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Examples of Xylochemistry: Colorants and Polymers

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Dedicated to Prof. Dr. Hans-Günther (Hagga) Schmalz on the occasion of his 60th birthday

Against the backdrop of modern sustainable chemistry and valorization of biomass for chemical raw materials, the syntheses of indigo dyes and polyamides as representatives of two classes of everyday chemical products based on xylochemicals are described. Wood-derived starting materials were transformed into functional materials using the principles of *green chemistry* to expand the scope of products gained from renewable resources. The indigo dyes were synthesized in a short, straightforward sequence starting from vanillin without the use of organic solvents. Two polyamides, representatives of todays most important class of polymers, were obtained from 4-propylcyclohexanol, which is one of the longest known (and most abundant) hydrogenative depolymerization products of lignin.

promising feedstock in the past decades.

Introduction

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The current chemical infrastructure relies mainly on petroleum and other fossil resources, the supplies of which are finite and which become increasingly difficult to extract from underground deposits. Furthermore, their use leads to a carbon imbalance in our ecosystem¹ and they contribute to a significant degree to the anthropogenic pollution of our environment. As a result of these issues, a paradigm change in the chemical infrastructure towards a sustainable production and use of chemical intermediates needs to be established. Possible solutions have been presented in the concepts of Anastas and Warner, who also postulated the 12 principles of green chemistry. One major aspect of these principles is the use of renewable feedstocks to provide chemical building blocks, intermediates and reagents.² Attention is recently turning to the use of biomass as a new raw material for energy and chemical production^{3, 4} which bears several advantages such as an ecologically benign production and the "renewability" of the resources in contrast to the continual depletion of coal and petroleum. Besides these ecological factors there are also chemical advantages including the abundance of complex substituents and groupings found in naturally occurring chemical building blocks such as the presence of functional groups or heteroatoms, and, importantly, the chiral content of these materials.⁵ Such preexisting functionalities should be maintained and utilized rather than destroyed and rebuilt in order to seize the full potential of the raw material employed. In the area of

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biomass valorization, lignin has received great attention as a

30% of the organic carbon in the biosphere. It consists of

phenylpropanoid units derived from p-coumaryl, coniferyl and

sinapyl alcohol.6 These assemble through C-O and C-C bonds to the

unique heterogenic, aromatic, hyperbranched polymer lignin

(figure 1), which can serve as a starting point for the preparation of a

depolymerization of lignin is known since 1938,⁷ great effort has

been put into its valorization as an effective source of low-

variety of useful chemical intermediates. Although

Lignin is part of lignocellulose and accounts for approximately

Figure 1 Conversion of lignin through key xylochemicals to dyes and bifunctional A_2/B_2 monomers.

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molecular-weight compounds in recent years.⁸ A variety of depolymerization methods have been developed to this end which include pyrolysis, hydrolysis, hydrogenolysis, liquid-phase reforming, chemical oxidation, and gasification. These methods mainly produce aromatic compounds of six to nine carbon atoms with functional groups such as hydroxyl, carbonyl or carboxyl.⁹

We recently reported the xylochemical synthesis of the berberine-type alkaloid Ilicifoline B in a sequence in which all carbon atoms are exclusively derived from wood.^{10, 11} In order to enhance the portfolio of products available through this strategy, we now report a synthesis of chemically well-defined colorants and unconventional polyamides based on wood derived molecules (xylochemicals). Furthermore, all steps of the synthesis are conducted with methods according to the principles of *green chemistry* to maximize the sustainability of the entire process and minimize environmental impact.

Indigo dyes as well as polyamides belong to the most common functional materials and have a long history in chemical industry and marketplace. Indigo itself is known and used since the time of the ancient Egyptians and has received even more attention since its structural elucidation by von Baeyer in 1883.¹² A variety of indigo syntheses and derivatives have since been developed. Furthermore new applications for indigos have been investigated, for example their use as semiconductors.¹³

Polyamides received popularity by the development of the synthetic fibers nylon (polyamide 6,6, PA66) by Carothers in 1937¹⁴ and Perlon[®] (polyamide 6, PA6) by Schlack in 1938.¹⁵ Because of their unmatched stability and unique properties like high toughness and good wear properties, polyamides are still an important class of materials. Today's production of indigo dyes as well as that of polyamides heavily relies on petroleum raw materials and environmentally deleterious processes.^{16, 17} Here, we present an alternative and sustainable access to both compound classes.

