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Exploring Oxidative NHC-Catalysis as Organocatalytic Polymerization Strategy Towards Polyamide Oligomers

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Abstract: The polycondensation of diamines and dialdehydes promoted by an N-heterocyclic carbene (NHC) catalyst in the presence of a quinone oxidant and hexafluoro-2-propanol (HFIP) is herein presented for the synthesis of oligomeric polyamides (PAs), which are obtained with a number-average molecular weight (M_n) in the range of 1.7-3.6 kg mol⁻¹ as determined by NMR analysis. In particular, the utilization of furanic dialdehyde monomers (2,5-diformylfuran, DFF; 5,5'-[oxybis(methylene)]bis[2-furaldehyde], OBFA) to access known and previously unreported bio-based PAs is illustrated. The synthesis of higher molecular weight PAs (poly(decamethylene terephthalamide, PA10T, M_n = 62.8 kg mol⁻¹; poly(decamethylene 2,5-furandicarboxylamide, PA10F, M_n = 6.5 kg mol⁻¹) by a two-step polycondensation approach is also described. The thermal properties (TGA and DSC analyses) of the synthesized PAs are reported.

Introduction

Polyamides (PAs) are among the most useful class of polymers, which find a wide range of applications as fibers, films, and highperformance specialty materials in different types of industries.^[1] High chemical and heat resistance are important features of PAs arising from intermolecular hydrogen bonding interactions between the amide portions of polymeric chains. Conventional routes for the synthesis of PAs involve the polycondensation of diamines with diacids or their derivatives (acyl chlorides and esters), the self-polycondensation of ω -amino acid esters, and the ring-opening polymerization (ROP) of lactams or N-carboxyamino acid anhydrides through standard techniques (melt, interfacial, and solution polymerization).^[2] Less common is the catalytic polyamidation of diols and diamines through iterative dehydrogenation promoted by the Ru-based Milstein catalyst (Figure 1).^[3] The implementation of organocatalytic approaches, which have proven to effectively complement metal-catalysis in the production of polyesters (PEs), polyurethanes (PUs) and polycarbonates (PCs), is more rare in the synthesis of PAs despite the benefits associated with this polymerization strategy;

these include catalyst stability and avoidance of metal contamination that is particularly favorable for applications in the electronic and biomedical fields.^[4] Indeed, examples of organocatalytic synthesis of PAs are mainly limited to the utilization of guanidine (TBD) and phosphazene (*t*-BuP₄) Brønsted bases in the ROP of lactams.^[5]



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

Also, the strong basic character of (latent) N-heterocyclic carbene (NHC) catalysts has been exploited by DuPont in 2006 for the polymerization of ε -caprolactam^[6] and later by the group of Buchmeiser for the preparation of PA12 and PA6,12.^[7] In addition to the Brønsted base behavior, NHCs are also distinguished by ambiphilic (α -basicity, π -acidity) and moderate nucleophilic attributes,^[8] which can be conveniently considered for the polymerization of different monomers such as epoxides, lactones,

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anhydrides, carbonates, acrylates, siloxanes, and also aldehydes. $^{\left[9,10\right] }$

Our group recently contributed in this area of research describing the unprecedented polycondensation of dialdehydes and diols promoted by NHCs under oxidative conditions to access PEs by the step-growth polymerization technique.^[11] Key step of this approach is the oxidation of the Breslow intermediate to generate the corresponding acyl azolium, which is susceptible of nucleophilic attack by the diol for completing the formal aldehydeto-ester conversion in an iterative fashion (Scheme 1).^[12] As a logical extension of that study, we herein report our results on the synthesis of polyamide oligomers by the same strategy using dialdehydes as mild acylating monomers of diamines. Actually, downsides of common routes to PAs may be represented by the elevated polycondensation temperatures and the need of reduced pressures to remove the condensate, as well as the use of hazardous halogenating reagents (e.g. thionyl chloride) in case of more reactive diacyl chloride monomers. At the same time, the ROP strategy may require the multi-step synthesis of starting lactams, that is a time-consuming process especially if functional PAs are targeted.^[5b,c] Therefore, an alternative route to PAs based on iterative, NHC-catalyzed aldehyde-to-amide conversion occurring under mild reaction conditions from readably available aldehyde monomers is worth of investigation (Scheme 1). In the present contribution we describe advantages and limitations of the envisaged strategy, which has been applied to the synthesis of fossil-based and also bio-based polyamide oligomers. As a matter of fact, there is an increasing interest in the utilization of renewable resources for the development of sustainable PAs due to their impact as high-performance materials in specific fields of polymer chemistry such as automotive and biomedical sectors.^[1,13]



