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# Diamines for Polymer Materials via Direct Amination of Lipid- and Lignocellulose-based Alcohols with $NH_3$

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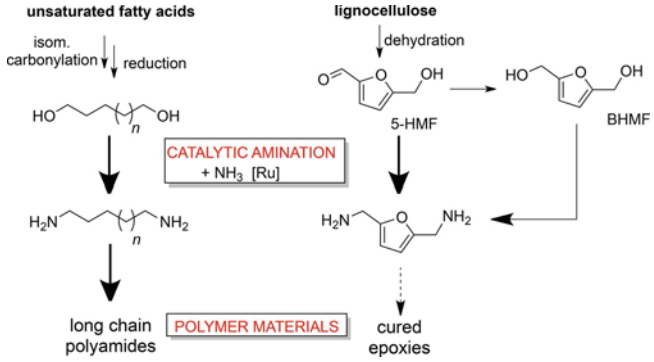
Via an all-catalytic route, long-chain diamines were prepared by the catalytic direct amination of long-chain diols, derived from plant oils. High conversion was achieved with good selectivity, with the amount of nitrile impurities formed suppressed to a low level. From the lignocellulose-based 5-hydroxymethylfurfural (5-HMF), or from bis(hydroxymethyl)furan, 2,5-bis(aminomethyl)furan (BAMF) was generated. 5-HMF was converted in a one-pot, one-step direct amination and reductive amination using ammonia. In both cases, the reaction proceeded very efficiently. In the combined amination and reductive amination, the $H_2$ concentration is a rate-limiting factor. Reducing the partial pressure of $H_2$ also shortened the reaction time required significantly. Polycondensation of the long-chain diamines with long-chain diacids led to higher molecular weight polyamides, illustrating the quality of the diamines obtained by this synthetic approach as monomers.

## Introduction

The preparation of polymers from renewable resources is an attractive prospect, not only considering the gradual depletion of fossil feedstocks but more importantly because nature also provides unique molecular structural motifs. Notably, the particular methylene chain sequences of fatty acids from plant oils can serve as the source of mid- and long-chain monomers X-$(CH_2)_n$-X for polycondensates.[1] The particular composition of carbohydrates via multiple dehydration affords furanic building blocks X-$CH_2$-furan-2,5-diyl-$CH_2$-X to be used as rigid segments in polyesters.[2]

In the synthesis of monomers from plant oils, the unsaturated fatty acids or esters are especially interesting for further functionalization.[3] Long chain α,ω-diesters and α,ω-diols are accessible already via various catalytic routes (Scheme 1, upper left part). An attractive chemical transformation towards diesters is the isomerizing alkoxycarbonylation.[4–6] In this reaction, the entire fatty acid is effectively incorporated into the product and no stoichiometric by-products are formed.[4,6–8] The highly kinetically controlled nature of the reaction results in the selective formation of a terminal ester or carboxylic acid group, far from the original site of the double bond.[9,10] The products obtained fulfil the stringent requirements on monomer purity required for polycondensation reactions, as given by the Carothers equation, and high molecular weight long-chain polyesters can be obtained.




**Scheme 1.** Overview of the synthesis of monomers and polymers pursued in this work.

Cellulose, and in particular hemicellulose as an abundant low-cost feedstock can be converted into 5-hydroxymethylfurfural (5-HMF, Scheme 1, upper right part) by acid-catalyzed dehydration.[11–20] Subsequent conversions of this platform chemical provide desirable compounds such as hexanediol, 2,5-furan dicarboxylic acid, 2,5-bis(hydroxymethyl)furan (BHMF)[21–23] and dimethyl furan.[24,25] For example 2,5-furan dicarboxylic acid can be used as an alternative to terephthalic acid in the production of polyesters materials.[26,27] These possess beneficial traits such as a higher gas barrier versus poly(ethylene terephthalate) (PET).

Compared to polyesters, fewer new polyamides[28,29] from renewables have been studied or introduced over the last decades. This is largely due to a lack of suitable routes to novel diamine monomers. Polyamides are most commonly generated by melt polycondensation of diacids with diamines.[30,31] Polyamides generally have relatively high melting points due to hydrogen bonding between the amide groups. Compared to

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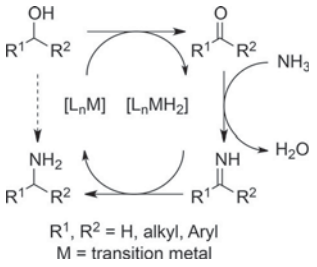
short-chain polyamides such as nylon-6,6 ($T_m$ ca. 260 °C), longer-chain monomers significantly reduce the melting point and also the water-uptake which enhances dimensional stability.[32,33] Beyond polyamides, diamines (and multifunctional amines) are also widely employed in epoxies and other resins, making use of the high nucleophilicity and reactivity of amine groups.

However, as mentioned straightforward routes to diamines based on renewable sources are lacking. Access to long-chain α,ω-diamines for polyamides still require multi-step procedures.[5,34] Commercial polyamides PA6,10, PA10,10 and PA11 are produced from ricinoleic acid, the major component of castor oil, which is, however, a rather limited resource.[1,35] Also in case of 5-HMF derived amines, no direct catalytic, atom-efficient routes are currently available and still rely on multi-step routes producing significant amounts of waste.[34,36–39]

Alcohols and alcohol derivatives (ketones, aldehydes) are easily accessible already from biomass and can be exploited in the synthesis of amines via the direct amination of alcohols with $NH_3$. The reaction follows the so-called "Hydrogen Shuttling" or "Borrowing Hydrogen" methodology with water as the only by-product (Scheme 2).[40–42] To date, several systems




