TUTORIAL REVIEW

Applications of xylochemistry from laboratory to industrial scale

Jonathan Groß,† Jonas Kühlborn† and Till Opatz [ID] *

Xylochemicals and their utilisation in total synthesis and industrial applications are highlighted in this review. This class of chemicals consists of bio-based molecules or building blocks derived from renewable feedstocks like plant-biomass, lignocellulose as well as waste-streams. The advantages over petroleum-based chemicals are presented with the aid of specific examples ranging from the total synthesis of natural products, relevant industrial applications to the exploitation of CO_2 as a C_1 feedstock. This review contributes to the trend of a "greener" and a more sustainable chemistry.

1. Introduction

Xylochemicals are synthetically valuable organic building blocks derived from renewable lignocellulose or other fractions of woody biomass and therefore theoretically CO_2-neutral.[1,2] Apart from an often useful degree of oxygenation, some xylochemicals also retain stereochemical information, which can be exploited for subsequent synthetic purposes.[3] In contrast, petroleum-based chemicals have lost the majority of the formerly contained heteroatoms during the process of kerogenesis[4] so that desired functionalities need to be reinstalled in often resource-intensive sequences.[5,6]

Lignocellulose is the most abundantly available type of biomass on planet earth. More precisely, agricultural waste products such as corn stover or rice husks, wood-waste streams *e.g.* wood processing residues like stalks and wood chips or municipal plant waste as well as switchgrass as ground cover for soil conversion, constitute promising renewable feedstocks for biofuels and platform chemicals.[3,7,8] Food supply chain waste streams (*e.g.* apple pomace,[9] brewer's spent grain[10] or waste frying oil[11]) are also abundant, readily available, and still contain valuable and functionalized compounds like antioxidants, carbohydrates or phenolics, which can be exploited for the production of chemicals.[12–15]

Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10–14, 55128 Mainz, Germany. E-mail: opatz@uni-mainz.de

† These authors contributed equally.

Jonathan Groß obtained his Bachelor's (2017) and Master's degree (2018) in Chemistry from the Johannes Gutenberg-University Mainz studying natural product synthesis and the valorization of renewable resources for the synthesis of functional materials. He is currently a graduate student in the group of Professor Till Opatz since 2019. In 2016/7, he spent six months with Professor Doug Stephan at the University of Toronto, Canada, researching on new frustrated Lewis-pairs for the activation of small molecules. His research interests are green chemistry and using computational chemistry for structure elucidation.

Jonathan Groß

Jonas Kühlborn obtained his Bachelor's (2014) and Master's degree (2016) in Biomedical Chemistry from the Johannes Gutenberg-University Mainz studying natural product synthesis and the valorization of renewable resources for the synthesis of functional materials. He is currently a graduate student in the group of Professor Till Opatz since 2016. In 2018, he spent four months with Professor Charles de Koning at the University of the Witwatersrand, Johannesburg, researching on the utilization of cashew nut shell liquid for organic synthesis. His research interests are green chemistry and total synthesis based on biomass-derived molecules.

Jonas Kühlborn
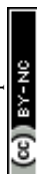
In the context of renewable feedstocks, a major benefit for the chemical industry was the switch from first to second generation biofuels. First generation fuels rely mainly on alcohols (bioethanol) and oils (biodiesel) which are available through well understood technologies for processing food crops, while for the second generation biofuels, non-edible feedstocks such as lignocellulose biomass or algae crops are utilised.[8,16] The limited or absent interference with the food and feed industry solved the so-called food *versus* fuel debate and the ethical problems associated with it.[17–19]

There are several approaches to produce platform chemicals or synthesis gas from biomass which have already been well-presented in the current literature (including both biorefinery concepts as well as chemical processes).[13,20–23] For these procedures, the pre-treatment of biomass proved crucial to achieve an efficient conversion or processing due to the complex structure of lignocellulose. A suitable pre-processing is highly dependent on the source of feedstock and can be performed biologically, chemically, thermally or mechanically (detailed information can be found in the cited literature).[13,24,25]

Prominent examples of xylochemical platform chemicals are vanillin (**1**),[26–28] the sugar alcohols sorbitol (**2**), xylitol (**3**) and mannitol (**4**)[29] or furfural (**5**).[30] These compounds can be upgraded to more advanced platform chemicals like levulinic acid (**6**),[31–33] succinic acid (**7**),[34,35] furan-2,5-dicarboxylic acid (**8**),[36,37] itaconic acid (**9**),[36] 5-(chloromethyl)furfural (**10**, CMF),[38] 5-(hydroxymethyl)furfural (**11**, HMF)[39–42] or γ-valerolactone (**12**) (Fig. 1).[43] For further examples of biomass conversion into value-added products, the reader is referred to the existing literature.[44–49]