Results and discussion

Indigo dye syntheses

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The synthesis of the indigo derivatives started from veratraldehyde (8) which can be directly isolated from biomass or can be obtained from vanillin (1) by O-methylation with dimethyl sulphate¹⁸ (available from the reaction of methanol with oleum or SO₃). The conversion of lignin to vanillin through chemical oxidation¹⁹ or electrolysis²⁰ is widely explored. Veratraldehyde was nitrated as described in the literature with 65% aqueous nitric acid to the corresponding 6-nitro derivative (9) in 91% yield (figure 2).²¹



Figure 2 Synthetic route to the indigos 3 and 4 based on the xylochemical 1.



Figure 3 Alternative sustainable route to 3 based on 2.

The latter could be transformed into 5,5⁺,6,6⁺-tetramethoxyindigo (**3**) in 23% yield according to a procedure by Harley-Mason through reaction with acetone and aqueous sodium hydroxide in a Baeyer-Drewsen indigo synthesis.²² Acetone and methanol (also known as wood alcohol) are available from wood by the long known processes of wood pyrolysis and distillation.²³ The Baeyer-Drewsen indigo synthesis is the oldest synthetic method to produce indigo derivatives.¹² Although it was eventually replaced by routes starting from aniline, it represents the most sustainable route because of the use of aromatic aldehydes and acetone, which can easily be obtained from renewable sources.⁸ Its low yield was suspected to be a result of the complex reaction mechanism. Indigo derivative **3** could further be transformed into 5,5⁺,6,6⁺-tetrahydroxyindigo (**4**) in 32% yield with HBr/acetic acid (figure 2).

While this route already fulfils the criteria of xylochemistry, we sought to prepare **3** by an alternative procedure to maximize synthetic efficiency. Starting from aldehyde **9**, a catalytic Henry-reaction with Ba(OH)₂·8H₂O and nitromethane in water provided the corresponding nitroaldol product **10** in 94% yield (figure 3).²⁴ This compound could be converted to indigo **3** using a method also developed by Harley-Mason. Treatment of **10** with sodium dithionite in aqueous alkaline solution and subsequent aerial oxidation produced **3** in 81% yield.²⁵

Although the synthesis of indigos from 1-(2-nitrophenyl)-2nitroethanol derivatives is a very rarely used, it is in accord with the principles of *green chemistry*. Nitromethane can be generated from dimethyl sulfate and potassium or sodium nitrite in high yield and purity on an industrial scale.²⁶ All steps of the synthesis were conducted in water using catalytic methods and mild reaction conditions.

Like most indigo dyes, indigos **3** and **4** are poorly soluble in organic solvents and water. Compounds **3** and **4** are known since 1948^{22} and 1947,²⁷ respectively, but apart from a report on some photophysical properties of **3** by De Melo et al.,²⁸ no further information or spectroscopic data have been reported. Indigo **3** can be used for vat dyeing textiles after dithionite reduction (see ESI, S50).

Polyamide syntheses

For the synthesis of the polyamide monomers, we chose 4-propylcyclohexanol (2) as the key xylochemical. It is one of the first compounds obtained through the depolymerization pathway by means of catalytic hydrogenolysis of hardwood lignin over copper chromite developed by Adkins et al. in 1938 with 11 wt% yield.^{7, 8} Because of the more suitable implementation on a laboratory scale, we prepared 2 from inexpensive 4'-hydroxypropiophenone (11) through hydrogenation over Pd/C in the presence of lactic acid to obtain 2 in 92% yield (figure 4).²⁹ As with the actual xylochemical, 2 was obtained as a mixture of both possible diastereomers with a ratio of cis:trans 1:1 (¹H-NMR, see the ESI, S27). These could easily be separated by flash chromatography for characterization, but all

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further syntheses were carried out with the isomeric mixture. Based on 2, the corresponding ε -lactam 5 as well as the corresponding hexanedioic acid 6 and hexanediamine 7 were synthesized. These compounds represent xylochemical versions of the most common monomers for polyamide synthesis.

Lactam 5 was produced according to an industrial ε -caprolactam synthesis³⁰ by oxidation of 2 to the ketone 12 which was converted to the corresponding oxime 13 followed by Beckmann-rearrangement (figure 4).