**Scheme 2.** "Hydrogen shuttling" for direct amination of alcohols with ammonia.[41]

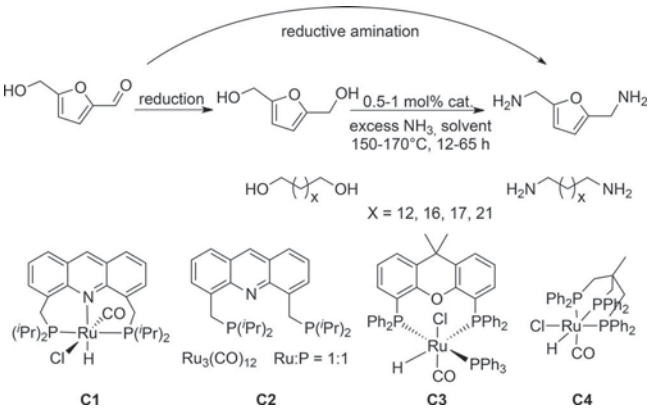
have been developed that efficiently convert primary and secondary alcohols to primary amines.[40–45] However, only two examples of a long-chain diol direct amination have been reported, both for the case of 1,19-nonadecane diol, and the conversion of the product to polymers as a probe of their suitability to this purpose has been lacking.[46,47,51] This is, however, crucial as it is also a sensitive probe whether the amination reaction is sufficiently selective and the formation of problematic (e.g. mono-functional) side-products is below an appreciable limit.

We now report insights on the pathways, and side-products and intermediates occurring in the target amination reactions. The rational derived allows for a direct di-amination of 5-HMF, and of plant oil-based long-chain diols to polymerization grade long chain diamines.

## Results and Discussion

### Diamine synthesis

A set of ruthenium complexes were screened for the direct amination of diols with $NH_3$ to the target amines (Scheme 3).




**Scheme 3.** Amination procedures and catalysts studied.

The choice of catalysts was based on their proven utility for direct amination reactions.

**C1**, reported early on in the development of catalytic amination chemistry, is based on an acridine diphosphine ligand developed by the Milstein group.[40] Moreover, this system seems to be most promising as this and derivatives of this, have been employed successfully in the direct amination of various diols, including a branched dimer fatty acid ($C_{36}$) diol.[46,51] System **C2** is also based on the acridine-based diphosphine ligand, but with ruthenium carbonyl as metal source, providing a somewhat more robust system.[44] Another system based on $RuHCl(CO)(PPh_3)_3$ and Xantphos as ligand, developed by the Beller group, was reported to be effective for diols and long-chain (mono)alcohols.[43] The most recent catalyst (**C4**) is based on $RuHCl(CO)(PPh_3)_3$ and the Triphos ligand,[45] which is also known to be a good hydrogenation catalyst.[48]

At 150 °C with a catalyst loading of 0.5 mol% only **C1** and **C4** showed activity in the amination of the α,ω-diols. However, **C4** did not lead to full conversion in these experiments and gave a broad mixture of products and was therefore not pursued further here (Tables S1 and S4, Supporting Information).

Studying 1,14-tetradecanediol as a substrate, the diol was completely converted but only 11% of primary diamine was produced. To rationalize the amination procedure, the as-obtained product mixture was fully characterized. Although high conversion was achieved, mainly secondary and cyclic amines were produced (Table 1, entry 1). This suggests that the availability of ammonia is not sufficient in these cases. In order to drive the reaction towards the primary diamine product, a sufficiently high amount of ammonia of 120 equivalents with respect to the diol was found to be key. This led to a higher selectivity of 89% (Table 1, entry 2). The increased ammonia concentration strongly reduced the formation of secondary and cyclic amines. One other notable by-product, the mono-nitrile, remained present to a small extent, which however did not hamper polycondensations (vide infra). Essentially similar observations were made for longer chain $C_{18}$ to $C_{23}$ diols. In all cases a large excess of ammonia was necessary and led to high selectivity to the corresponding diamines (Table 1, entry 3 vs. 4, 5 vs. 6). Further variations for optimization can be found in the supporting information (Table S1, entries 8–12). Interest-

**Table 1.** Screening and optimization of the direct amination of long chain diols with $NH_3$ using **C1**.

| Entry[a] | Diol (mmol) | Solvent [mL] | $NH_3$ (mmol) [mL] | Conversion [%][a] | Primary amine selectivity[a] | Secondary/cyclic amine selectivity[a] | Nitrile selectivity[a] |
|---|---|---|---|---|---|---|---|
| 1 | 1,14 (1.67) | 5 | 97.5 (2.5) | 99 | 11 | 83 | 6 |
| 2 | 1,14 (5) | 15 | 585 (15) | 92 | 89 | 6 | 5 |
| 3 | 1,18 (1.67) | 5 | 97.5 (2.5) | 99 | 11 | 80 | 9 |
| 4 | 1,18 (5) | 15 | 585 (15) | 99 | 87 | 4 | 9 |
| 5 | 1,19 (1.67) | 5 | 97.5 (5) | 100 | 74 | 17 | 9 |
| 6 | 1,19 (5) | 15 | 585 (15) | 100 | 95 | 0 | 5 |
| 7 | 1,23 (5) | 20 | 585 (15) | 100 | 96 | 0 | 4 |

Conditions: **C1** (0.5 mol%), toluene, 150 °C, 64 h. [a] Determined by $^1$H NMR (298 K, 400 MHz, $CDCl_3$) analysis based on the signal of $NH_2$-C$H_2$ (2.69 ppm) for primary amine groups, C$H_2$-NH-C$H_2$ (2.59 ppm) for secondary and cyclic amine groups and NC-C$H_2$ for nitrile groups (2.33 ppm).

ingly it was noted that with increasing chain length, the selectivity also increased.