Scheme 1. NHC-based strategy to polyesters (PEs) and polyamides (PAs)

Results and Discussion

The polycondensation of ethylenediamine (EDA) **1a** with terephthalaldehyde **2a** was selected as the model reaction using a slight excess of diamine **1a** (1.1 equiv.) to promote the formation of oligomeric poly(p-ethylene terephthalamide) (PETA)^[14] **3aa** with terminal amine groups (Table 1). At the beginning of this research, we were aware that the direct oxidative N-acylation with aldehydes^[15] may be precluded in the case of primary amines because of the competing imine formation and that this issue can be addressed by the addition of nucleophiles as additives^[15a,b,c,f] or by the execution of a two-step procedure with activated ester

intermediates.^[15d,g] Actually, application of the reaction conditions previously optimized for synthesis of PEs by the same oxidative strategy^[11] (triazolium salt **C1** (5 mol%) as the pre-catalyst, 1,8diazabicyclo[5.4.0]undec-7-ene (DBU, 12.5 mol%) as the base and quinone **4** (1 equiv.) as the external oxidant in anhydrous THF), resulted in no formation of the target oligomer **3aa** because of the formation of a complex reaction mixture containing low molecular weight (LMW) mixed aldehyde and imine derivatives of **2a** (mainly monomers and dimers) as judged by ESI-MS analysis (entry 1).

Table 1. Screening of reaction conditions for the synthesis of PETA oligomers



Entry	NHC HX	Oxidant/ Additive	Conv. (%) ^[b]	3aa (%) ^[c]	<i>M_n</i> (kg/mol) ^[d]
^r 1	C1	4/-	>95	-	-
2	C1	5/-	88	-	-
3	C1	5/6	>95	-	-
4	C2	4/7	>95	-	-
5 ^[e]	C3	4/8	>95	-	-
6 ^[f]	C1	4/9	>95	90	1.9
7 ^[f,g]	C1	4/9	>95	91	1.9
8 ^[f,h]	C1	4/9	80	71	1.2
9 ^[f,i]	C1	4/9	>95	86	1.9
10 ^[f,j]	C1	4/9	>95	76	1.5
11 ^[f,k]	C1	4/9	>95	82	1.1
12 ^[I]	C1	4/9	>95	92	1.9

^[a]Conditions: **1a** (0.88 mmol), **2a** (0.80 mmol), **NHCHX** (0.08 mmol), DBU (0.20 mmol), oxidant (1.60 mmol), additive (0.32 mmol), THF (6.0 mL). ^[b]Detected by ¹H NMR of the crude reaction mixture (durene as internal standard). ^[c]Isolated yield via precipitation technique (see the Experimental Section). ^[d]Calculated by ¹H NMR after precipitation of the polymer. ^[e]Imidazole **8**: 1.76 mmol. ^[f]HFIP **9**: 2.40 mmol. ^[G]Reaction time 24 h. ^[h]Reaction time 8 h. ^{[IR}Reaction run in the presence of 4 Å molecular sieves. ^{[II}Temperature: 50 °C. ^[K]Anhydrous DCM as solvent. ^{[II}Conditions: **1a** (11.0 mmol), **2a** (10.0 mmol), **C1** (1.00 mmol), **4** (20 mmol), DBU (2.5 mmol), **9** (30.0 mmol), THF (60 mL).

The utilization of phenazine **5** as oxidant had no effect on the reaction outcome producing the same results as the quinone **4** (entry 2). Addition of the nucleophilic co-catalyst 1,2,4-triazole **6** (20 mol%) to the couple **C1/5** as reported by Connon and co-workers^[15m] for amidation of primary amines suppressed imine formation but, unexpectedly, it produced a mixture of mono- and bis-amide derivatives of **2a** without evidence of oligomeric species (¹H NMR and ESI-MS analyses, entry 3). Also, unsatisfactory results with lack of chain elongation were detected applying the oxidative amidation procedures of primary amines developed by the groups of Rovis^[15b] and Bode^[15a] involving, respectively, the utilization of **C2** (20 mol%) in combination with 1-hydroxy-7-azabenzotriazole (HOAt) **7** (20 mol%; entry 4), and of **C3** (20 mol%) with imidazole **8** (1.1 equiv.; entry 5).