For the oxidation of **2**, several green aerobic oxidation methods were evaluated. Aerobic procedures can be considered as the most sustainable oxidation methods because they guarantee good atomeconomy and the only side-product is water.⁵ While the most common procedures based on the nitroxyl radical TEMPO (**14a**)³¹ did not show any conversion of **2** (table 1, entries 1–3) other nitroxyl radicals like ABNO (**14b**),³² keto-ABNO (**14c**)³³ or PINO (**14d**)³⁴ led to moderate yields of **12** (table 1, entries 4–6). Remarkably, only the *cis*-diastereomer of **2** could be converted to the ketone **12** with keto-ABNO (**14c**, table 1, entry 5).

The best yield (87%) among the aerobic oxidation procedures was provided by a method based on Pd(OAc)₂/triethylamine in a toluene/THF mixture under oxygen atmosphere (table 1, entry 7).³⁵

 Table 1 Used nitroxyl radicals and tested reaction conditions for the aerobic oxidation of 2 to 12.

		A.	° Ano.		ı–o [:]
	14a	14b	14c	14d	
Entry	Oxidation system		Solv	ont	Conditions
Entry			5017	ciit	(yield, %)
1	14a , NH_4NO_3 , HCl, air		Met	٦N	60 °C, 35 h
1			meen		(0)
2	14a, Cu(OAc) ₂ , air		MeCN	:H ₂ O	r.t., 18 h (0)
3	14a, NaNO ₂ , HBr, air		Me	CN	r.t., 38 h (0)
4	14b , Fe(NO ₃) ₃ ·9H ₂ O, air		Me	CN	r.t., 6 h (60)
5	14c , NaNO ₂ , HNO ₃ , O ₂		Me	CN	r.t., 38 h (40) ^a
6	14d , Fe(NO ₃) ₃ ·9 H ₂ O, O ₂		Me	CN	r.t., 48 h (45)
7	Pd(OAc) ₂ (3 mol%), NEt ₃ (6 mol%), O ₂		PhMe	THF	r.t., 48 h (87)
8	NaOCl (1.2 eq)		AcO	ΟH	r.t., 5 h (98)

^{*a*} full conversion of *cis*-2; *trans*-2 could still be detected by TLC and NMR.

The failure of the nitroxyl radical based methods is suspected to be the result of steric hindrance. As an inexpensive and simple alternative procedure, treatment with NaOCl in acetic acid readily oxidized **2** to **12** in 98% yield on a 10 gram scale (table 1, entry 8).³⁶ The following synthesis of the oxime **13** was conducted with hydroxylamine hydrochloride and sodium carbonate in methanol and water in 96% yield.³⁷ Beckmann-rearrangement with polyphosphoric acid at 55 °C³⁸ provided **5** in 87% yield.

The monomers for the A_2/B_2 -type polyamide, compounds **6** and **7**, could be obtained from alcohol **2** by acidic dehydration and catalytic oxidative cleavage or from ketone **12** by oxidation to yield diacid **6** followed by ammonolysis of the corresponding acyl chloride and reduction to obtain diamide **7** (figure 5).

Direct oxidation of 2 to 6 with tungstic acid and H_2O_2 , with NaOCl under sonication or RuCl₃·xH₂O and Oxone[®] failed. Thus, dehydration was performed by catalytic amounts of sulfuric acid at 150 °C.³⁹ The resulting cyclohexene was then subject to catalytic oxidative cleavage with sodium periodate as the oxidizing agent using RuCl₃·xH₂O as a catalyst.⁴⁰ Through this sequence, **6** could be obtained in 74% yield over two steps. The outcome of this reaction strongly depends on the amount of oxidizing reagent. While the use of two equivalents of NaIO₄ gives the corresponding dialdehyde, three or more equivalents are necessary to obtain the dicarboxylic acid.⁴⁰ Although the use of large amounts of oxidizing reagent is in contrast to the precepts of sustainable chemistry, the periodate could be regenerated from the formed iodate by electrochemical oxidation.⁴¹ Alternatively **12** could be oxidized to **6** in 70% yield using the water soluble and inexpensive Oxone[®], in combination with as little as 0.5 mol% of RuCl₃·xH₂O as a catalyst and water as the solvent.⁴² After conversion of 6 into the acyl chloride with thionyl chloride, ammonolysis with aqueous ammonia provided diamide 15 in 75% yield over two steps.43 This diamide could be reduced to the corresponding diamine 7 either with lithium aluminium hydride (LAH) in MTBE in 71% yield or with borane. THF complex in THF in 74% yield.⁴⁴ The reduction step can still be further optimized to improve its sustainability and e.g.