The amination of 2,5-bis(hydroxymethyl)furan (BHMF) has been addressed in a recent patent application.[51] However, a direct and combined reductive amination-alcohol amination of 5-HMF as a one-pot procedure would be highly desirable but has not been studied before. In view of this target the aforementioned conditions for the amination of long chain diols were adapted to the amination of BHMF as a model reaction. These furan-based molecules can be susceptible to various side reactions, especially at the reaction temperatures required for the amination. In addition, the product, 2,5-bis(aminomethyl)furan (BAMF) is known to form resins and to being oxidized relatively easily under ambient conditions.[36,49] In general, it is a highly reactive amine, which is advantageous for low temperature curing.[50]

Monitoring of the reaction over time revealed that BHMF was consumed within 6 hours with considerable amounts of the intermediate aminoalcohol accumulating, which was then slowly converted to the diamine product. The reaction eventually went to completion within about 7 hours (Graph S1, Table S2). After the solvent was removed, BAMF was isolated as a brown oil.[51] As suspected by the color of the mixture, some impurities were found in the $^1$H NMR spectrum, which were not observed by GC analysis. This suggests that they are higher molecular weight secondary products formed from BAMF.[49,52]

In view of a straightforward and efficient process, the combined reductive amination-alcohol amination of 5-HMF was studied. Clearly, this requires the combination of $H_2$ and $NH_3$ in order to arrive at the diamine. After addition of $NH_3$, the pressure in the autoclave was 7.5 bar (the standard pressure of $NH_3$ at room temperature). The autoclave was further pressurized to a total pressure of 10 bar with $H_2$.

The reaction profile shows a very fast consumption of 5-HMF (Figure 1 B). In about 30 minutes all 5-HMF is converted to the intermediate aminoalcohol. At the reaction temperature, it can be expected that the aldehyde is immediately converted to the imine, due to its high reactivity but also due to the excess of ammonia. The hydrogenation step appears to be fast, which indicates that the catalyst takes up the added $H_2$, and hydrogenates the imine.[53] The subsequent conversion of the aminoalcohol to the diamine is much slower. The amount

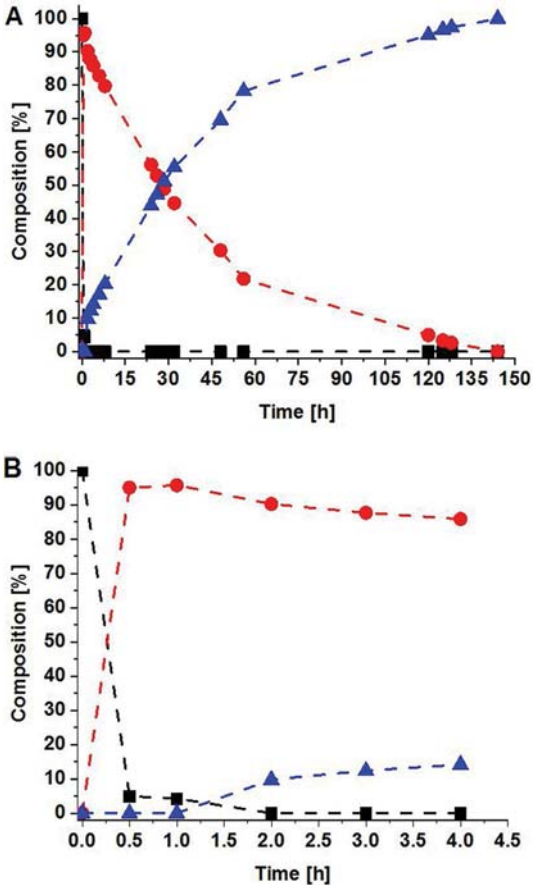



**Figure 1.** Reaction profile of the direct amination of 5-hydroxymethylfurfural with $NH_3$ and $H_2$ using catalyst **C1**. Conditions: Milstein catalyst, **C1** (0.5 mol%), 5-HMF (5 mmol), tert-amyl alcohol (15 mL), $NH_3$ (5 mL, 195 mmol), $H_2$ (2.5 bar), 150 °C. Full reaction profile (A), zoom in on the first 4 hours (B). ■ = 5-HMF, ● = aminoalcohol, ▲ = BAMF diamine. Conversion and selectivity were determined via GC-analysis.

of aminoalcohol gradually decreases over 140 h, while the amount of produced diamine (BAMF) constantly increases (Figure 1 A). This is a strong indication that the catalyst is saturated by the hydrogen in the system, and for a large part unavailable for the required alcohol dehydrogenation. In order to reduce the ratio of $H_2$ to catalyst, the reaction was scaled-up, while the $H_2$ amount was kept constant. Under these conditions the reaction time was reduced to 12 hours until completion (Fig-

ure 2 A). Again 5-HMF was consumed rapidly (Figure 2 B), leaving only the aminoalcohol after 30 min, which then smoothly converted to BAMF.

