion of fossil resources have stimulated extensive research on the polymerization of monomers derived from renewable feedstocks.^[6,13,14] Therefore, after a propaedeutic study on the synthesis of PET and polyethylene isophthalate (PEI) oligomers,

the potential of the revealed methodology for engineering polymers has been validated by the polycondensation of bio-based furanic monomers, glycerol, and isosorbide to access polyester oligomers of interest for the development of environmentally benign macromolecular materials. Indeed, oligoesters can be exploited not only to prepare thermoplastic polyesters in a subsequent polycondensation step but also as components in thermosetting resin formulations in combination with curing agents such as isocyanates (polyurethane), urea (polyester-urea) or anhydrides (alkydic resins) to obtain high-performance composites, adhesives, coatings or inks.

Results and Discussion

The polycondensation of ethylene glycol **1a** and terephthalaldehyde **2a** was selected as a benchmark for the optimization of the reaction conditions with the inexpensive triazolium salt **A** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); in our previous studies, in fact, this pre-catalyst/base couple proved to be effective in the NHC-promoted esterification of aldehydes under different oxidative conditions.^[15] A prerequisite of the present investigation was the utilization of a slight excess of diol **1a** (1.1 equiv) to promote the formation of bis-hydroxyl-terminated polymers.

Initially, the biomimetic system of electron-transfer mediators (ETMs) developed by Bäckvall^[16] and Sundén^[17] groups was applied to evaluate the possible use of air as the terminal oxidant in our polymerization procedure (Table 1). Accordingly, a catalytic amount of the low-cost alcohol **4** generated the quinone oxidant **5** (ETM) in situ, which was responsible for the oxidation of the Breslow intermediate with formation of the reactive acyl azolium and the reduced species **5'**. This latter could be re-oxidized to **5** by atmospheric oxygen in the presence of catalytic iron(II) phthalocyanine **6** (ETM'). Unfortunately, the above oxidation conditions were only moderately effective, furnishing low aldehyde conversions (20–22%) in anhydrous tetrahydrofuran (THF) after 16 hours at room temperature or 60 °C as determined by ¹H NMR analysis (entries 1–2).

Gratifyingly, the utilization of a stoichiometric amount of oxidant **5** represented a major step forward, allowing a good reaction conversion (75%) in 2 hours and the isolation of **3aa** (precipitation into excess of methanol) with a number-average molecular weight (M_n) of 4.2 kg mol⁻¹ based on ¹H NMR spectroscopic analysis (entry 3). An increase of oligomer length (M_n = 6.5 kg mol⁻¹) was achieved by extending the reaction time to 16 hours (entry 4). Disappointingly, the addition of molecular sieves to prevent competitive nucleophilic attack by water, heating of the reaction mixture (60 °C), and the replacement of THF with anhydrous DCM or with the biomass-derived Me-THF did not improve the polymer growth (entries 5–8). Furthermore, unsatisfactory reaction outcomes were detected with different oxidants such as phenazine **7** (entry 9) and azobenzene **8** (entry 10), with the latter being completely ineffective. Finally, the optimized conditions detailed in entry 4 were successfully applied to the gram-scale synthesis of **3aa** (1.69 g, 88% yield) starting from 10 mmol of aldehyde **2a** (entry 11).

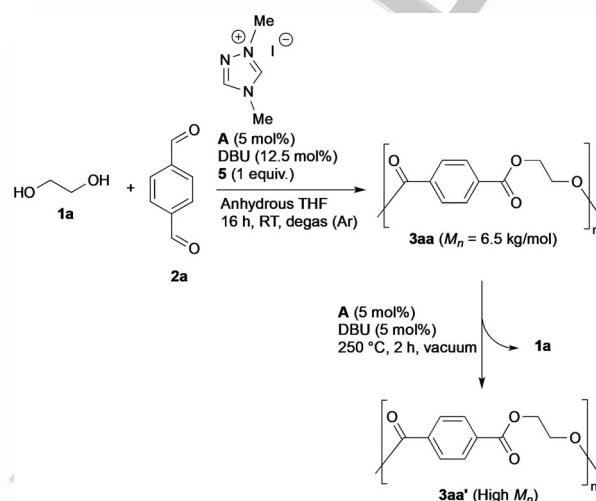
Table 1. Screening of reaction conditions for the synthesis of PET oligomers **3aa**.^[a]

Entry	Oxidant [mol%]	Time [h]	Conv. ^[b] [%]	3aa ^[c] [%]	M_n ^[d] [kg mol ⁻¹]
1	air, 4 / 6 ^[e]	16	20	10	n.d.
2 ^[f]	air, 4 / 6 ^[e]	16	22	11	n.d.
3	5 (100)	2	75	61	4.2
4	5 (100)	16	> 95	82	6.5
5 ^[g]	5 (100)	16	> 95	80	6.5
6 ^[f]	5 (100)	16	> 95	71	6.2
7 ^[h]	5 (100)	16	> 95	80	6.3
8 ^[i]	5 (100)	16	> 95	78	5.8
9	7 (100)	2	61	44	1.9
10	8 (100)	2	–	–	–
11 ^[j]	5 (100)	16	> 95	88	6.5