In light of the above disappointing findings, the one-pot two-step amidation strategy via hexafluoroisopropyl esters proposed by Studer and co-workers^[15d] was next investigated. Accordingly, the mixture of aldehyde 2a, C1 (5 mol%), DBU (12.5 mol%), 4 (1 equiv.), and hexafluoro-2-propanol (HFIP) 9 (1.5 equiv.) in anhydrous THF was reacted for two hours, then diamine 1a (1.1 equiv.) was added and the mixture stirred under inert atmosphere (Argon) for an additional 16 hours (entry 6). Gratifyingly, this procedure allowed for the isolation of 3aa (precipitation technique) in 90% yield with a number-average molecular weight (M_n) of 1.9 kg mol⁻¹ based on ¹H NMR spectroscopic analysis. Extending the reaction time to 24 hours did not increase the oligomer length (entry 7), while a shorter time (8 hours) afforded **3aa** with lower yield (70%) and M_n (1.2 kg mol⁻¹; entry 8). Disappointingly, the polymer growth could not be improved either by adding molecular sieves to avoid water nucleophilic attack onto acyl azolium (entry 9) or by heating the reaction mixture to 50 °C (entry 10). The replacement of THF with anhydrous DCM determined a significant decrease of M_n (1.1 kg mol⁻¹) likely because of the lower solubility of the growing polymer chain in this halogenated solvent (entry 11). Satisfyingly, the optimized conditions of entry 6 could be applied to the gram-scale synthesis of 3aa (1.75 g, 92% yield) from 10 mmol of 2a (entry 12). Of note, this experiment also served to demonstrate that the cost and the environmental impact of the disclosed polyamidation procedure can be considerably reduced thanks to the simple recovery and reutilization of both HFIP 9 (evaporation) and quinone 4 (regeneration by air oxidation of the reduction product o,o'-di-tertbutyl-p-bisphenol; see the Supporting Information for details).

The reaction mechanism hypothesized for the NHC-promoted polyamidation relies on an ionic pathway in agreement with Studer proposal^[15d] and the general mechanism of oxidative NHCcatalysis (Scheme 2).^[12] Hence, deprotonation of C1 pre-catalyst by DBU, followed by nucleophilic attack of the generated carbene I on the dialdehyde 2 affords the Breslow intermediate II, which in turn is oxidized by the quinone 4 to the corresponding acyl azolium III. Next, nucleophilic attack by HFIP 9 results in the formation of the hexafluoroisopropyl monoester IV and the release of the NHC catalyst. The aldehyde functionality of monoester IV is then involved in a second catalytic cycle affording the hexafluoroisopropyl diester V (the concurrent oxidative esterification of both aldehyde functionalities of 2 seems to be unlikely but it cannot be excluded). Diester V is, however, the key substrate of the subsequent amidation step as confirmed by NMR and IR analyses (see the Supporting Information for details). At this stage, the diamine 1 introduced in the reaction mixture attacks the highly reactive diester **V** with formation of the amide bond and release of HFIP in an iterative manner yielding PAs **3**.



Scheme 2. Proposed mechanism for the synthesis of PAs 3.

Oligomeric PETA 3aa is typically prepared by polycondensation of terephthaloyl acid/chloride with ethylenediamine and, in virtue of its thermal stability and flame retardancy, is conveniently used as charring agent for the synthesis of halogen-free flame retardant polypropylene-based composites.[14c,d] In order to establish strengths and limitations of the proposed methodology, other semi-aromatic and fully-aromatic PAs 3 of synthetic relevance were addressed by the iterative N-acylation of diamines 1 with dialdehyde monomers 2 (Table 2). High molecular weight (HMW) poly(decamethylene terephthalamide (PA10T) displays excellent heat and mechanical resistance together with low water adsorption and good dimensional stability.^[1] Because of these favorable features and easy accessibility of 1,10-decanediamine (1,10-DDA) 1b from renewable castor oil, bio-based PA10T is produced by several companies and widely employed in electronics and automotive industry.[16] Implementation of our optimized protocol with diamine 1b and terephthalaldehyde 2a afforded PA10T oligomers 3ba in good isolated yield (88%) and satisfactory molecular weight ($M_n = 2.6 \text{ kg mol}^{-1}$; entry 2).

Next, by mimicking the two-step polycondensation approach applied for the production of HMW PAs,^[16a,c,d,17] oligomeric **3ba** was utilized as the prepolymer for the synthesis of HMW PA10T **3ba'** (Scheme 3 and Table 2, entry 3).



Scheme 3. Two-step procedure for the synthesis of high molecular weight (HMW) PA10T 3ba'.

Accordingly, terephthaloyl chloride **10** was added at 0 °C to a mixture of isolated oligomers **3ba**, N,N-diisopropylethylamine (DIPEA) and LiCI in N,N-dimethylacetamide (DMA), and the polymerization continued at room temperature for 48 hours affording **3ba'** (85%) with increased molecular weight (M_n = 62.8 kg mol⁻¹), as evidenced by the diminished integral values of the end group signals at 3.04 ppm in the ¹H NMR spectrum (1:1 CDCl₃-HFIP, Figure 2).