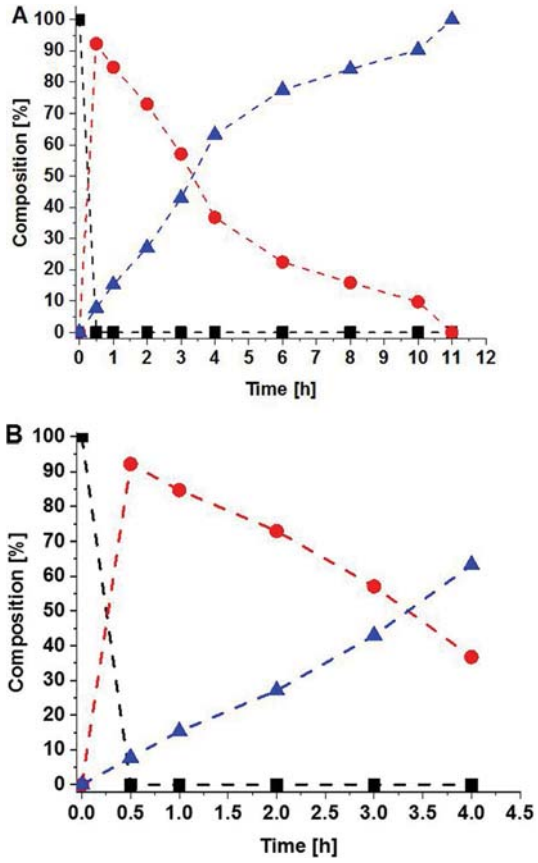



**Figure 2.** Reaction profile of the amination of 5-hydroxymethylfurfural with $NH_3$ and $H_2$ using system **C1** with a decreased $H_2$ concentration. Conditions: Milstein catalyst, **C1** (0.5 mol%), 5-HMF (10 mmol), tert-amyl alcohol (55 mL), $NH_3$ (10 mL, 390 mmol), $H_2$ (2.5 bar), 150 °C. Full reaction profile (A), zoom in on the first 4 hours (B). ■ = 5-HMF, ● = aminoalcohol, ▲ = BAMF diamine. Conversion and selectivity were determined via GC-analysis.

The $^1$H NMR spectrum of the product essentially is identical to that of the product from amination of BHMF, with two singlet resonances at 6.0 and 3.8 ppm, as anticipated (Graph S16). Some minor additional peaks reveal that the reaction is not perfectly clean and some by-products occur which do not show in GC. Therefore, the exact selectivity and product purity were determined via $^1$H NMR and were found to be slightly lower namely 85% selectivity while GC analysis suggested a product purity of 90–100%. This compares favorably to GC purity data reported in a patent by Schaub and co-workers[51] for diamine produced from the separately prepared diol. The minor additional signals in $^1$H NMR were reduced by lowering the reaction temperature to 140 °C, which also decelerated the reaction, resulting in a reaction time of 24 hours for complete conversion.

## Polycondensation

Melt-polycondensations were carried out under elevated pressure in a 25 mL stainless steel reactor.[54] Stoichiometric amounts of the diamine and the diacid were reacted in the initial presence of excess water as a reaction medium (Table 2).

**Table 2.** Molecular weights and melting points of the polycondensation products of various chain length diamines and diacids.

| Entry | Polyamide PA | $M_n$ [g/mol][a] | $T_m$ [°C][b] |
|---|---|---|---|
| 1[c] | 7,19 | 13 700 | 180 |
| 2[c] | 8,19 | 19 300 | 183 |
| 3 | 12,12 | 12 400 | 187 |
| 4 | 12,18 | 28 100 | 171 |
| 5 | 12,19 | 19 500 | 170 |
| 6 | 19,19 | 18 700 | 158 |
| 7 | 23,23 | 21 600 | 149 |

Polyamides were obtained by melt polymerization in the initial presence of degassed (mL) water pre-pressurized with 10 bar nitrogen pressure and heated to 210 °C for 2.5 hours, subsequently 2 hours vacuum. [a] Molecular weights determined by $^1$H NMR spectroscopy at 403 K in $C_2D_2Cl_4$ with addition of phenol via endgroup analysis. [b] Melting points determined by DSC. [c] Vacuum was applied for 1.75 hours.

Generally, the obtained polyamides were white to yellow materials. For comparison, with commercial monomers such as 1,12-diamine and 1,18-diacid or with 1,19-diacid from isomerizing carbonylation, molecular weights varying from $1.2\times10^4$ to $2.8\times10^4$ g mol$^{-1}$ were obtained (Table 2, entries 1–5). The polyamides with the (catalytically) synthesized long chain diamines exhibited comparatively high molecular weights of about $1.8\times10^4$ and $2.1\times10^4$ g mol$^{-1}$, respectively (entries 6 and 7, Table 2). Note that these molecular weights match with those of typical commercial polyamides.[55]

The linear increase of the melting point with a lower chain-length of the monomers is evident for the materials studied here (Figure 3), and matches with previous observations on

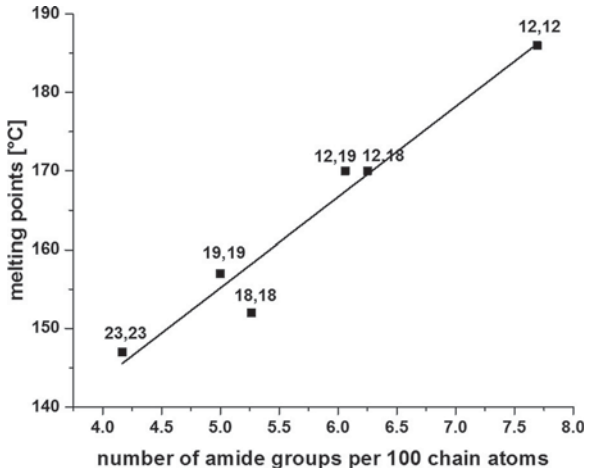



**Figure 3.** Variation of the melting point depending on the $CH_2$ to CONH ratio. Generally pronounced odd/even effects are found for the melting behavior of aliphatic polyamides.

these polyamides generated through other routes.[1,56] As the formation of hydrogen bonds also depends on the odd or even number of carbon atoms in the chain, the melting points of odd/odd, even/even and odd/even polyamides variate.