[a] Conditions: **1a** (0.88 mmol), **2a** (0.80 mmol), **A** (0.08 mmol), DBU (0.20 mmol), THF (6.0 mL). [b] Detected by ¹H NMR analysis of the crude reaction mixture (durene as internal standard). [c] Isolated yield via precipitation into excess methanol (see the Experimental Section). [d] Calculated by ¹H NMR analysis after precipitation of the polymer. [e] ETM'/ETM'' system: **4** (10 mol%), **6** (2.5 mol%). [f] T = 60 °C. [g] Reaction run in the presence of 4 Å molecular sieves. [h] Anhydrous DCM as solvent. [i] Me-THF as solvent. [j] Conditions: **1a** (11.0 mmol), **2a** (10.0 mmol), **A** (1.00 mmol), **5** (20 mmol), DBU (2.5 mmol), THF (60 mL).

In parallel, the possibility of recycling both the DBU base and the oxidant **5** was investigated for the setup of a more sustainable polymerization procedure; accordingly, the reaction mixture containing **3aa** was concentrated and the resulting solid residue was triturated several times with Et₂O for the solubilization of DBU and alcohol **5'**, which was formed quantitatively at complete reaction conversions. After washing with acidic aqueous solution, the protonated DBU and **5'** could be separated and alcohol **5'** quantitatively re-oxidized to quinone **5** with air in the presence of catalytic phthalocyanine **6** (see the Supporting Information for details).

Subsequently, thanks to the ability of NHCs to work as effective transesterification agents^[9] and mimicking the approach for the production of commercial PET, the synthesis of high molecular weight PET was addressed by an NHC-promoted two-step procedure in analogy with the studies of Waymouth,^[8] Hedrick,^[8] Sardon,^[18] and their co-workers (Scheme 2;



Scheme 2. NHC-promoted two-step procedure for the synthesis of high molecular weight PET **3aa'**.

Table 2, entry 2). Hence, isolated **3aa** ($M_n = 6.5 \text{ kg mol}^{-1}$) was heated at 250 °C for 2 hours under vacuum in the presence of triazolium pre-catalyst **A** (5 mol%) and DBU (5 mol%), affording PET **3aa'** with high molecular weight, as evidenced by the disappearance of the end group signals in the ¹H NMR spectrum (4:1 CDCl₃-TFA; see the Supporting Information).

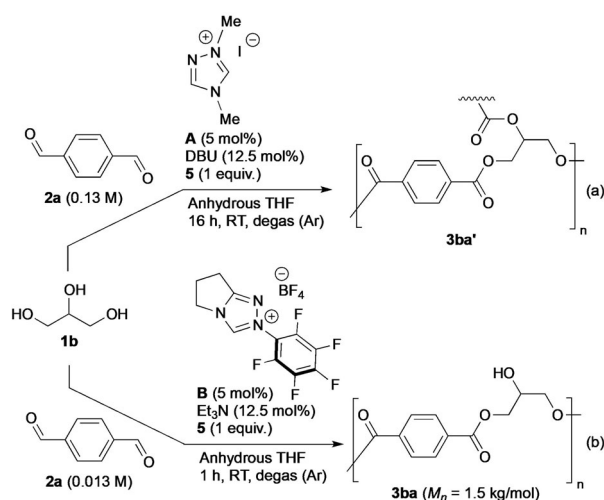
Polyethylene isophthalate oligomers **3ab** ($M_n = 6.5 \text{ kg mol}^{-1}$; 77% yield) were readily obtained by the optimized protocol starting from diol **1a** and isomeric isophthalaldehyde **2b** (Table 2, entry 3).

As anticipated, we also aimed to exploit the organocatalytic procedure for the synthesis of bio-based polymers from renewable monomers, including the abundant and inexpensive glycerol. Polyesters derived from glycerol find important applications in pharmaceutical and biomedical fields as drug-delivery agents,^[19] surgical adhesives,^[20] and tissue engineering scaffolds.^[21] Given that the physical properties of poly(glycerol esters) strongly depend on the linear or branched microstructure of the glycerol unit,^[22] the development of a selective, metal-free strategy for the synthesis of glycerol PEs with a controlled degree of acylation is highly desirable.^[23,24] In this direction, our optimized polymerization procedure was performed with terephthalaldehyde **2a** and glycerol **1b** and we observed the rapid and quantitative formation of poly(glycerol terephthalate) (PGT) **3ba'** as a gel-like material, which was insoluble in common organic solvents (DCM, THF, DMSO, DMF) likely because of the high content of triacylglycerol units (Scheme 3, eq. a). The synthesis of linear PGT was next addressed and, after a long period of experimentation with different azolium salt promoters and conditions, we found that the more steri-