Figure 6 Anionic ring-opening polymerization of 5 to the corresponding polyamide 16.



Figure 7 SEC result (top left: elution volume, right: molar mass) and MALDI-ToF spectrum (below) A) full spectrum, B) enlarged region (m/z = 2000-4000) of AB-type polyamide 16.

electrochemical reductions⁴⁵ or catalytic hydrogenations⁴⁶ of amides to amines have been developed to this end.

Polymerizations

We have investigated several polymerization/oligomerization methods for **5** (which was previously claimed to be barely polymerizable due to an inhibitory effect of the propyl moiety).^{47, 48} While anionic ring-opening polymerization (AROP) with sodium hydride and *N*-acteyl caprolactam as well as nucleophilic polymerization with octylamine and tin(II) 2-ethylhexanoate did not lead to promising results, AROP with potassium as the initiator and benzoyl chloride as a termination agent worked well (figure 6).⁴⁹

The resulting polyamide **16** is soluble in most organic solvents except for ethereal solvents and chloroform. The yield was diminished due to the volatilization of the monomer **5** at the high temperature and low pressure that were necessary for the polymerization. In order to obtain entirely monomer-free polyamide **16**, dialysis was conducted while washing with hexane/ethyl acetate and water or precipitation in cold diethyl ether did not remove low molecular compounds to a sufficient extent to allow analytical characterization. Characterization of the polyamide thus obtained was performed by SEC, MALDI-ToF-MS and NMR, all of which indicated a successful polymerization. The NMR data show the aliphatic main chain and the terminal benzoyl group (ESI, S45).

Determination of the chain length with the end group analysis method leads to n = 25 and therefore $M_n = 4200 \text{ g mol}^{-1}$ including





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the terminal groups. This is in accordance with the result of the SEC experiment showing a value of 8600 g mol⁻¹ for $M_{\rm w1}$ and 4200 grave I^{-1} for $M_{\rm n}$ with a dispersity (*D*) of 2.05 (figure 7). The high dispersity is ascribed to the bulk polymerization, which leads to quick solidifycation and poor stirring of the mixture. Consequently not all chains can be terminated at the same time after addition of the termination agent. This leads to unequal distribution of the chain length and of the molecular weight. SEC shows a unimodal product distribution.

The MALDI-ToF experiment (figure 7) also shows successful polymerization, but two peak series with the peak distance of the repeating unit (M = 155.13 g mol⁻¹) can be identified. According to our calculations, one series originates from the polyamide with the benzoyl group (M = 105.03 g mol⁻¹) attached to the terminal nitrogen and with a terminal carboxylic acid moiety as a potassium adduct (figure 7, **B**)). The second peak series results from polyamide matrix adducts (HABA-Matrix (M = 242.07 g mol⁻¹), figure 7, **B**)). The MALDI experiment therefore confirms that the benzoyl group is attached to the polyamide and no cyclic polymers were formed. Furthermore, the terminal lactam ring was hydrolyzed to the corresponding amino acid, most probably during the work up of the polymer.

The recorded spectra cannot be used to determine the average molecular weight or dispersity of the polymer since the peak intensity cannot be considered proportional to the abundance (mass discrimination). These properties are rather determined using SEC or NMR experiments.

The thermal behavior of **16** was investigated by differential scanning calorimetry (DSC) displaying a glass transition temperature (T_g) of 15 °C, but no distinct melting point $(T_m, \text{ figure 8})$. The most important factor influencing T_g is the efficiency of hydrogen bonding of the amide group between the polymer chains. As expected, the flexible propyl side chain in **16** reduces the ability to form interchain hydrogen bonds and of effective alignment of the polymer chains in comparison with T_g of Nylon 6 $(T_g = 51 \text{ °C})$.⁵⁰ The substitution increases the flexibility of the polymer.