The mentioned waste streams and raw materials result in platform chemicals, all carbon atoms of which are wood-based and hence renewable on a short timescale.[1] With these xylo-
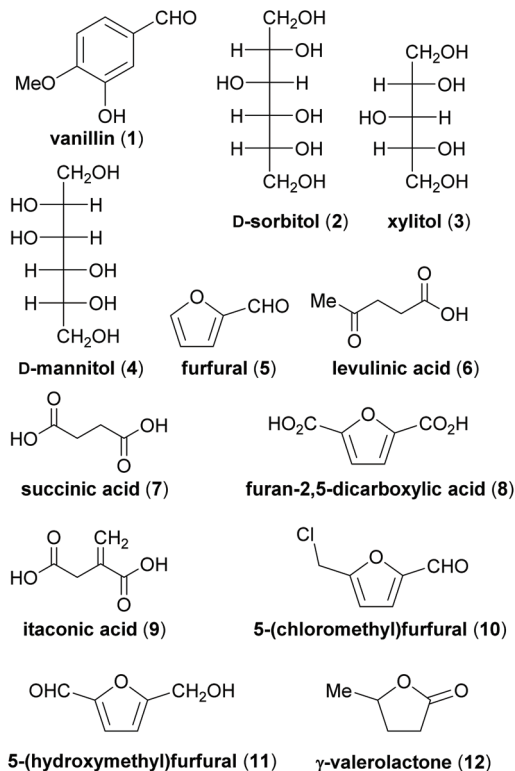

Fig. 1 Examples of xylochemical platform chemicals.

chemical platform chemicals (or xylochemicals), the synthesis of functional materials as well as natural products[50] can be the basis of processes with an improved carbon footprint and ideally with little or even no input of fossil carbon. While the complete re-engineering of process cascades for the sake of environmental production and to avoid the increasing costs of fossil fuels is one option, xylochemical routes to valuable intermediates already integrated in today's value chains might be a more convenient first step towards a sustainable chemical economy.[51]

In the present review, selected examples of the synthesis of natural products as well as of functional materials are presented to illustrate the application of the above-mentioned options for eco-friendly synthesis.

Till Opatz

Till Opatz is currently a Professor of Organic Chemistry at the Department of Chemistry, Johannes Gutenberg-University, Mainz, Germany. After receiving his diploma in 1997 with Professor Johann Mulzer at the Goethe-University Frankfurt, he obtained his doctorate with Professor Horst Kunz at the Johannes Gutenberg-University Mainz in 2001. After a postdoctoral stay with Professor Rob Liskamp at the University of Utrecht (Netherlands), he completed his Habilitation in 2006 at Johannes Gutenberg-University Mainz. In 2007, he was appointed associate and later full Professor at the University of Hamburg and returned to Mainz in 2010. His research interests are method development, natural products, and sustainable chemistry.

2. Examples of xylochemistry

2.1. Total synthesis of natural products

2.1.1. (–)-Thebaine. Opatz, Waldvogel and Schäfer *et al.* have developed an enantioselective total synthesis of (–)-thebaine ((–)-**13**) *via* a regioselective intramolecular anodic coupling of a laudanosine derivative **14** in an undivided constant-current setup (Scheme 1).[52,53] The desired 4a-2′-coupling was achieved with a 3′,4′,5′-trioxygenated laudanosine derivative **14** possessing an unsymmetrical substitution pattern which was synthesised from the three xylochemicals methanol, homoveratrylamine (**15**), and methyl gallate (**16**).[54–56]
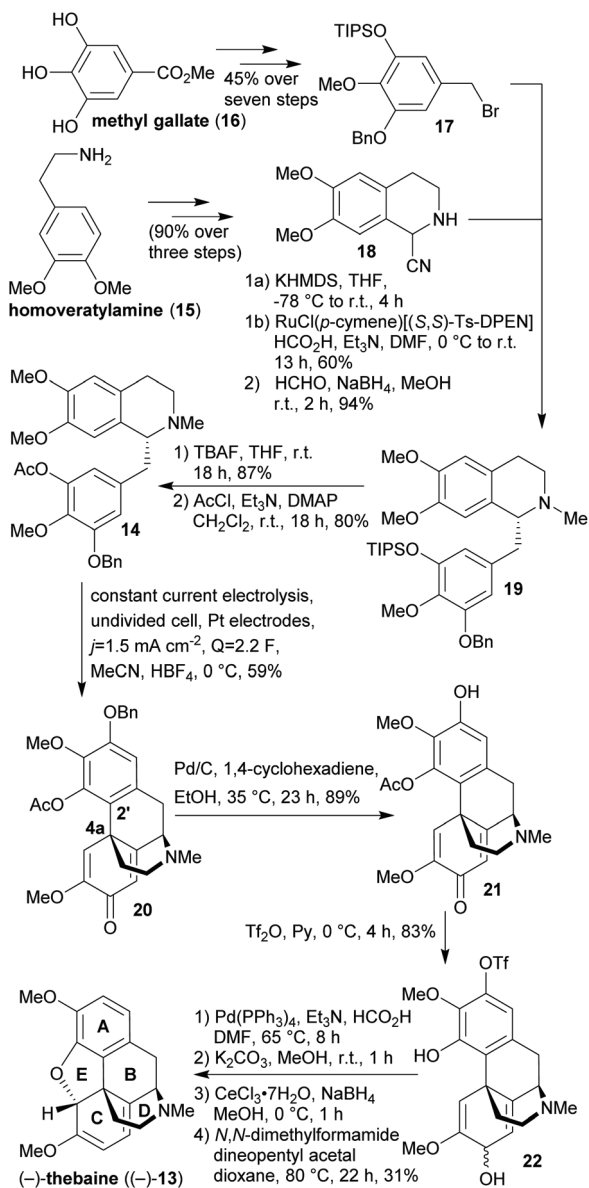
Scheme 1 Total synthesis of (−)-thebaine ((−)-**13**) from xylochemicals (DPEN = diphenylethylene diamine, TBAF = tetrabutylammonium fluoride).