Table 2. Scope of the oxidative polycondensation of diols **1** and dialdehydes **2**.^[a]

Entry	Diol	Dialdehyde	Polyester	Polyester acronym	Yield ^[b] [%]	M_n ^[c] [kg mol ⁻¹]
1				PET	82	6.5
2 ^[d]				PET (high M_n)	78	-
3				PEI	77	6.5
4				PGT (cross-linked)	90	-
5 ^[e]				PGT (linear)	71	1.5
6				PEF	68	1.5
7				PEOBF	73	3.5
8				PBHMT	81	3.1
9				PBHMF	78	7.8
10				PIT	71	2.8
11				PIF	72	2.7

[a] Conditions: **1** (0.88 mmol), **2** (0.80 mmol), **A** (0.08 mmol), DBU (0.20 mmol), **5** (1.60 mmol), THF (6.0 mL). [b] Isolated yield. [c] Calculated by ¹H NMR analysis after precipitation of the polymer. [d] See Scheme 2 and the Experimental Section for reaction conditions. [e] Performed with pre-catalyst **B** (0.08 mmol), Et₃N (0.20 mmol), THF (60 mL).



Scheme 3. Optimized conditions for the synthesis of cross-linked and linear poly(glycerol esters) **3 ba'** and **3 ba**.

cally hindered pre-catalyst **B**, in combination with triethylamine in dilute solution, produced linear PGT oligomers **3 ba** ($M_n = 1.5 \text{ kg mol}^{-1}$) in 71% yield after precipitation (eq. b). Actually, following the detailed study by Slawko and Taylor on the characterization of glycerol-based PEs,^[24] the formation of triacyl and 1,2-diacylglycerol motifs in **3 ba** could be excluded by quantitative ^{13}C NMR analysis ($[\text{D}_6]\text{DMSO}$) using chromium(III) acetylacetonate as relaxation agent.

Although high molecular weight linear PGT **3 ba** could not be obtained by using our strategy, this proof-of-concept study on glycerol demonstrated that the structural variation of NHC catalyst might allow the regioselective activation of the polyol substrate to produce polyesters with a well-defined architecture; an additional advantage is the maintenance of polyester microstructure thanks to the mild reaction conditions that preclude acyl group migration during the polycondensation.

The compatibility of the oxidative polycondensation protocol with respect to variation of the bio-based dialdehyde was then verified by the utilization of furan aldehydes derived from 5-hydroxymethyl furfural (HMF); namely, 2,5-diformylfuran (DFF) **2 c** and 5,5'-oxybis(methylene)bis2-furaldehyde (OBFA) **2 d** (Table 2). In recent years, DFF and difuranic OBFA have been employed as monomers to prepare furan-urea resins and imine-based polymers,^[25,26] but also as suitable precursors of the corresponding diacids, that are 2,5-furandicarboxylic acid (FDCA)^[27] and 5,5'-oxybis(methylene)bis2-furancarboxylic acid (OBFC).^[28] Today, FDCA is widely recognized as an effective equivalent of terephthalic acid for the synthesis of PEs from renewable resources; in particular, poly(ethylene furanoate) (PEF) has emerged as an innovative alternative to PET with attractive mechanical and barrier properties,^[29] and some companies are presently building plants for its production on a large scale. Similarly, the difuranic-diacid OBFC is under investigation for the synthesis of novel polyester-ether materials, including the promising poly(ethylene 5,5'-(oxybis(methylene)bis(2-furancarboxylate))) (PEOBF).^[28] Hence, PEF and PEOBF oligomers **3 ac** ($M_n = 1.5 \text{ kg mol}^{-1}$) and **3 ad** ($M_n = 3.5 \text{ kg mol}^{-1}$) were readily prepared by using our complementary oxidative strategy, di-

rectly starting from DFF and OBFA dialdehydes **2 c,d** in place of the corresponding acids FDCA and OBFC (entries 6–7).