## Conclusion

The direct amination of various long-chain diols is feasible employing an acridine-based diphosphine ruthenium complex, previously reported by Milstein. A high excess of ammonia is key to prevent the formation of cyclic and secondary amines. In a single amination step, long-chain diamines were obtained, sufficiently pure for subsequent polycondensation, previously not demonstrated in this type of catalytic synthesis of diamines. In contrast to previous methods, no intensive purification was required. A one-pot, combined reductive amination-alcohol amination of 5-HMF yielded 2,5-bis(aminomethyl)furan (BAMF). The reaction requires additional hydrogen, which dramatically slowed down the entire reaction. By minimizing the partial pressure of $H_2$ the diamine was produced at the same rate as in the direct amination of the separately prepared diol. This new one-step procedure is particularly attractive due to the ready availability of 5-HMF as a lignocellulose-based platform chemical. Lignocellulosic waste material does not compete with food use of renewable feedstocks, and notably also the long-chain feedstocks used here can be generated from microalgae oils.[62,63]

## Experimental Section

### General considerations

All syntheses were carried out under inert gas atmosphere using standard Schlenk or glovebox techniques unless stated otherwise. All catalytic reactions were carried out under inert gas atmosphere. Toluene was dried in a solvent purification system over aluminum oxide and stored under inert gas. THF was dried over sodium benzophenone and stored under inert gas. Water was distilled under nitrogen atmosphere and stored under inert gas. 4,5-Bis-(di-*iso*-propylphosphinomethyl)acridine (Milstein acridine ligand) was prepared following a published procedure.[40] The long-chain dimethyl esters $C_{18}$, $C_{19}$, $C_{23}$ were prepared according to a published procedure.[5] 5-(Hydroxymethyl)furfural, 2,5-bis(hydroxymethyl)furan and bis(aminomethyl)furan were bought from Carbosynth. 1,12-Diaminododecane was purchased from TCI and 1,12-dodecanedioic acid, 1,12-diaminododecane (98%) from Sigma–Aldrich. 1,18-Octadecanedioic acid was purchased from Elevance and recrystallized from toluene before use. 1,6-Diaminohexane (97%) and 1,8-diaminooctane (98%) were purchased from Fluka. Ammonia was acquired from BOC in micrographic grade 99.998% in a 5.0 L cylinder equipped with a BS10 dual port valve and was dosed using a Bronkhorst Liquid-Flow mass flow controller. Hydrogen for the amination was purchased from BOC in industrial grade with a purity of 99.99%. Amination reactions were carried out in 75 mL stainless steel autoclaves equipped with a Pt-100 thermocouple, a gas inlet, a pressure gauge, a sampling unit for 50 μL samples and an inlet for reagents. Polymerizations were performed in 20 mL autoclaves equipped with a 15 mL glass inlay, two gas inlets and a pressure gauge. Deuterated solvents were bought from Eurisotop except for $CDCl_3$, which was received from Sigma–Aldrich and stored over 4 Å molecular sieves. $CD_3OD$ was dried over 3 Å molecular sieves. NMR spectra were recorded on Bruker Avance III 400 MHz, Bruker Avance III 500 MHz, Bruker Avance DRX 600 spectrometers or a Varian Unity INOVA 400 MHz spectrometer. $^1$H NMR spectra were recorded at 400 MHz, 500 MHz, and 600 MHz. The splitting patterns in the NMR spectra are listed as followed: chemical shift (δ) in ppm, multiplicity, coupling constant in Hertz, integral, label of the protons. Following abbreviations were used: (s) for singlet, (d) for doublet, (t) for triplet and (m) for multiplet. Acquired data was processed and analyzed using MestReNova software. Amination of 5-HMF or BHMF as substrate were monitored over time and analysis was conducted via gas chromatography using a Shimadzu GC-2010 instrument equipped with a flame-ionization detector (FID) and an Ultra-19091B-102 column (25.0 m, 0.20 mm ID, 95% dimethyl polysiloxane, 5% phenylmethyl polysiloxane). The column flow was 0.69 mL min$^{-1}$ with helium as carrier gas and a linear velocity of 26.1 cm s$^{-1}$. Injection was conducted at 270 °C, and the sample was detected at 290 °C. The method started at 80 °C and within 18 minutes the temperature was increased to 215 °C and within 3 minutes the temperature was raised to 270 °C which was held for another 3 minutes. Further GC analyses were carried out on a PerkinElmer Clarus 500 GC system equipped with a flame-ionization detection (FID) over a PerkinElmer Elite-5 capillary column (30 m, 0.25 mm, 0.25 μm, 5% phenylmethyl polysiloxane 95% dimethyl polysiloxane) and a PerkinElmer Elite-5MS column (15 m, 0.32 mm, 0.1 μm, 5% phenylmethyl polysiloxane 95% dimethyl polysiloxane). The injection volume of the automatic sampler was set to 1 μl. The sample was injected at 300 °C and detected at 280 °C. For both columns the same method was used, which started at 90 °C and maintained this temperature for 1 min before heating to 280 °C within 30 min. The final temperature was kept constant for another 8 min.

#### 1,14-Tetradecanediol to 1,14-tetradecane diamine:

Into a 75 mL autoclave, 1.15 g (5 mmol) of 1,14-octadecane diol and 15.1 mg (0.025 mmol, 0.5 mol%) [RuHCl(acridine-$^i$Pr-PNP)(CO)] were weighed. The autoclave was equipped with a cross-shaped stirring bar, closed and purged several times with argon. Via syringe, 15 mL toluene was added. Subsequently, 15 mL (585 mmol) of $NH_3$(l) was added via a mass flow controller. The autoclave was then heated to 150 °C and stirred for 65 hours. After cooling to room temperature, the reactor was vented, and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and an off-white powder was obtained. The powder (1.08 g, 4.73 mmol) was subsequently dissolved in 75 mL heptane at 90–95 °C. It should be noted that above 95 °C, a brown, fluffy solid precipitated. The solution was filtrated hot to remove all the insoluble parts. After cooling to 8 °C, an off-white precipitate formed which was filtrated and dried under vacuum. The product was isolated as an off-white powder (0.94 g, 4.12 mmol, 82%) in 90% purity. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 2.67 (t, $^3J_{HH}$ = 7.0 Hz, 4H, H-2), 1.45 (m, 4H, H-3), 1.28 (m, 28H, H-6). See Graph S7 for assignment.