The electrochemical approach is a sustainable alternative to the conventional approach of using partly toxic or harmful stoichiometric oxidants such as $VOCl_3$,[57] thallium tris(tri-fluoroacetate),[58] manganese dioxide[59] or potassium ferricyanide[60,61] for the aryl–aryl coupling of reticuline-type scaffolds. Every carbon and oxygen atom in (−)-thebaine ((−)-**13**) can be derived from woody biomass in the present synthesis. Furthermore, tetrahydroisoquinoline **18** was prepared in three steps from **15** according to known procedures without chromatographic purification.[62–64] The iodomethane required for the O-methylation of methyl gallate (**16**) can be obtained by reacting methanol ("wood spirit") with hydrogen iodide.[65] For the conversion of homoveratrylamine (**15**) into 6,7-dimethoxy-

3,4-dihydroisoquinoline (not shown), formic acid is required which is accessible via a biorefinery process.[23] Formaldehyde, which is employed in the reductive alkylation reaction leading to **19**, can e.g. be obtained by the rapid pyrolysis of milled wood lignin.[66] Unfavourable aspects in the light of "green" chemistry are the switching and the general use of protecting groups as well as the use of several undesired solvents and reagents. Moreover, the majority of the chemicals employed in the synthesis are conventional and hence petrochemistry-based. In a very similar sequence, the same group managed to synthesise (−)-oxycodone (not shown)[67] while its "non-natural" enantiomer (+)-oxycodone (not shown) was prepared by the Hudlický lab in an enzyme-catalysed approach, in which all carbon atoms are derivable from renewable resources and employing several "green" solvents. Yet, petrochemistry-derived protecting groups as well as toxic reagents were used in the latter synthesis, too.[68]

2.1.2. Ilicifoline B. In 2015, Opatz et al. published the first total synthesis of ilicifoline B (**23**), a dimeric berberine-type alkaloid first isolated from *Berberis ilicifolia* (Scheme 2).[1,2,69]
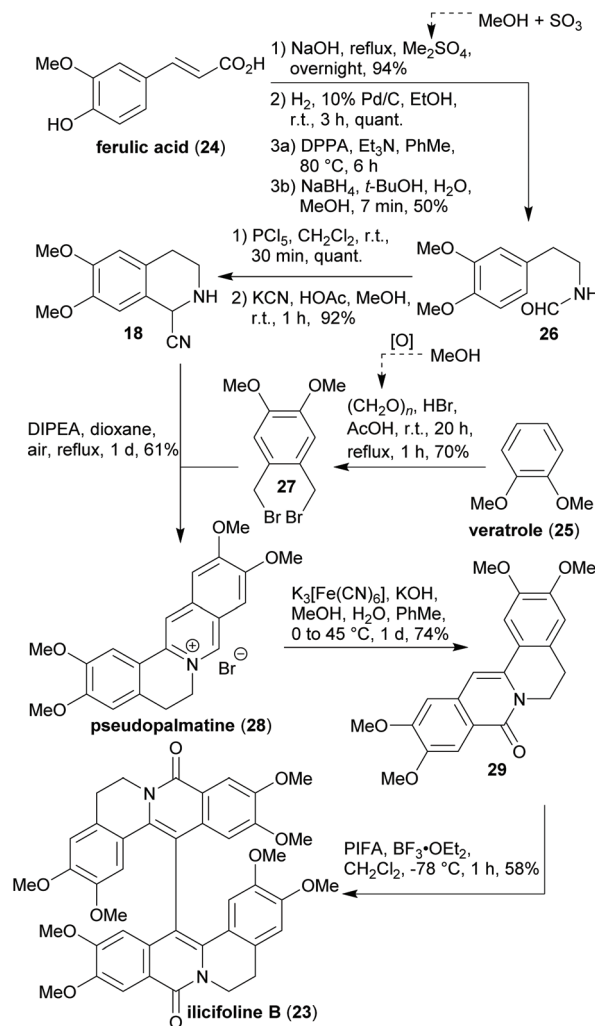
Scheme 2 Total synthesis of ilicifoline B (**23**) (DPPA = diphenyl phosphoryl azide, PIFA = [bis(trifluoroacetoxy)iodo]benzene).