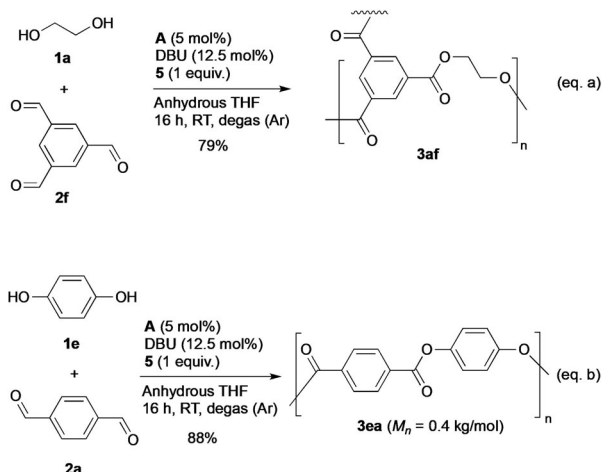
The scope of the polycondensation was next extended to the use of 2,5-bis(hydroxymethyl)furan (BHMF) **1 c**,^[30] which is an HMF-derived diol that is widely employed to prepare PEs and PUs.^[31] Thus, polymerization of **1 c** with terephthalaldehyde **2 a** produced poly(2,5-furandimethylene terephthalate)^[32] (PBHMT) oligomers **3 ca** ($M_n = 3.1 \text{ kg mol}^{-1}$) with good efficiency (81% yield) under the optimized oxidative conditions (entry 8).

Satisfyingly, the replacement of **2 a** with 2,5-diformylfuran **2 c** afforded the fully furan-based polyester poly(2,5-furandi-methylene 2,5-furandicarboxylate) (PBHMF)^[31] **3 cc** with the highest molecular weight registered in this study ($M_n = 7.8 \text{ kg mol}^{-1}$; entry 9). It is important to stress the mild polycondensation procedure presented herein appears well suited for the utilization of BHMF, as this diol has been reported to suffer from low thermal stability in solution polymerizations.^[31a]

Secondary alcohols were also effective in the NHC-promoted polyesterification with dialdehydes. Indeed, additional monomer combinations involved isosorbide (IS) **1 d**, which is a renewable diol (1,4:3,6-dianhydro-D-glucitol) available from glucose and cellulose with high efficiency. Isosorbide has recently been attracting increasing interest in polymer chemistry by virtue of its rigid structure, chirality, and nontoxicity.^[33] In particular, poly(isosorbide)terephthalate^[31a,34] (PIT) and poly(isosorbide 2,5-furandicarboxylate)^[35] (PIF), which are the isosorbide-based counterparts of PET and PEF, respectively, display excellent thermal and structural properties, making them suitable for packaging applications. In our study, PIT oligomers **3 da** ($M_n = 2.8 \text{ kg mol}^{-1}$) and PIF oligomers **3 dc** ($M_n = 2.7 \text{ kg mol}^{-1}$) were prepared in good yields (71–72%; entries 10–11) with the terminal isosorbide units enchainned through the more nucleophilic C5 hydroxyl group, as proven by ^1H NMR analysis and comparison with authentic samples of C2 and C5 benzoyleated isosorbide derivatives (see the Supporting Information).

Scope and limitation were further investigated by analysis of challenging combinations involving *ortho*-difunctionalized or tri-functionalized aromatic monomers as well aromatic alcohols, which are known to be poorly reactive substrates in NHC-promoted esterifications (Scheme 4).^[12] Whereas the polymerization of *o*-phthalaldehyde **2 e** with ethylene glycol **1 a** produced a complex mixture of compounds with no evidence of ester linkage formation (NMR analysis), the reaction of benzene-1,3,5-tricarboxaldehyde **2 f** with **1 a** afforded the target polyester **3 af** in 79% yield after purification (eq. a). This polymer was insoluble in all common organic solvents because of its highly cross-linked structure, as confirmed by thermal analysis (see below). Hydroquinone **1 e** reacted efficiently with terephthalaldehyde **2 a**, furnishing the fully aromatic **3 ea** in 88% yield but with low molecular weight ($M_n = 0.4 \text{ kg mol}^{-1}$, eq. b).^[37] Disappointingly, the aromatic triol 1,3,5-trihydroxybenzene (phloroglucinol) **1 f** was found to be unreactive in the polycondensation with **2 a** under the disclosed polymerization conditions.

All synthesized polyesters were characterized by thermogravimetric analyses (TGA). The collected relevant parameters,



Scheme 4. Use of tricarboxaldehyde **2f** and hydroquinone **1e** in the disclosed polycondensation procedure.

namely the onset of thermal degradation (T_{di}), the temperature of maximum degradation rate (T_d), and the residuum after degradation at 850 °C, are summarized in Table 3.

Table 3. Onset of thermal degradation (T_{di}), temperature of maximum degradation rate (T_d), and residuum after degradation (residuum) from TGA analyses; glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and melting enthalpy (ΔH_m) from DSC analyses of polyesters **3**.