Figure 2. ¹H NMR spectra of oligomeric PAT10 3ba and HMW PA10T 3ba' (1:1 CDCI₃-HFIP).

Validation of the method for M_n determination by NMR analysis was performed for HMW PA10T by viscometry. Indeed, size exclusion chromatography (SEC) of semi-aromatic PAs is complicated by their low solubility in common organic solvents and the requirement of sophisticated equipment compatible with pure HFIP as eluent. On the other hand, viscometry is widely recognized as a reliable method for the determination of molecular weight for this class of polymers.[16e,18] In particular, Mathias and co-workers found a correlation between the numberaverage molecular weight estimated by NMR and the intrinsic viscosity ([η]) of a series of PAs^[18a] with M_n in the range of ca. 2-25.2 kg mol^{-1.[18]} Hence, our study started with the synthesis of an authentic sample of PA10T with a molecular weight to fall in the calibration range (**3ba**", $M_n = 20.2$ kg mol⁻¹. See the Supporting Information). Then, 3ba" was fully solubilized in sulfuric acid (96%) at a concentration of 0.5 g dL⁻¹ (12 hours mixing). Singlepoint intrinsic viscosity measurements were performed by means of an Ubbelohde viscometer in a 25 °C controlled water bath. Specific viscosity (η_{sp}) and relative viscosity (η_{rel}) were obtained from flow time data of sulfuric acid and 3ba" (average of four values, ±0.2 s). Single point intrinsic viscosity ([n]) was then determined using the Solomon-Ciută equation $1^{[19]}$ ([n] = 1.93). The number-average molecular weight of 3ba" was estimated with the Mark-Houwink equation 2 considering $K = 5.58 \times 10^{-4} \text{ dL}$ g^{-1} and α = 0.81. These constants were initially calculated for PA12T^[18a] and subsequently adopted for PA10T due to the similar

with that determined by NMR analysis ($M_n = 20.2 \text{ kg mol}^{-1}$).

$$[\eta] = \frac{\sqrt{2 \left[\eta_{sp} - \ln(\eta_{rel})\right]}}{C} \quad (\text{eq 1})$$
$$M_n = \sqrt[\alpha]{\frac{\left[\eta\right]}{K}} \quad (\text{eq 2})$$

Oligomeric poly(hexamethylene terephthalamide) (PA6T)^[16d] **3ca** ($M_n = 2.5 \text{ kg mol}^{-1}$) and poly(hexamethylene isophthalamide) (PA6I)^[20] **3cb** ($M_n = 1.7 \text{ kg mol}^{-1}$) were readily prepared with good efficiency (84% and 78% yield) by the polycondensation of 1,6-hexanediamine (1,6-HDA) **1c** with terephthalaldehyde **2a** and isophthalaldehyde **2b**, respectively (entries 4-5).

Furan-based polyamides are promising sustainable alternatives to polyphthalamides featuring improved solubility and enhanced processability, which make them of great commercial interest as innovative, high performance materials for diversified applications.^[21,22] This special class of PAs is suitably accessed by chemical and enzymatic methods using diamines and 2,5furandicarboxylic acid (FDCA)^[23] monomers, the latter serving as an effective equivalent of terephthalic acid. Therefore, the compatibility of the disclosed oxidative step-growth polyamidation methodology with respect to furanic-aliphatic PAs was also demonstrated by the synthesis of oligomeric poly(decamethylene furanamide) (PA10F)^[17,21] 3bc and poly(hexamethylene furanamide) (PA6F)^[17,21c,d,22] 3cc starting from 2,5-diformylfuran (DFF) 2c.^[24] This bio-based dialdehyde monomer is produced from the platform chemical 5-hydroxylmethyl furfural (HMF) and it has been recently employed to prepare furan-urea resins,^[25] imine-based polymers,^[26] and polyesters.^[27] Satisfyingly, oligometric polyamides **3bc** ($M_n = 1.6$ kg mol⁻¹) and **3cc** ($M_n = 1.7$ kg mol⁻¹) were obtained in good yields (81% and 72%) by our complementary oxidative strategy using DFF 2c in the place of the corresponding acid FDCA (entries 6-7). In analogy with the synthesis of HMW PA10T 3ba', oligomeric 3bc was utilized as the prepolymer to prepare chain-extended CE-PA10F 3bc' (Table 2, entry 8). Accordingly, 2,5-furandicarbonyl dichloride 11 was added at 0 °C to a mixture of 3bc, DIPEA and LiCI in DMA, and the polymerization let to proceed at room temperature for 48 hours affording **3bc'** (76%) with increased molecular weight (M_n) = 6.5 kg mol⁻¹) as determined by NMR analysis (Scheme 4).