All of the carbon atoms in the product were derived from sustainable sources. The oxygenation pattern of the starting aromatic residues was preserved throughout the sequence.[1,2] The starting materials, ferulic acid (24) and veratrole (25), are available from wood or other types of biomass.[70,71] The employed reagents, dimethyl sulfate for the O-methylation of the phenolic hydroxy group of 16, and formaldehyde for the double bromomethylation of veratrole (25), can be directly obtained from methanol.[66,72,73] The authors used the solvents MeOH, H$_2$O, EtOH and toluene, which are classified as benign according to the principles of "green" chemistry.[74] Moreover, toluene is available through hydrodeoxygenation of lignin[75] while ethanol can be prepared by fermentation from sugars available by catalytic hydrolysis of cellulose and hemicelluloses.[8] Yet, the use of undesired solvents such as dichloromethane should generally be avoided. Also, a switch to a non-toxic cyanide source (e.g. potassium ferricyanide)[76,77] would have been welcome.

2.1.3. Aminophenoxazinones. Veratraldehyde (30) was also utilised by Opatz et al. as a building block in their xylochemical synthesis of 2-aminophenoxazinone-type natural products.[78] Aldehyde 30 can either be isolated directly from woody biomass[79,80] or be obtained by O-methylation of vanillin (1) with dimethyl sulfate[81] (xylochemical, vide supra).[73] The conventional oxidative synthesis of these interesting compounds from o-aminophenols requires the stoichiometric use of strong oxidants which generally lead to decreased yields due to the lack of selectivity. The authors therefore opted for a "greener" method with higher selectivity for the oxidation of the 2-aminophenol starting materials 31–36 to avoid the formation of undesired products. This should allow a selective cross coupling when two different o-aminophenols were deployed. A combination of the mild, eco-friendly oxidant H$_2$O$_2$ with the electron rich 4,5-dimethoxy-2-aminophenol (31) was found to provide optimum results. The latter could be synthesised from 30[82] and was reacted with various less electron rich o-aminophenols 31–36 which are also derivable from renewable sources to produce the respective natural products or intermediates 37–39 (Table 1). The only "waste" products of this method are methanol and water.

With this method, the natural products peristrophine (37), questiomycin A (38), maroxazinone (39) as well as 2-amino-6-hydroxy-3H-phenoxazin-3-one (40) could be synthesised in generally high overall yields. The hydroxy derivative 41 served as an intermediate for the synthesis of chandrananimycin A (43), which was obtained by acetylation and subsequent ester cleavage (Scheme 3A). Exfoliazone (44), viridobrunnine A (45) and venezueline E (46) were synthesised from 42 by N-acetylation, deprotection and esterification (Scheme 3B). Since aminophenoxazinones are known for their biological activities and particularly for their cytotoxicity, the synthesised natural products were subjected to an MTT viability assay with HeLa cells in which they showed promisingly low IC$_{50}$ values from 8.87 to 23.65 μM.

2.2. Dyes

The production of dyestuffs was one of the key driving forces for industrial scale synthetic organic chemistry and began with

Table 1 Results and conditions of the key oxidative coupling in the synthesis of 2-aminophenoxazinone natural products by Opatz et al.

| #	Starting material	R^1	R^2	R^3	R^4	Product, %
1	31	H	OMe	OMe	H	37, 98
2	32	H	H	H	H	38, 100
3	33	H	H	CO$_2$Me	H	39, 66
4	34	OH	H	H	H	40, 14
5	35	H	H	H	OH	41, 76
6	36	H	H	CH$_2$OTHP	H	42, 91
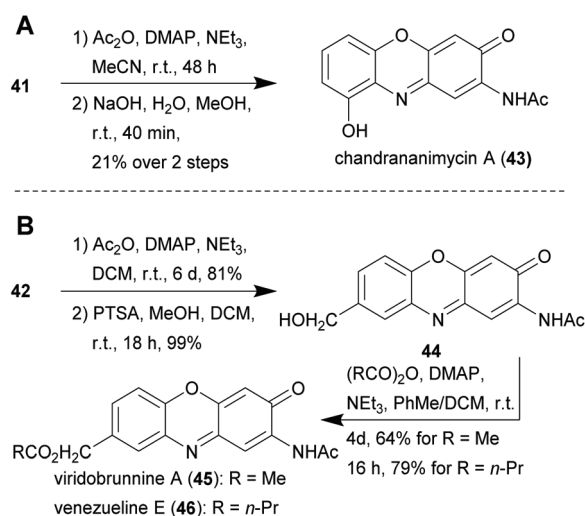
Scheme 3 Synthesis of chandrananimycin A (43) from 41 (A) as well as exfoliazone (44), viridobrunnine A (45) and venezueline E (46) from 42 (B).

Perkin's synthesis of mauveine.[83] The structure elucidation and first total synthesis of indigo by von Baeyer[84–86] in the second half of the 19th century is another highly important milestone. On the other hand, the advent of synthetic dyestuffs boosted the use of fossil carbon sources like coal tar and later petroleum by the chemical industry. With increasing production volumes, petrochemical starting materials became indispensable for the manufacturing of most chemical products.[87,88]