	TGA			DSC			
	T_{di} [°C]	$T_d^{[a]}$ [°C]	Res. ^[b] [%]	$T_g^{[c]}$ [°C]	$T_m^{[d]}$ [°C]	T_c [°C]	ΔH_m [J g ⁻¹]
3aa	410	444	5.3	65	242	209	53
3aa'	419	447	7.3	83	244	214	42
3ab	404	442	4.1	53	–	–	–
3ac	327	354	10.2	52	186	139	48
3ad	< 200	342/392	25.6	–	–	–	–
3af	< 200	442	13.4	–	–	–	–
3ca	247	258/364	7.3	60	181	142	39
3ba	205	407	29.0	91	–	–	–
3ba'	212	422	1.1	176	–	–	–
3da	399	421	1.9	136	–	–	–
3cc	< 200	333	6.9	–	–	–	–
3dc	373	409	3.3	140	–	–	–
3ea	224	540	18.9	389	445 ^[e]	–	84.6

[a] Temperature of the peak minimum in the DTGA plots. [b] Residuum at 850 °C. [c] Values at the midpoint. [d] Values at the peak maximum. [e] Maximum of the observed endothermic peak.

The PET oligomer **3aa** showed a degradation plot (Figure 2) that was comparable to those reported for a commercial PET and for the same polymer prepared under different conditions.^[37,38] The thermal stability of **3aa** was high, with a T_{di} value of the main degradation process at 410 °C. The weight loss measured between room temperature and 300 °C was minimal (3.1%) and mainly due to a step with onset temperature at 100 °C, which was attributed to the loss of moisture and to the dehydration of terminal hydroxyl groups.^[37] Accordingly, this step disappeared completely after chain-elongation in **3aa'**, in good agreement with its ¹H NMR spectrum, which

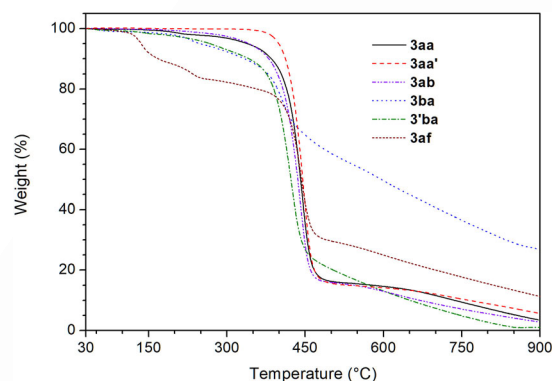


Figure 2. Comparison of the TGA curves of polyesters prepared from terephthalaldehyde/isophthalaldehyde/benzene-1,3,5-tricarbaldehyde and ethylene glycol/glycerol (**3aa**, **3aa'**, **3ab**, **3ba**, **3'ba**, **3af**).

displayed no detectable CH₂-OH groups (see the Supporting Information).

Polyesters **3aa** and **3aa'** both exhibited melting and crystallization peaks in the heating and cooling steps of DSC analysis (Figures 3 and 4). Indeed, the solid-state PET with a regular sequence is well known to be a semicrystalline polymer with a melting temperature between 245 and 265 °C, depending on

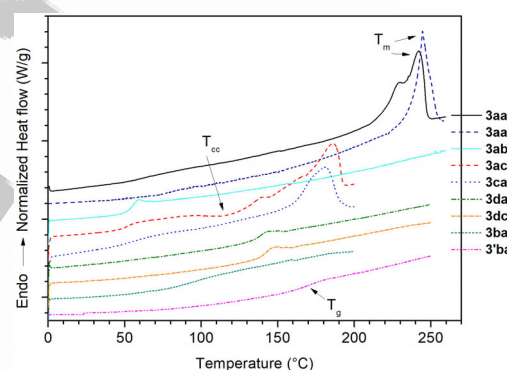


Figure 3. Second heating step in the DSC thermograms of polyesters **3** indicated in the legend. Plots have been arbitrary shifted vertically for clarity and a selection of significant transitions have been indicated as examples.

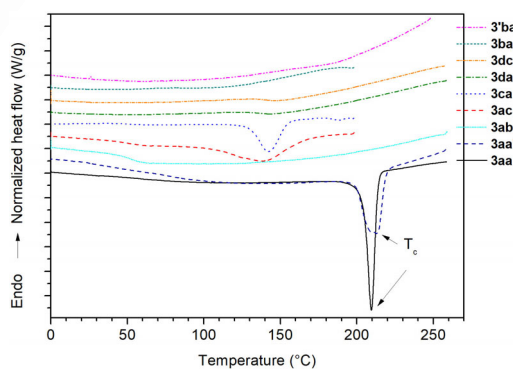


Figure 4. Cooling step in the DSC thermograms of polyesters **3** indicated in the legend. Plots have been arbitrary shifted vertically for clarity. Two crystallization peaks have been indicated as examples.

the cooling protocol, the macromolecular features (e.g., molecular weight, existence of defects), and the presence of residual or additives.^[39]

The melting peaks of **3aa** and **3aa'** were observed at the minimum of the range noted above, in accordance with the adopted measurement protocol. In particular, the melting peak of **3aa'** is shifted at little higher temperature and does not include the shoulder toward low temperatures that is instead present in **3aa** (Figure 3).