Scheme 4. Two-step procedure for the synthesis of CE-PA10F 3bc'.

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Table 2. Scope of the oxidative polyamidation of diamines 1 with dialdehydes 2.^[a]

		H_2N $H_2 + H$ H_2	C1 (5 mol%) DBU (12.5 mol%) 4 (1 equiv.) HFIP 9 (1.5 equiv.) Anhydrous THF RT, degas (Ar) 3	n		
Entry	Diamine	Dialdehyde	Polyamide	Polyamide acronym	Yield (%) ^[b]	M _n (kg/mol) ^[c]
1	H ₂ N NH ₂ 1a (EDA)	0 0 2a		РЕТА	90	1.9
2	H ₂ N (M ₈ NH ₂	°		PA10T	88	2.6
	1b (1,10-DDA)	2a	- 3ba - n F			
3 ^[d]	H ₂ N () ₈ NH ₂			HMW PA10T	85	62.8
	1b (1,10-DDA)	2a	L 3ba' ^J n			
4	H ₂ N (H ₄ NH ₂			PA6T	84	2.5
	1c (1,6-HDA)	2a	1 3ca			
5				PA6I	78	1.7
			0 ⁴ HN+			
	1c (1,6-HDA)	0 2b	3cb			
6	H ₂ N H ₂ N H ₂	° L O O O		PA10F	81	1.6
	1b (1,10-DDA)	2c (DFF)	3bc			
7	H_2N H_2N H_2 H_2 H_2			PA6F	72	1.7
	1 C (1,6-HDA)	2c (DFF)	3cc			
8 ^[e]	H ₂ N H ₂ N H ₂			CE-PA10F	76	6.5
	1b (1,10-DDA)	2c (DFF)	L Jn			
9	H ₂ N H ₃ NH ₂			PA10FF	95	3.2
	1b (1,10-DDA)	2d (OBFA)		n		
10	H_2N H_2N H_2 1c (1,6-HDA)			- PA6FF	90	3.6
		Y				
11	H ₂ N O NH ₂			PAFAT	86	1.9
	1d (BAF)	2a	3da			

^{[[a]}Conditions: **1** (0.88 mmol), **2** (0.80 mmol), **C1** (0.08 mmol), DBU (0.20 mmol), **4** (1.60 mmol), HFIP **9** (2.40 mmol), THF (6.0 mL). ^[b]Isolated yield. ^[c]Calculated by ¹H NMR after precipitation of the polymer. ^[d]See Scheme 3 and the Experimental Section for reaction conditions. ^[e]See Scheme 4 and the Experimental Section for reaction conditions.

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Unfortunately, M_n evaluation of **3bc'** by viscosity measurements was not possible due to the absence of known Mark-Houwink coefficients for PA10F and the degradation of the sample in concentrated sulfuric acid likely because of instability of the furan ring under strong acidic conditions for the prolonged time necessary for viscosity analysis.

The synthesis of novel furan-based polyamides was also addressed in our study by considering unprecedented monomer combinations to access PAs with unexplored potential in the polymer field. Hence, the polycondensation of 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA)^[27] **2d** with diamines **1b** and **1c** gave the oligomers **3bd** (PA10FF; M_n =

3.2 kg mol⁻¹) and **3cd** (PA6FF; M_n = 3.6 kg mol⁻¹), respectively, displaying the unusual polyamide-ether repeating unit (entries 9-10). Finally, the polyamidation of 2,5-bis(aminomethyl)furan (BAF)^[28] **1d** with terephthalaldehyde **2a** furnished the furanic-aromatic polyamide **3da** (PAFAT; M_n = 1.9 kg mol⁻¹) endowed with a stiffer backbone structure (entry 11).^[29]

In order to evaluate the thermal stability of the prepared PAs, thermogravimetric analysis was carried out under standard conditions in nitrogen atmosphere (Table 3). The PA10T oligomer **3ba** displayed a very good thermal stability exhibiting a main degradation process with T_d at 486 °C (Figure 3).

Table 3. Decomposition temperature at 5% weight loss ($T_{d,5\%}$), temperature of maximum degradation rate (T_d) and residuum after degradation (Res.) 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 polyamides **3**.