We have tested several polycondensation methods with derivatives of dicarboxylic acid 6 for the synthesis of A₂/B₂-type polyamides, but neither the activated pentachlorophenyl ester nor the diethyl ester of 6 reacted with 7. On the other hand, polycondensation of the acyl chloride with diamine 7 in N,N-dimethylacetamide (DMAc) in the presence of triethylamine at room temperature worked well (figure 9).⁵¹ Again, the polyamide proved to be soluble in most organic solvents except for ethereal solvents and chloroform. It was also purified using dialysis for analytical characterization. It is suspected that the preceding formation of the acid chloride lowered the yield because it might not have resulted in quantitative conversion, but rather in formation of the cyclic anhydride and therefore leads to a slight excess of diamine although dicarboxylic acid and diamine were used in equimolar amounts. Nevertheless, a moderate yield of 62% of polymer 17 was achieved.



Figure 9 Synthesis of A₂/B₂-type polyamide 17



Figure 10 SEC result (top left: elution volume, right: molar mass) and MALDI-ToF spectrum (below) of A_2/B_2 -type polyamide 17.

The polyamide thus obtained was investigated by SEC, MALDI-ToF-MS and NMR and indicated a successful polymerization. The NMR data show two sets of alkyl side chains as well as two carbonyl groups (ESI, S47-S48). In lack of an end group, the molecular weight could only be determined using SEC (figure 10). This experiment results in values of 3400 g mol⁻¹ for M_n and 6200 g mol⁻¹ ¹ for $M_{\rm w}$ with a dispersity (D) of 1.82. MALDI-ToF data also confirm successful polymerization, but three peak sets with a peak distance of the repeating unit ($M = 310.26 \text{ g mol}^{-1}$) can be identified (figure 10). The most intensive peaks belong to the sodium adduct of the cyclic polymer. The second intensive peak set originates from the corresponding linear polymer 17 (figure 10, sodium adduct). The difference between these two peak sets adds up to $M = 18 \text{ g mol}^{-1}$. The third peak series belongs to a polyamide with two terminal amine functionalities. This polyamide is most probably the result of the acid depletion mechanism outlined above.

Differential scanning calorimetry (DSC) investigations of 17 resulted in a glass transition (T_g) of 28 °C and, as with 16, no distinct melting point was observed (figure 10), which is clearly due to the branched nature of the monomer units. The propyl branches impede crystallization and lead to strong softening, i.e., low T_g of the A₂/B₂-type polyamides compared to the T_g of unsubstituted PA66 ($T_g = 70 \text{ °C}$)⁵² as in the case of the AB-type polyamide. The low T_g is based on the impeded order of the polyamide main chains and conesequently the reduced possibility of hydrogen bonding between the chains. On the other hand, the hydrogen bonding capability of the A₂/B₂-type polyamides, as is manifest in the higher value for T_g of 17 compared to 16. We believe the monomers 5–7 are of interest as a component in other polyamides to reduce melting points and degree of crystallization.

Conclusion

We have successfully established a sustainable synthesis for two colorants, the indigo dyes 3 and 4, as well as for the polyamide monomers 5-7 along with the respective polymers from the xylochemicals vanillin (1) and 4-propylcyclohexanol (2). 6-

Nitroveratraldehyde (9), available from vanillin in two steps, was transformed to 3 along two different routes. Baeyer: Drewsen indigo synthesis with acetone and NaOH²² provided 3 with low yield in a single step, whereas the two-stage synthesis using a catalytic Henryreaction and subsequent reduction provided 3 with an overall yield of 89% over three steps. Both sequences were conducted without using organic solvents and extensive purification. Cleavage of the methyl ether moieties of 3 yielded tetrahydroxy-indigo 4. Starting from the xylochemical 4-propylcyclohexanol (2), the polyamide monomers 5-7 were synthesised in moderate to high yields using methods of green chemistry. Lactam 5 was produced in 93% yield over three steps using a sequence of catalytic aerobic oxidation of 2 followed by oxime synthesis and Beckmann-rearrangement. The A₂/B₂-type polyamide monomers were obtained by acid catalyzed elimination of 2 followed by catalytic oxidative olefin cleavage or by direct oxidation of 12 to obtain 6 in 74% or in 84% over two steps, respectivley. Subsequent formation of the acid chloride of 6, ammonolysis and reduction provided the diamine 7 in 63% over five steps. Polymerization of these monomers was achieved using anionic ring-opening polymerization for 5 and polycondensation for 6 and 7, leading to polyamides with unusual properties. The xylochemistryderived monomers could also be used for copolymerization to tune the aggregation behavior of classical polyamides. In summary, sustainable and straightforward synthetic procedures of functional materials like colorants and polymers were established that could potentially substitute petroleum based methods and products. All carbon atoms in the products originate from renewable resources.

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