This behavior is consistent with the higher molecular weight of **3aa'** and thus with the presence of a lower number of chain ends. In fact, chain ends usually behave like defects in polymer crystallization, affecting the kinetics and the thermodynamics of the process and, consequently, the melting temperature.^[40]

Furthermore, the glass transition temperature of **3aa'** was observed at ca. 80 °C, in good agreement with the expected value for this polymer in the semi-crystalline form.^[41] On the other hand, the lower T_g value of **3aa** (65 °C) indicates a plasticization effect by the high number of chain ends present in the sample because of its low molecular weight.

Poly(ethylene isophthalate) (PEI) is a polymer similar to PET except for the lower ability to crystallize.^[42] Accordingly, PEI oligomers **3ab** exhibited a thermal stability under nitrogen atmosphere similar to that of **3aa** (Figure 2) and only a glass transition temperature at 53 °C and no detectable melting and crystallization peaks by DSC analysis (Figures 3 and 4). These features are consistent with the results by Lee and co-workers, who reported a T_g value of 56 °C for a PEI with a molecular weight of 21 000 kg mol⁻¹ and residual crystallinity of only 2%.^[43]

The insoluble polymer **3af**, derived from the polycondensation of ethylene glycol and the tricarboxaldehyde **2f**, showed a thermal stability comparable to those of PET and PEI, with the onset of the main degradation step at 419 °C (Figure 2). Additional weight loss steps were also observed at lower temperatures likely because of the degradation of the low molecular weight branches or the presence of impurities that could not be efficiently removed from the rigid cross-linked structure. Indeed, based on DSC analysis, the polymer did not show any thermal transition in the analyzed range (up to 280 °C), thus suggesting a higher value of the glass transition due to the rigidity of the aromatic cross-linker (Figure S1).

Substitution of ethylene glycol with glycerol in the polycondensation with terephthalaldehyde afforded the linear oligomer **3ba**, which displayed lower thermal stability (Figure 2) compared with **3aa** in the region in which the dehydration of hydroxyl groups is expected to occur (150–400 °C). Actually, the T_{di} of **3ba** was found at 205 °C; this functional oligomer, however, did not degrade completely in nitrogen atmosphere, leaving a quite high residuum even at 900 °C (ca. 30%; Table 3). In contrast, the insoluble cross-linked analogue **3ba'** exhibited similar thermal behavior before 400 °C but a plot more comparable to those of PET and PEI above this temperature, with negligible residuum at 900 °C. This result indicates that the presence of the secondary free hydroxyl groups in each repeating unit of the regular **3ba** affects its degradation

mechanism but further investigation is needed to clarify this effect.

As previously reported,^[24] cross-linked and linear poly(glycerol esters) **3ba'** and **3ba** were found to be amorphous, exhibiting only a heat capacity jump while crossing the T_g during DSC analysis and no peaks in the heating-cooling scan (Figures 3 and 4). The observed glass transition temperature of **3ba'** and **3ba** were quite different to that of **3ba**, which is lower by 85 °C, thus revealing a higher chain mobility in this sample in agreement with the presence of a negligible number of crosslinks.

The oligoester **3da** from terephthalaldehyde and isosorbide was also found to be an amorphous solid with high T_g and good thermal stability, as previously reported for the corresponding polymer prepared by polycondensation of isosorbide and terephthaloyl dichloride.^[34a] The thermal stability of **3da** was similar to that of PET oligomer **3aa**, being shifted by only 10 °C toward lower temperature (Figure 5).

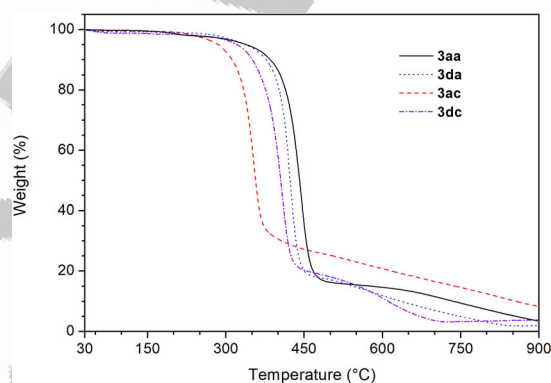


Figure 5. Comparison of TGA curves of oligoesters prepared from terephthalaldehyde/diformylfuran and ethylene glycol/isosorbide (**3aa**, **3da**, **3ac**, **3dc**).