	T _{d,5%} (°C)	T _d ^[a] (°C)	Res. ^[b] (%)	Tg[c] (°C)	T _{m^[d] (°C)}	T _c (°C)	∆H _m (J/g)	M _n (kg/mol)	REF
PETA (3aa)	264	431	31.0±0.5	n.d.	n.d.	n.d.	n.d.	1.9.	
PETA (lit.)	250	450	n.a.	n.a.	n.a	n.a	n.a	4.2	31
	~420	~450	20-30	n.d.	n.d.	n.d.	n.d	>10	32
PA10T (3ba)	377	486	2.5±0.5	106	220	185	19	2.6	
PA10T (3ba'')	364	482	1.8±0.5	117	235	198	15.3	20.2	
HMW PA10T (3ba')	291	465	2.5±0.5	117	200, 287, 296	177, 273	3.2, 43.4 ^[e]	62.8	
PA10T (lit.)	n.a.	n.a.	n.a.	n.a.	304, 317	n.a.	90	4.2	16e ^[f]
	436	491	n.a.	132.3	302, 313	287.7	100	11	30b
	n.a	n.a	n.a.		279	n.a.	n.a.	14	33
	420-440	479	< 5	132.6	313	276	n.a.	21	30a
	426	482	n.a.	113	290	n.a.	n.a.	26	33
PA6T (3ca)	355	472	6.5±0.5	146	277	217	16	2.5	
PA6T (lit.)	>380	480-484	2.4-5.2	n.a.	374-379 ^[f]	n.a.	108-146	3.8-3.9	34
	245	471	n.a.	170	270	n.d	n.d.	15.6	22a
	428	~450	~5	n.a.	368	n.d	n.d.	>10	32
PA6I (3cb)	176	475	3.6±0.5	105	n.d.	n.d.	n.d.	1.7	
PA6I (lit.)	409	455	n.a.	132	n.d.	n.d.	n.d.	15.7	22b
PA10F (3bc)	159	462	11.5±0.5	90	n.d.	n.d.	n.d.	1.6	
CE-PA10F (3bc')	310	455	21.8±0.5	132	n.d.	n.d.	n.d.	6.5	
PA10F (lit.)	n.a	350-450	n.a.	71	n.d.	n.d.	n.d.	5.3	21d
	366	473	n.a	98	135	n.a.	n.a	13.4	21d
PA6F (3cc)	171	404	34.5±0.5	90-110	n.d.	n.d.	n.d.	1.7	
PA6F (lit.)	380		_	95				2.4	22b
	n.a	350-410	n.a.	110	n.d	n.d.	n.d.	5.2	21b
	322	460	n.a.	119	162	n.a	n.a	13.4	21d
	287-309	355-408	n.a.	86-64	n.d.	n.d.	n.d.	30-62	22a
PA10FF (3bd)	292	456	21.0±0.5	69	n.d.	n.d.	n.d.	3.2	
PA6FF (3cd)	225	357	28.0±0.5	73	n.d.	n.d.	n.d.	3.6	
PAFAT (3da)	157	349	19.5±0.5	n.d.	n.d.	n.d.	n.d.	1.9	

^[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]Total area of the peaks with maximum at 287 °C and 296 °C; n.d. = not detected; n.a. = not available; ^[f]data collected at 20 °C/min as scan rate.

Surprisingly, the value is higher than that of PA10T samples of higher M_n (3ba' and 3ba''), which were obtained by subsequent chain extension with terephthaloyl chloride, and the stability decrease is highest for the polymer with the highest M_n. In any case, the values are comparable to those of PA10T obtained by other polymerization methods (Table 3 and references therein) and the differences lie within the range often observed among similar samples prepared in different batches.^[34] The differences among the temperature at the maximum degradation rate reflect the differences among the temperature of 5% mass loss. Regarding the mass loss at low temperature, this is usually associated to the chain ends. In the case of the high molecular weight polymers the shift of the temperature can be associated to the increase of the polydispersity (PDI) in the second step process. Indeed, step growth polymerization is known to give polymers with $PDI \ge 2$, depending on the reagent ratio. The control over the reagent ratio can be difficult for laboratory scale preparation, and it becomes critical over multistep processes. In fact, it can be usually overcome by scaling to industrial production where appropriate measure to reduce reagent volatilization can be implemented.

PA6T **3ca** was observed to degrade between **3ba'** and its precursor oligomer **3ba**, with a 5% weight loss at 355 °C (Table 3). The corresponding onset temperature of **3ca** is 455 °C, value that is close to the ones reported for PA6T obtained by solid-state polycondensation from salt precursors^[16a] or by interfacial polycondensation.^[30]



Figure 3. Comparison among the TGA curves of terephthalaldehyde- and isophthalaldehyde-derived polyamides.