#### 1,18-Octadecanediol to 1,18-octadecane diamine:

Into a 75 mL autoclave, 1.43 g (5 mmol) of 1,18-octadecane diol and 15.1 mg (0.025 mmol, 0.5 mol%) [RuHCl(acridine-$^i$Pr-PNP)(CO)] were weighed. The autoclave was equipped with a cross-shaped stirring bar, closed and purged several times with argon. Via syringe, 15 mL toluene was added. Subsequently, 15 mL (585 mmol) of $NH_3$(l) was added via a mass flow controller. The autoclave was

then heated to 150 °C and stirred for 65 hours. After cooling to room temperature, the reactor was vented, and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and an off-white powder was obtained. The powder (1.408 g, 4.949 mmol) was dissolved in 75 mL heptane at 90–95 °C. It should be noted that above 95 °C, a brown, a fluffy solid precipitated. The solution was filtrated hot to remove all the insoluble parts. After cooling to 8 °C, an off-white precipitate formed which was filtrated and dried under vacuum. The product was isolated as an off-white powder (1.00 g, 3.515 mmol, 71 %) in 90 % purity und could not be purified further. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 2.67 (t, $^3J_{HH}$ = 7.0 Hz, 4 H, H-2), 1.42 (m, 4 H, H-3), 1.27 (m, 28 H, H-6). See Graph S8 for assignment.

**1,19-Nonadecanediol to 1,19-nonadecane diamine:**

Into a 75 mL autoclave, 1.50 g (5 mmol) of 1,19-nonadecane diol and 15.1 mg (0.025 mmol, 0.5 mol %) [RuHCl(acridine-$^i$Pr-PNP)(CO)] were weighed. The autoclave was equipped with a cross-shaped stirring bar, closed and purged several times with argon. Via syringe, 15 mL toluene was added. Subsequently, 15 mL (585 mmol) of $NH_3$(l) was added via a mass flow controller. The autoclave was then heated to 150 °C and stirred for 65 hours. After cooling to room temperature, the reactor was vented, and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and an off-white powder was obtained consisting of 96 % of the desired diamine with 4 % of 1-amino-19-nitrile as by-product and could not be purified further. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 2.67 (t, $^3J_{HH}$ = 7.0 Hz, 4 H, H-2), 1.42 (m, 4 H, H-3), 1.27 (m, 30 H, H-6). See Graph S9 for assignment.

**1,23-Tricosanediol to 1,23-tricosane diamine:**

Into a 75 mL autoclave, 1.79 g (5 mmol) of 1,23-tricosane diol and 15.1 mg (0.025 mmol, 0.5 mol %) [RuHCl(acridine-$^i$Pr-PNP)(CO)] was weighed. To this, a cross-shaped stirring bar was added, and the autoclave was closed. After purging several times with argon, 15 mL of toluene was added via syringe. Subsequently, 15 mL (585 mmol) of $NH_3$(l) was added via a mass flow controller. The autoclave was then heated to 150 °C and stirred for 65 hours. After cooling to room temperature, the reactor was vented, and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and an off-white powder was obtained consisting of 90 % of the desired amine with 10 % of 1-amino-23-nitrile as by-product. In 80 mL heptane, (1.66 g, 4.69 mmol) 1,23-diaminotricosane was dissolved at 95 °C. It should be noted that above 95 °C, a brown, fluffy solid precipitated from the solution. The solution was filtrated hot to remove all insoluble parts. After cooling to 8 °C, an off-white precipitate occurred which was filtered off and dried under vacuum. The product was isolated as an off-white solid in 1.40 g (3.955 mmol, 84 %) yield with a purity of 94 % according to $^1$H NMR analysis. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 2.67 (t, $^3J_{HH}$ = 7.0 Hz, 4 H, H-2), 1.43 (m, 4 H, H-3), 1.25 (m, 36 H, H-6). See Graph S10 for assignment.

**2,5-Bis(hydroxymethyl)furan to 2,5-bis(aminomethyl)furan (BAMF):**

Into a 75 mL autoclave, 640 mg (5 mmol) of bis(hydroxymethyl)furan and 15.1 mg (0.025 mmol, 0.5 mol %) [RuHCl(acridine-$^i$Pr-PNP)(CO)] were weighed. A cross-shaped stirring bar was placed in the autoclave after it was closed and purged several times with argon. Via syringe, 15 mL of *tert*-amylalcohol was added followed by 5 mL (195 mmol) $NH_3$(l) via a mass flow controller. The autoclave was then heated to 150 °C and stirred for 7 hours. After cooling to room temperature, the autoclave was vented, and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and the diamine was isolated as a viscous brown liquid (isolated: 410 mg, 3.25 mmol, 65 %). The reaction was monitored by taking samples at specific time intervals and GC analysis was conducted subsequently. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 6.04 (s, 2 H, H-1), 3.79 (s, 4 H, H-2). See Graph S16 for assignment.