Comparison of the TGA plots of terephthalaldehyde-based oligoesters **3aa** and **3da** with those of diformylfuran-based oligoesters **3ac** and **3dc** (Figure 5) reveals a lower thermal stability of the latter two because of the higher instability of the furan moiety.^[44] Instead, the replacement of ethylene glycol with an isosorbide unit improves the thermal stability of isosorbide-based oligoesters **3da** and **3dc** compared with ethylene glycol-derived oligoesters **3aa** and **3ac**. This behavior is likely due to a different mechanism of degradation resulting from the change of chemical structure and not to chemical-physical differences: both isosorbide-based oligoesters **3da** and **3dc** are amorphous materials with very similar glass transition temperature values (Table 3), and both ethylene glycol-based oligoesters **3aa** and **3ac** are semicrystalline. Indeed, **3ac** is a low molecular weight PEF exhibiting both melting and crystallization peaks in DSC analysis (Figures 3 and 4). The detected values were a little lower than those reported for PEF, which has been described as a semicrystalline material with T_g = 70–90 °C, T_m = 200–215 °C, and T_c = 150–165 °C,^[31a,35c,44,45] however, this decreasing trend with the reduction of molecular weight has already been observed for other polymers.^[46]

Oligoesters **3cc**, **3ad**, and **3ca** displaying a 5-substituted furan-2-yl-moiety as a repeating unit were all found to have thermal stability lower than PEF **3ac** (Figure 6). The more stable oligoester of this series was **3ca**, derived from terephthalaldehyde; in spite of its lower molecular weight, **3ca** was found to be a semicrystalline polymer with T_g higher than room temperature (60 °C) and T_m of ca. 180 °C, thus indicating this oligoester as a promising candidate to prepare transparent thermoplastic films.

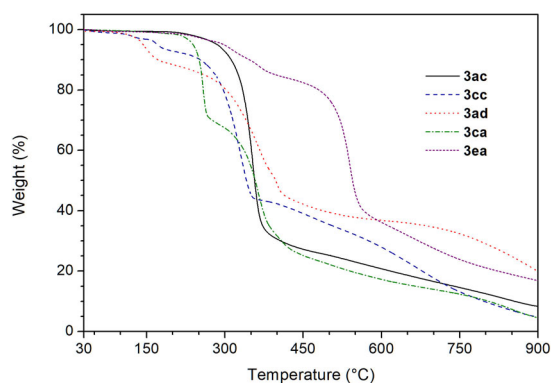


Figure 6. Comparison of the TGA curves of PEF oligomer **3ac**, oligoesters displaying the 5-substituted furan-2-yl-moiety (**3cc**, **3ad**, **3ca**), and the fully aromatic oligoester **3ea**.

The fully aromatic polyester **3ea** was observed to degrade by a quite complex process consisting of several steps, the largest one having onset temperature at 515 °C and the lowest at 225 °C (Figure 6). Nevertheless, **3ea** can be considered to show a good thermal stability in relation to its low molecular weight, since the degradation processes at low temperature can be attributed to the loss of the chain-end groups. The DSC analysis of **3ea** showed a heat capacity jump at 390 °C and an endothermic peak with a maximum at 455 °C (Figure S2). The former can be easily attributed to a glass transition process, whereas the latter can be due to a melting even if the corresponding crystallization was not observed on cooling. It must be pointed out that, in the case of the present sample, the first heating step was carried out up to 400 °C to eliminate any process responsible for the observed weight loss step in TGA that occurred before this temperature. In fact, the assignment of the above-mentioned peak to any degradation process is unlikely because no weight loss processes were detected by TGA in this range. The observed characteristic temperatures (T_g and T_m) of **3ea** are a little different from those reported in the literature;^[47] this discrepancy, however, can be explained by the difference of molecular weight and chain-end groups.

Conclusions

We have described a novel strategy for the synthesis of polyesters (PEs) based on the polycondensation of diols and dialdehydes promoted by an *N*-heterocyclic carbene (NHC) catalyst in the presence of an external oxidant. While PEs of relatively low molecular weight were obtained ($M_n = 1.5\text{--}7.8 \text{ kg mol}^{-1}$),

the disclosed mild procedure proved to be effective for the preparation of a series of synthetically relevant bio-based polyesters from furanic monomers, glycerol, and isosorbide. Additionally, the results of the present study have demonstrated the compatibility of the obtained oligoesters with a subsequent NHC-catalyzed chain-elongation step to achieve PEs with higher molecular weight as well as the possibility of controlling the microstructure (linear or cross-linked) of poly(glycerol esters) by modulation of the steric hindrance of the NHC catalyst. Further investigation aimed at extending this methodology to other polymer classes (e.g., polyamides) is under way in our laboratories and results will be reported in due course.

Experimental Section

General procedure for the synthesis of polyesters **3**

A mixture of diol **1** (0.88 mmol), aldehyde **2** (0.80 mmol), oxidant **5** (1.60 mmol), and pre-catalyst **A** (0.08 mmol) in anhydrous THF (6.0 mL) was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times. DBU was then added (0.20 mmol), and the reaction was stirred at RT for 16 h. The mixture was concentrated and the resulting residue was triturated with fresh portions of Et₂O or DCM (3×10 mL) and centrifuged. The organic solutions were collected for the recovery of DBU and oxidant **5**; the solid residue was dissolved in the minimum amount of appropriate solvent, and precipitated by dropwise addition into a poor solvent at 0 °C (see the Supporting Information for details).