In spite to the observed differences among samples having different molecular weight, all synthetized PA10Ts as well as PA6T have good thermal stability (Figure 3). This feature is also connected to their semicrystalline structure evidenced by DSC analysis (Table 3). Indeed, all above mentioned polymers exhibited melting and crystallization peaks with a higher value for PA6T compared to PA10T (Table 3), in agreement with literature.^[35] PA10T **3ba**" was found to have a higher melting temperature and enthalpy than its precursor **3ba**, as expected, based on the higher molecular weight (Figure 4). Extra peaks at higher temperatures were also observed in **3ba**', having a

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still higher molecular weight and these peaks can be ascribed to crystals made of HMW chains. The low temperature peak can be assigned to the low molecular weight (LMW) sample fraction or to crystals including many chain ends. Indeed, polymers obtained by step-growth polymerization are known to have polydispersity index larger than 2. And the value is as much high as the reagent ratio in the feed differs from 1. This event may occur also if the two reagents have different volatility so that the reagent ratio may change during the ongoing of the polymerization under vacuum as in the case of the PA10T oligomeric precursor and terephthaloyl chloride. The high polydispersity of the sample is also supported by the observed difference between the characteristic temperatures of the polymer prepared by the herein proposed method and by salt condensation. Indeed, in the latter mentioned case, the characteristic temperature values are a little bit higher, thus supporting the lower polydispersity. The consistency of the data herein presented is corroborated by the intermediate characteristic temperatures observed for PA10T 3ba" having intermediate molecular weight with respect to 3ba and 3ba'. Furthermore, chain extended PA10Ts showed glass transition temperature larger than the oligomer precursor, as expected, and the value is comparable to the one of PA10T exhibiting a similar melting value.^[33] In fact, this last value is a little bit lower with respect to the other reported values, but this is strongly affected by the conditions adopted for sample isolation, as well as by the analysis conditions, such as heating rate, isothermal steps, etc..[16c]



Figure 4. DSC analysis at 10°C/min of PA10T 3ba (red lines), 3ba' (black lines) and 3ba'' (blue lines). Dashed lines are cooling steps performed after pre-heating. Solid lines are 2nd heating steps accomplished after the cooling ones.

All others synthesized polymers **3** did not show any melting peaks in the analyzed temperature range. This result is in accordance with the literature in the case of PA10F and PA6F: For both polymers, melting peaks were observed only for samples with molecular weight larger than the ones described in the present paper (Table 3). In the case of PA10FF, PA6FF and PAFAT no data on the thermal behavior have been previously reported.

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All amorphous polymers, except PETA **3aa** and PAFAT **3da**, showed glass transition processes ranging in between 69 °C and 146 °C. The temperature at which the transition was observed is in good accordance with previous reported data in the case of terephthalate polymers, when polymers with comparable molecular weight are considered (Table 3).

In the case of PETA **3aa** and of the fully aromatic PAFAT **3da** neither melting or glass transition processes could be observed (Table 3). These polymers are characterized by a very rigid main-chain structure and thus most likely they have transitions at temperatures above the investigated temperature range, or transitions occur with a very low change in specific heats c_p , so that they cannot be properly identified.

Comparison the stability among thermal of and terephthalaldehydeisophthalaldehyde-derived polyamides (Figure 3) showed large differences among amorphous and semicrystalline PAs. Indeed, both PETA 3aa and PA6I 3cb degrade by a substantial two-step process, the first in the 200-300 °C temperature range, and the second at around 400 °C. The former step accounts for the degradation of the samples corresponding to the LMW fraction of the polymers.^[32] An additional difference between the degradation plots of PAs in Figure 3 is the residuum after thermal degradation (Table 3), which is highest for PETA, medium for PA6T and PA6I, and lowest for PA10T, in agreement with previous literature finding (Table 3 and references therein). This parameter, in fact, depends on the N/C ratio and, typically, the higher the ratio, the more this parameter increases.

All furan-based PAs synthesized herein displayed a general low thermal stability with the exception of PA10F **3bc**' and PA10FF **3bd**, which are stable at least up to 310 °C (Table 3). All the other furan-based PAs start to degrade in between 130 and 206 °C (Figure 5).



Figure 5. Comparison among the TGA curves of furan-based polyamides.

The reasons for the higher thermal stability of PA10FF **3bd** cannot be easily explained. Although this polymer did not show any crystallization and melting peaks during cooling and the subsequent heating (up to 250 °C), it may have some crystallinity phase with melting temperature above the degradation. However, further investigation is needed to confirm this hypothesis. The same hypothesis cannot support

the data for PA10F **3dc'**, which is much more stable than the precursor **3bc'** at lower molecular weight. In fact, this polymer was previously reported to give crystallization with melting temperature at 138 °C, which is close to the glass transition. In any case, the still scarce data on these polymers do not allow to unambiguously explain the observed thermal behavior.