**5-Hydroxymethylfuran to 2,5-bis(aminomethyl)furan (BAMF):**

Into a 75 mL autoclave, 1.280 g (10 mmol) 5-hydroxymethylfurfural and 30.2 mg (0.05 mmol, 0.5 mol %) [RuHCl(acridine-$^i$Pr-PNP)(CO)] were weighed and a cross-shaped stirring bar was added. Then the autoclave was closed and purged several times with argon. To the autoclave, 25 mL *tert*-amylalcohol was added via syringe followed by 10 mL (390 mmol) $NH_3$(l) via a mass flow controller. Subsequently, the reactor was further pressurized to 10 bar with $H_2$(g). The autoclave was heated to 140 °C and stirred for 11 hours. After cooling to room temperature, the autoclave was vented and the reaction mixture was transferred into a 100 mL round bottom flask. The solvent was removed in vacuo and the diamine was isolated as a viscous brown liquid (isolated: 731.7 mg, 5.8 mmol, 85 %). The reaction was monitored by taking samples at specific time intervals and GC analysis was conducted subsequently. $^1$H NMR ($CDCl_3$, 298 K, 400 MHz, $\delta$ = ppm): 6.04 (s, 2 H, H-1), 3.79 (s, 4 H, H-2). See Graph S16 for assignment.

**General procedure for the preparation of long-chain X,X polyamides:[54]**

Stoichiometric amounts of diamine and diacid (ca. 1 g substrates) were weighed into a 15 mL glass inlay and placed in a 20 mL autoclave. The reactor was closed and purged several times with nitrogen. Then 10 mL degassed water was added with a syringe through the gas inlet. The autoclave was subsequently pressurized with nitrogen to 10 bar and heated to 210 °C for 2.5 hours. The pressure was released within 10 minutes and vacuum was applied for another 2 hours. After the reaction the autoclave was vented with nitrogen and cooled to room temperature.

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## Conflict of interest

*The authors declare no conflict of interest.*

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[1] F. Stempfle, P. Ortmann, S. Mecking, *Chem. Rev.* **2016**, *116*, 4597 – 4641.
[2] Y. Xia, R. C. Larock, *Green Chem.* **2010**, *12*, 1893 – 1909.
[3] J. C. Mol, *Green Chem.* **2002**, *4*, 5 – 13.