Synthesis of high molecular weight PET **3aa'**

Isolated **3aa** (126 mg, 0.66 mmol of repeating unit, $M_n = 6.5 \text{ kg mol}^{-1}$) was heated at 250 °C for 2 hours under vacuum in the presence of triazolium pre-catalyst **A** (7.5 mg, 0.03 mmol) and DBU (4.5 μL, 0.03 mmol). After this period the flask was cooled, the reaction mixture was triturated with DCM and centrifuged (3×10 mL). Final drying under vacuum afforded **3aa'** with high molecular weight, as confirmed by ¹H NMR analysis.

Synthesis of cross-linked PGT **3ba'**

A mixture of glycerol **1b** (65 μL, 0.88 mmol), terephthalaldehyde **2a** (107 mg, 0.80 mmol), oxidant **5** (654 mg, 1.60 mmol), and pre-catalyst **A** (18 mg, 0.08 mmol) in anhydrous THF (6.0 mL) was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times. DBU was then added (30 μL, 0.20 mmol), and the reaction was stirred at RT for 16 h. Solvent removal under reduced pressure, trituration of the reaction mixture with DCM and subsequent centrifugation (3×10 mL) followed by drying under vacuum afforded **3ba'** (160 mg, 90%) as an off-white solid.

Synthesis of linear PGT **3ba**

A mixture of glycerol **1b** (65 μL, 0.88 mmol), terephthalaldehyde **2a** (107 mg, 0.80 mmol), oxidant **5** (654 mg, 1.60 mmol), and pre-catalyst **B** (29 mg, 0.08 mmol) in anhydrous THF (60 mL) was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times. Et₃N was then added (28 μL, 0.20 mmol), and the reaction was stirred at RT for 1 h. After solvent removal under reduced pressure, trituration with DCM and subsequent centrifugation (3×10 mL), the resulting solid was dissolved

in a minimum amount of DCM and MeOH (4:1, v/v) and precipitated from 2-propanol (10 volumes) at 0°C. Filtration followed by washing with cold 2-propanol and drying under vacuum afforded **3ba** (126 mg, 71%, $M_n = 1.5 \text{ kg mol}^{-1}$) as an off-white solid.

Synthesis of polyester **3af**

A mixture of diol **1a** (74 μL , 1.32 mmol), trialdehyde **2f** (130 mg, 0.80 mmol), oxidant **5** (981 mg, 2.40 mmol), and pre-catalyst **A** (18 mg, 0.08 mmol) in anhydrous THF (6.0 mL) was degassed under vacuum and saturated with argon (by using an Ar-filled balloon) three times. DBU was then added (30 μL , 0.20 mmol), and the reaction was stirred at RT for 16 h. Solvent removal under reduced pressure, trituration of the reaction mixture with DCM and subsequent centrifugation ($3 \times 10 \text{ mL}$) followed by drying under vacuum afforded **3af** (158 mg, 79%) as a pale-yellow solid.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenes · organocatalysis · oxidation · polyesters · polymerization

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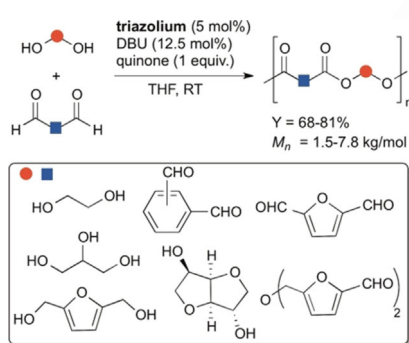
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FULL PAPER


Metal-free polymerization: Fossil- and bio-based polyesters are obtained under mild ambient conditions by polycondensation of diols and dialdehydes promoted by *N*-heterocyclic carbenes in the presence of an external oxidant. The catalyst-controlled definition of polyester architecture (cross-linked or linear) is also illustrated with the trifunctional glycerol monomer (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

**Polymerization**

D. Ragno, G. Di Carmine, A. Brandolese, O. Bortolini, P. P. Giovannini, G. Fantin, M. Bertoldo, A. Massi*



Oxidative NHC-Catalysis as Organocatalytic Platform for the Synthesis of Polyester Oligomers by Step-Growth Polymerization

 Fossil- and bio-based polyesters are obtained @UniFerrara under mild ambient conditions by polycondensation of diols and dialdehydes promoted by *N*-heterocyclic carbenes in the presence of an external oxidant. **SPACE RESERVED FOR IMAGE AND LINK**

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