Conclusion

In summary, we have presented a novel strategy for the synthesis of oligomeric polyamides (PAs) relying on the stepgrowth polycondensation of diamines and dialdehydes promoted by an N-heterocyclic carbene (NHC) catalyst in the presence of a quinone oxidant. While the optimized procedure required the addition of hexafluoro-2-proponal (HFIP) as a nucleophilic additive to guarantee the oligomer growth, the mild polyamidation conditions (ambient temperature) together with the simple recovery of both external oxidant and HFIP may represent operational advantages of the proposed methodology. The results of our study have also demonstrated that the obtained oligometric PAs ($M_n = 1.7-3.6$ kg mol⁻¹) are compatible with a subsequent chain-elongation step to achieve PAs with higher molecular weight, as exemplified by the synthesis of chain extended PA10T ($M_n = 62.8$ kg mol⁻¹) and PA10F ($M_n = 6.5$ kg mol⁻¹). Finally, important benefit of the disclosed iterative amine-to-aldehyde condensation may consist in the utilization of readily available dialdehyde monomers including those belonging to the furanic platform, thus allowing for the easy access to known and novel biobased PAs of interest for the development of environmentally benign macromolecular materials.

Experimental Section

General procedure for the synthesis of polyamides 3

A mixture of pre-catalyst **C1** (0.08 mmol) and hexafluoro-2-propanol (HFIP) (2.40 mmol) in anhydrous THF (6.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, DBU was added (0.20 mmol), and the reaction was stirred at room temperature for 5 minutes. Later, oxidant **4** (1.60 mmol) and aldehyde **2** (0.80 mmol) were added, and the reaction mixture was stirred at room temperature for 2 h. After complete consumption of aldehyde (verified by ¹HNMR analysis), diamine **1** (0.88 mmol) was added and the reaction was stirred for 16 h at the same temperature. After this period the mixture was concentrated and the resulting residue triturated with fresh portions of Et₂O (3 ×10 mL) and centrifuged. The organic solutions were collected for the recovery of DBU and oxidant **4** while the solid precipitate was dissolved in the minimum amount of appropriate solvent, and precipitated by dropwise addition into a poor solvent at 0 °C.

Synthesis of high molecular weight (HMW) PA10T 3ba'

To a 10 mL round bottom flask, under Ar atmosphere were added 200 mg of **3ba** (M_n = 2.6 kg/mol, 0.077 mmol), anhydrous N,N-dimethylacetamide (1 mL), lithium chloride (16 mg, 0.38 mmol) and N,N-diisopropylethylamine (40 µl, 0.23 mmol). The resulting mixture was stirred at room temperature until most of the prepolymer was dissolved, then the mixture was cooled to 0 °C. In a different flask, terephthaloyl chloride **10** (15 mg, 0.073 mmol) was dissolved in 0.5 mL of anhydrous N,N-dimethylacetamide. The solution was transferred in

an air tight syringe and injected in the prepolymer solution at 0 °C. After 10 minutes, the ice bath was removed and the mixture was stirred at room temperature for 48 h. After this period, the solution was slowly added to water (15 mL). The resulting solid precipitate was filtered and washed with methanol (15 mL) and diethyl ether (15 mL). Finally, the polymer was dried in vacuum at 100 °C for 4 h (183 mg, 85% yield, M_n = 62.8 kg/mol).

Synthesis of chain-extended CE-PA10F 3bc'

To a 10 mL round bottom flask, under Ar atmosphere were added 200 mg of **3bc** ($M_n = 1.6$ kg/mol, 0.068 mmol), anhydrous N,N-dimethylacetamide (1 mL), lithium chloride (14 mg, 0.34 mmol) and N,N-diisopropylethylamine (36 µl, 0.20 mmol). The resulting mixture was stirred at room temperature until most of the prepolymer was dissolved, then the mixture was cooled to 0 °C. In a different flask, 2,5-furandicarbonyl dichloride **11** (13 mg, 0.065 mmol) was dissolved in 0.5 mL of anhydrous N,N-dimethylacetamide. The solution was transferred in an air tight syringe and injected in the prepolymer solution at 0 °C. After 10 minutes, the ice bath was removed and the mixture was stirred at room temperature for 48 h. After this period, the solution was filtered and washed with methanol (15 mL) and diethyl ether (15 mL). Finally, the polymer was dried in vacuum at 100 °C for 4 h (162 mg, 76% yield, $M_n = 6.5$ kg/mol).

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Keywords: carbenes • organocatalysis • oxidation • polyamides • polymerization

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Organocatalytic step-growth polymerization: fossil- and bio-based polyamides are obtained under mild ambient conditions by polycondensation of diamines and dialdehydes promoted by an N-heterocyclic carbene in the presence of recyclable external oxidant and nucleophilic additive