The increasing depletion of these resources challenges today's scientists to develop new routes to known dyestuffs based on renewable starting materials and to search for novel dyes that can be produced in a more sustainable fashion as potential substitutes for the materials currently in use. In search for a xylochemical approach, the Opatz lab investigated the synthesis of the indigo derivatives 5,5′,6,6′-tetramethoxyindigo (47) and 5,5′,6,6′-tetrahydroxyindigo (48).[89]
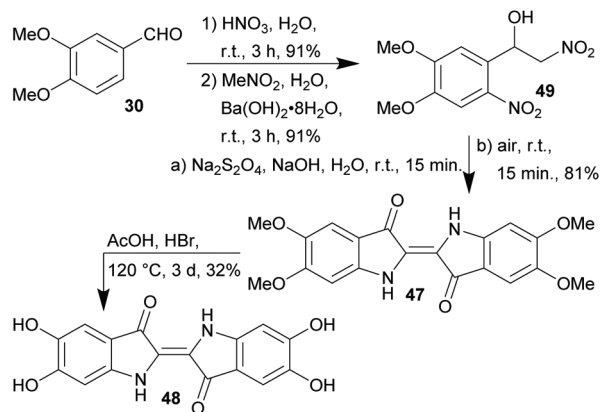
Scheme 4 Synthesis of indigo-type dyes by Opatz *et al.*

In a three step sequence, **47** was synthesised starting from veratraldehyde (**30**)[79] and nitromethane (available from methanol)[90] in 69% yield without the use of an organic solvent at ambient temperature (Scheme 4). This short and eco-friendly approach furthermore bears the advantage that the reductive cyclization in the last step of the synthesis of **47** directly yields a solution of the (reduced) leuko-form suitable for vat dyeing of any natural fabric without prior isolation of the dyestuff itself. Furthermore, all carbon atoms incorporated in the product were obtained from renewable starting materials.

The group of Mascal presented a sustainable synthesis of butenolide colorants based on bio-derived starting materials.[91] For this approach, they utilised the carbohydrate-derived, versatile renewable platform molecule 5-(chloromethyl)furfural (**10**, CMF) as well as the related angelica lactone (**50**, AL) which can also be prepared from CMF (**10**).[38] Condensation of lactone **49** with aldehyde **10** or with 2,5-diformylfuran (**51**, DFF) or vanillin (**1**) in 1,4-dioxane with Mn_2O_3 as a catalyst gave the butenolide dyes **52–54** in high yields of 87%, 82% and 85%, respectively (Table 2, entries 1a, 4 and 5). While DFF (**51**) is also accessible from carbohydrates,[92] vanillin (**1**) is a prime example of a lignin-derivable starting material and numerous methods for its preparation through lignin depolymerisation have been developed.[28,93–95] Although 1,4-dioxane is a less favourable solvent in terms of sustainability,[96] the superiority of these conditions in terms of chemical yield might justify its use. Other solvents caused side reactions which decreased the yields significantly or led to different products. The yield of **52** dropped to 22% in water with $BaCO_3$ due to predominant hydrolysis of AL **50** (Table 2, entry 1b), whereas the reaction of **50** with **51** in water without any additive produced the monocondensation product **55** in only 28% yield (Table 2, entry 3). Switching the solvent to ethanol gave the respective ethyl ether **56** through chloride displacement in 85% yield (Table 2, entry 2).

Both approaches to sustainable colorants not only relied exclusively on starting materials from renewable resources but also were devoid of extensive purification operations which are usually cost- as well as material-intensive and increase the

Table 2 Synthesised butenolide dyes **52–56** and conditions by Mascal *et al.*

#	R^1	Conditions	R^2
1	ClH₂C (**10**)	(a) 1,4-Dioxane, H_2O, Mn_2O_3, reflux, 2 h (b) H_2O, $BaCO_3$, reflux, no **49**	HOH₂C **52**, a) 87%, b) 22%
2	ClH₂C (**10**)	EtOH, Mn_2O_3, reflux, 1.5 h	EtOH₂C **56**, 85%
3	OHC (**51**)	H_2O, 80 °C, 1 h	OHC **55**, 28%
4	OHC (**51**)	1,4-Dioxane, Mn_2O_3, reflux, 2 h	**53**, 82%
5	MeO/HO (**1**)	1,4-Dioxane, Mn_2O_3, reflux, 14 h	MeO/HO **54**, 85%

environmental burden of a given process.[97] All intermediates and products could instead be separated by simple extraction or filtration.

2.3. Polymers

While the valorisation of lignin for applications in polymer chemistry (composites, carbon nanofibers or dispersing agents) is a highly active research field,[98–101] several pure bulk chemicals obtained from lignocellulose have also been successfully applied for future polymer production (*vide infra*).[37,102]

2.3.1. Polyamides. A rather unusual but also one of the longest known xylochemicals, 4-propylcyclohexanol (**57**),[103] was used by Opatz *et al.* for the synthesis of polyamides as xylochemical counterparts of nylon-6 and nylon-6,6 (its monomer lactic acid (**64**) can be obtained *via* fermentation of pure carbohydrates, corn or sugar beets).[89,104] Polyamides currently belong to the most popular chemical consumer products but are also tightly linked to classical petrochemistry. Therefore, there is an urgent need for eco-friendly alternatives.[105–109] The xylochemical approach regarding the starting materials of Opatz *et al.* was complemented using sustainable methods and solvents throughout the syntheses (Scheme 5).