[4] D. Quinzler, S. Mecking, *Angew. Chem. Int. Ed.* **2010**, *49*, 4306 – 4308; *Angew. Chem.* **2010**, *122*, 4402 – 4404.
[5] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, *Macromolecules* **2011**, *44*, 4159 – 4166.
[6] C. Jiménez-Rodriguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* **2005**, *8*, 878 – 881.
[7] M. R. L. Furst, R. L. Goff, D. Quinzler, S. Mecking, C. H. Botting, D. J. Cole-Hamilton, *Green Chem.* **2012**, *14*, 472 – 477.
[8] M. R. L. Furst, T. Seidensticker, D. J. Cole-Hamilton, *Green Chem.* **2013**, *15*, 1218 – 1225.
[9] P. Roesle, L. Caporaso, M. Schnitte, V. Goldbach, L. Cavallo, S. Mecking, *J. Am. Chem. Soc.* **2014**, *136*, 16871 – 16881.
[10] V. Goldbach, L. Falivene, L. Caporaso, L. Cavallo, S. Mecking, *ACS Catal.* **2016**, *6*, 8229 – 8238.
[11] I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose, R. Palkovits, *Chem. Rev.* **2016**, *116*, 1540 – 1599.
[12] Y.-C. Lin, G. W. Huber, *Energy Environ. Sci.* **2009**, *2*, 68 – 80.
[13] B. F. M. Kuster, *Starch/Staerke* **1990**, *42*, 314 – 321.
[14] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411 – 2502.
[15] C. M. Cai, T. Zhang, R. Kumar, C. E. Wyman, *Green Chem.* **2013**, *15*, 3140 – 3145.
[16] Y. Ma, S. Qing, L. Wang, N. Islam, S. Guan, Z. Gao, X. Mamat, H. Li, W. Eli, T. Wang, *RSC Adv.* **2015**, *5*, 47377 – 47383.
[17] Q. Cao, X. Guo, J. Guan, X. Mu, D. Zhang, *App. Catal. A* **2011**, *403*, 98 – 103.
[18] B. Saha, M. M. Abu-Omar, *Green Chem.* **2014**, *16*, 24 – 38.
[19] X. Qi, M. Watanabe, T. M. Aida, J. R. L. Smith, *Green Chem.* **2008**, *10*, 799 – 805.
[20] F. Benvenuti, C. Carlini, P. Patrono, A. M. Raspolli Galletti, G. Sbrana, M. A. Massucci, P. Galli, *Appl. Catal. A* **2000**, *193*, 147 – 153.
[21] Q. Cao, W. Liang, J. Guan, L. Wang, Q. Qu, X. Zhang, X. Wang, X. Mu, *Appl. Catal. A* **2014**, *481*, 49 – 53.
[22] J. Chen, F. Lu, J. Zhang, W. Yu, F. Wang, J. Gao, J. Xu, *ChemCatChem* **2013**, *5*, 2822 – 2826.
[23] S. Subbiah, S. P. Simeonov, J. M. S. S. Esperanca, L. P. N. Rebelo, C. A. M. Afonso, *Green Chem.* **2013**, *15*, 2849 – 2853.
[24] P. Zhou, Z. Zhang, *Catal. Sci. Technol.* **2016**, *6*, 3694 – 3712.
[25] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499 – 1597.
[26] A. Gandini, T. M. Lacerda, A. J. F. Carvalho, E. Trovatti, *Chem. Rev.* **2016**, *116*, 1637 – 1669.
[27] A. J. J. E. Eerhart, A. P. C. Faaij, M. K. Patel, *Energy Environ. Sci.* **2012**, *5*, 6407 – 6422.
[28] R. J. Palmer, S. Updated by, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., **2000**.
[29] R. J. Palmer, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., **2002**.
[30] A. E. Hamielec, H. Tobita, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.
[31] C. E. Schildknecht, I. Skeist, *Polymerization Processes*, Wiley, **1977**.
[32] W. G. Perkins, R. S. Porter, *J. Mater. Sci.* **1977**, *12*, 2355 – 2388.
[33] X. Cui, D. Yan, *J. Appl. Polym. Sci.* **2004**, *93*, 2066 – 2071.
[34] K. S. Hayes, *Appl. Catal. A* **2001**, *221*, 187 – 954.
[35] W. Keim, in *Kunststoffe*, Wiley-VCH, Weinheim, **2006**, pp. 325.
[36] A. Mitiakoudis, A. Gandini, *Macromolecules* **1991**, *24*, 830 – 835.
[37] N.-T. Le, A. Byun, Y. Han, K.-I. Lee, H. Kim, *Green Sustainable Chem.* **2015**, *5*, 115 – 127.
[38] S. Gabriel, *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 2224 – 2236.
[39] T. Haas, T. Tacke, J. Pfeffer, Christoph, F. Klasovsky, M. Rimbach, M. Volland, M. Ortelt, *Process for Producing 2,5-Diformylfuran and Derivatives Thereof*, **2012**, WO2012004069 (A1).
[40] C. Gunanathan, D. Milstein, *Angew. Chem. Int. Ed.* **2008**, *47*, 8661 – 8664; *Angew. Chem.* **2008**, *120*, 8789 – 8792.
[41] D. Pingen, C. Müller, D. Vogt, *Angew. Chem. Int. Ed.* **2010**, *49*, 8130 – 8133; *Angew. Chem.* **2010**, *122*, 8307 – 8310.
[42] S. Imm, S. Bähn, L. Neubert, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2010**, *49*, 8126 – 8129; *Angew. Chem.* **2010**, *122*, 8303 – 8306.
[43] S. Imm, S. Bähn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas, M. Beller, *Angew. Chem. Int. Ed.* **2011**, *50*, 7599 – 7603; *Angew. Chem.* **2011**, *123*, 7741 – 7745.
[44] D. Pingen, O. Diebolt, D. Vogt, *ChemCatChem* **2013**, *5*, 2905 – 2912.
[45] E. J. Derrah, M. Hanauer, P. N. Plessow, M. Schelwies, M. K. da Silva, T. Schaub, *Organometallics* **2015**, *34*, 1872 – 1881.
[46] G. Walther, J. Deutsch, A. Martin, F.-E. Baumann, D. Fridag, R. Franke, A. Köckritz, *ChemSusChem* **2011**, *4*, 1052 – 1054.
[47] Y. Shi, P. C. J. Kamer, D. J. Cole-Hamilton, *Green Chem.* **2017**, *19*, 5460 – 5466.
[48] K.-M. Sung, S. Huh, M.-J. Jun, *Polyhedron* **1998**, *18*, 469 – 479.
[49] K. I. Galkin, E. A. Krivodaeva, L. V. Romashov, S. S. Zalesskiy, V. V. Kachala, J. V. Burykina, V. P. Ananikov, *Angew. Chem. Int. Ed.* **2016**, *55*, 8338 – 8342; *Angew. Chem.* **2016**, *128*, 8478 – 8482.
[50] A. Panchenko, M. Charrak, K. Dahmen, M. Brinks, M. Schelwies, B. Blank, Benoit, M. Piepenbrink, R. Backes, *Use of 2,5-bis(aminomethyl)furan as curing agent for epoxy resins*, **2015** EP 2837645 (A1).
[51] T. Schaub, B. Buschhaus, M. K. Brinks, M. Schelwies, R. Paciello, J.-P. Melder, M. Merger, *Process for Preparing di-, tri- and polyamines by homogenously catalyzed alcohol amination*, **2012**, WO20120232293 (A1).
[52] C. Goussé, A. Gandini, P. Hodge, *Macromolecules* **1998**, *31*, 314.
[53] D. Pingen, M. Lutz, D. Vogt, *Organometallics* **2014**, *33*, 1623.
[54] E. Kaya, L. J. Mathias, *J. Appl. Polym. Sci.* **2012**, *123*, 92 – 98.
[55] B. Herzog, M. I. Kohan, S. A. Mestemacher, R. U. Pagilagan, K. Redmond, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.
[56] Y. Kinoshita, *Makromol. Chem.* **1959**, *33*, 1 – 20.
[57] Y. Jiang, D. Maniar, A. J. J. Woortman, G. O. R. Alberda van Ekenstein, K. Loos, *Biomacromolecules* **2015**, *16*, 3674 – 3685.
[58] S. Jeol, *Novel Polyamide*, *Process for Preparing same and uses Thereof* **2013**, WO2013007585 (A1).
[59] S. Jeol, *Curable Composition and Process for the Manufacture of an Epoxy Thermoset* **2015**, WO2015001061 (A1).
[60] M. Ortelt, E. Spyrou, J. C. Pfeffer, D. Fuchsmann, B. Kohlstruk, T. Haas, *Curable Compositions Based on Epoxy Resins Without Benzyl Alcohol* **2014**, WO2014037222 (A3).
[61] S. Jeol, *Polyimides*, *Processes for Producing said Polyimides and Articles Obtained From said Polyimides* **2014**, WO2014173876 (A1).
[62] P. Roesle, F. Stempfle, S. K. Hess, J. Zimmerer, C. Río Bártulos, B. Lepetit, A. Eckert, P. G. Kroth, S. Mecking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6800 – 6804; *Angew. Chem.* **2014**, *126*, 6918 – 6922.
[63] S. K. Hess, N. S. Schunck, V. Goldbach, D. Ewe, P. G. Kroth, S. Mecking, *J. Am. Chem. Soc.* **2017**, *139*, 13487 – 13491.