The key intermediate for the synthesis of the monomers for both types of polyamides was 4-propylcyclohexanone (**58**), which was synthesised by Pd-catalysed aerial oxidation of **57** in 87% yield. From there on, the respective ε-lactam **59** was synthesised through oxime formation and Beckmann rearrangement with neat polyphosphoric acid in 84% over two steps.
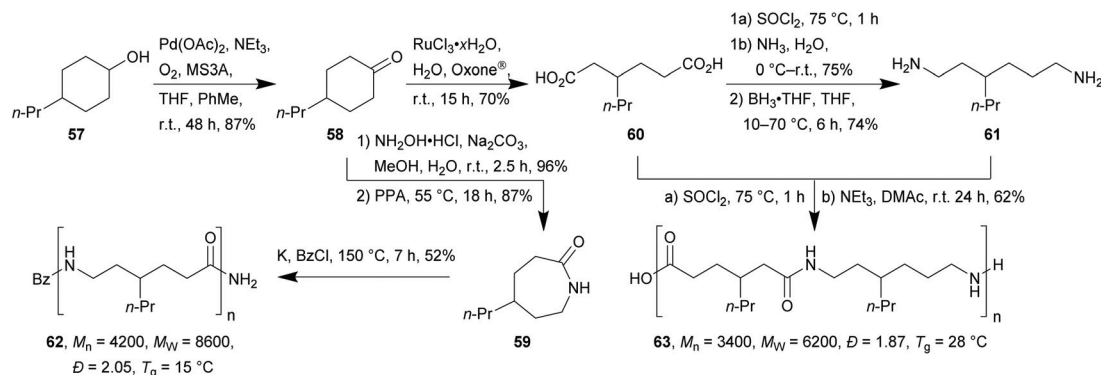
Scheme 5 Synthesis of polyamides **62** and **63** from xylochemical **57** by Opatz *et al.*

The monomers for the dipropyl analogue of nylon-6,6 polyamide, diacid **60** and diamine **61**, were synthesised by catalytic oxidative C–C-bond cleavage of **58**, subsequent conversion to the diamide followed by reduction of the latter to yield **61**. For the implementation of this step on a laboratory scale, the unfavourable borane–THF complex was used as the stoichiometric reducing agent. As an ecologically more acceptable alternative the Ru/triphos hydrogenation reaction developed by Beller *et al.* could be employed.[110]

Polymerisation of the respective monomers by means of an anionic ring opening polymerisation for **59** and polycondensation in the case of **60**/**61** led to xylochemical, propyl-functionalised versions of nylon-6 and nylon-6,6 with reasonable dispersity in moderate yields of 52% and 62%, respectively. Both resulting polymers show unusually low glass transition temperatures (T_g) of 15 °C in case of polylactam **62** and 28 °C for A_2B_2-type polyamide **63**.

2.3.2. Polylactic acid. Polylactic acid (PLA) is currently the most promising polymer available from renewable resources.[111,112] Its monomer lactic acid (**64**) can be obtained *via* fermentation of carbohydrates, corn or sugar beets.[104]

Biodegradation is not an inherent property of polymers, just because their monomers can be obtained from biomass. PLA however shows excellent biodegradability and decomposes only to H_2O, CO_2 and humus.[113,114] PLA finds application in biomedical-devices, coatings, 3D printing, fibres and packagings.[113,115,116]

Lactide (**65**), the dimeric self-condensation product of lactic acid (**64**), can also be used as a building block for polymerisations. Its ring-opening polymerisation (ROP) is one of the most promising synthetic methods (Scheme 6).[117,118]

Dependent on the relative configuration of the starting material (*i.e.* whether the *meso* lactide or the racemic mixture of (R,R)- and (S,S)-lactide is used), a variety of PLA structures (atactic, isotactic, heterotactic and syndiotactic) can be obtained, (**A** and **B**), which differ in their materials properties.[119–121] Companies (*e.g.* NatureWorks LLC) are already producing biobased polylactide polymers on an industrial scale (nameplate capacity of 150 000 t per year)[122] and have performed life cycle assessments as well as ecoprofile
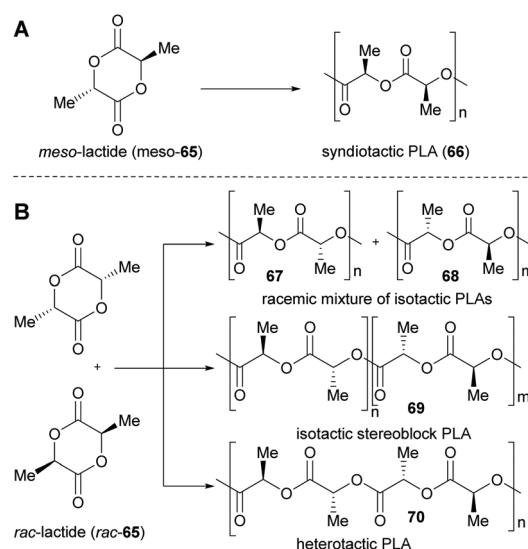

Scheme 6 Polymerisation of *meso*-**65** (A) and rac-**65** (B) to different PLA structures **66–70**.

investigations.[123,124] Furthermore, industry is currently assessing new technologies to use microorganisms to convert CO_2 and methane into lactic acid.[125,126]

2.3.3. CO_2 as C_1-feedstock. CO_2 is a cheap, nontoxic, and extremely abundant C_1 feedstock.[127,128] Since it acts as greenhouse gas and is believed to be a major contributor to the recent change of the global climate, the utilisation of CO_2 for synthetic purposes is highly desirable. The fixation and valorisation of CO_2 has triggered many research initiatives and has resulted in numerous examples in the literature (Scheme 7A–C).[129–131] Yet, the overall CO_2-balance including the consumed energy ultimately needs to be taken into account.

The copolymerisation of CO_2 and an epoxide (*e.g.* propylene oxide (**71**)) with organometallic catalysts (*e.g.* Et_2Zn) at ambient temperature was discovered in the 1960s by Inoue *et al.*[132] This opened up an alternative route to the phosgene process for the production of polycarbonates, which suffers from environmental and safety problems due to the involvement of the highly toxic and corrosive $COCl_2$.[133]
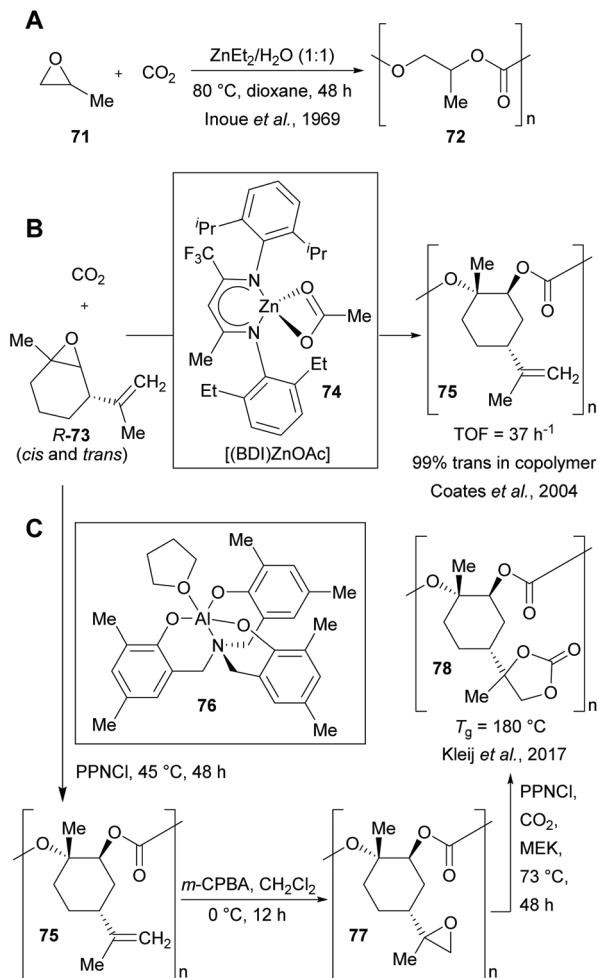
Scheme 7 Copolymerisation of CO_2 with propylene oxide (**71**, A) or (R)-limonene oxide ((R)-**73**) (B and C). ([(BDI)ZnOAc] (**74**) = β-diiminate zinc acetate complex, turnover frequency (TOF) = mol **73** (mol Zn)$^{-1}$ h^{-1}), PPNCl = (bis-triphenylphosphine iminium chloride).

In 2004, Coates et al. developed the alternating copolymerisation of CO_2 with (R)-limonene oxide ((R)-**73**, mixture of cis- and trans-diastereomer) to give a highly regio- and stereoregular, biodegradable polycarbonate.[134] Epoxide **73** is derived from limonene, the most common terpene (produced by >300 plant species) and major component of oils from citrus peels.[135,136] The Kleij lab is also very active in the field of CO_2/terpene epoxide copolymerization.[137–139]

2.3.4. Cyclic lactones. Renewable, cyclic alternatives to methyl methacrylate (**79**, MMA, Scheme 8A) are vinylidene lactones like α-methylene-γ-butyrolactone (**80**, MBL, Scheme 8B) or its methyl derivate γ-methyl-α-methylene-γ-butyrolactone (**81**, MMBL, Scheme 8B).[121,140] The former monomer is also known as tulipalin A due to its natural occurrence in tulips,[141,142] while the latter monomer can be obtained from biomass derived levulinic acid (**6**) and formaldehyde.[140]

PMMA (**82**)[143] is widely used as a substitute for glass[144] as well as for biomedical-,[145] sensor-,[146] or nanotechnology[147] applications. PMBL (**83**) can be used for high temperature
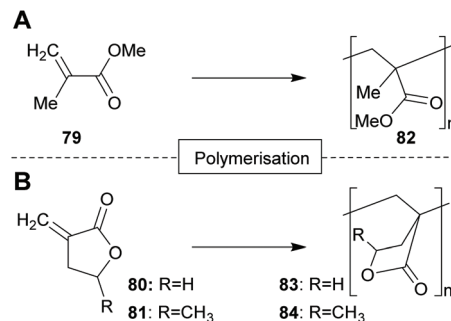
Scheme 8 Polymerisation of MMA **79** (A) vs. MBL **80** and MMBL **81** (B).

applications, due to its high thermal stability and the very high glass transition temperature.[148] PMMBL (**84**) possess a higher glass transition temperature than PMMA (**82**) and exhibits excellent resistance to common organic solvents.[149,150]

Another emerging platform chemical available from renewable resources is succinic acid (**7**). It can be produced by micro-organisms via an anaerobic conversion under consumption of CO_2.[151] Untreated whey, wood hydrolysate or corn steep liquor can be used as the raw material for this process.[152,153] Succinic acid (**7**) can either be transformed into commodity or fine chemicals,[39,40,154] or serve as a building block for the synthesis of poly(esteramides), polyamides or polyesters.[151,155,156] Its derivatives are also used in compositions for lubricants or as fuel additives.[157–159]

2.4. Oils and fatty acids

Another compound class suitable for the preparation of biodegradable polymers with industrial applications are fatty acids and plant oils, which can also be regarded as xylochemicals.[160–162] Vegetable oils from soy, rapeseed, cotton, peanut, sunflower, ricinus, olive, and coconut as well as tall oil, a side stream from wood pulping, are important sources for renewable raw materials. They are widely used for the production of surfactants, paint formulations, flooring materials, cosmetic products, and lubricants.[121,163–165] The mostly found fatty acids in the nature (stearic acid (**85**), palmitic acid (**86**), oleic acid (**87**), linoleic acid (**88**), linolenic acid (**89**) and ricinoleic acid (**90**)) are present as triglycerides in vegetable oils.[163,165]

Unsaturated fatty acids and vegetable oils can undergo various oxidation reactions like epoxidation-, bishydroxylation- or carbon–carbon-bond cleavage reactions.[166,167] For the formation of C–C-bonds, pericyclic-,[168] ionic-[169] and radical[170,171] reactions can be employed. Olefin metathesis reactions in lipids were first observed by a homogeneous WCl_6/Me_4Sn catalyst,[172] but can more conveniently be performed with well-known ruthenium catalysts.[173,174] This type of reaction was improved by Gooßen et al. by developing a bifunctional catalyst system consisting of a dimeric palladium(I) complex for a double-bond migration and a ruthenium complex for the olefin metathesis. With this system, fatty acids and esters can be transformed into olefin mixtures with controllable chain

length distributions adjustable in their mean and span.[175] These kinds of blends were tested as additives for biodiesel[176] or as building blocks in polymerisation reactions[177,178] and represent interesting recent examples of the integration of oleochemicals into the chemical value chain. The group of Biermann reported a protocol for the transesterification of calendula oil and tung oil with alcohols such as methanol, ethanol or isopropanol. The respective esters were then tested in coating formulations as reactive diluents for alkyd resins.[179] Conventional diluents are volatile organic compounds (VOCs) which are added to lacquers or resins to reduce their viscosity and evaporate during the drying process. In contrast, reactive diluents participate in the cross-linking process and remain in the resin while influencing the viscosity as well as the physical properties after curing.[180] The substitution of volatile organic solvents by reactive diluents is also reducing the emission of volatile substances into the atmosphere.[181] Mixed canola oil esters using methanol, ethanol or a mixture of both were synthesized by Dalai et al. for the use as lubricity additives for diesel fuels in order to compensate for the reduced sulphur content required by the authorities.[182]
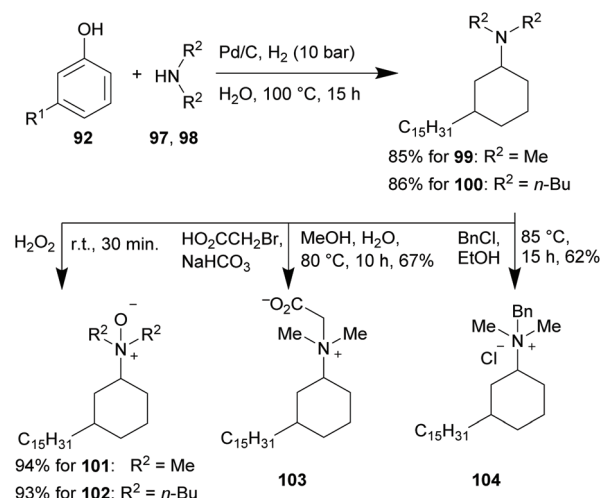
2.5. Surfactants

2.5.1. Cashew nut shell liquid. Cashew nut shell liquid (CNSL) is a sustainable, nonedible feedstock, which is recently gaining attention and application in various areas. The annual production of cashew nuts in 2017 added up to 3.97 million metric tons and they can therefore be seen as a major agricultural product.[183] Whereas the nut itself is the desired product for consumption, the shells usually end up as compostable waste or are incinerated for energy production. On the other hand, the cold ethanol extract of this waste product delivers the cashew nut shell liquid itself which stands out for its high content of up to 95% of pentadecyl(ene) substituted phenolics, namely anacardic acid (**91**), which makes up to 70%, cardanol (**92**) and cardol (**93**, Scheme 9A).[184–187] These unique compounds found use in natural product synthesis,[188] fuel research,[189] polymer chemistry,[190–192] and the synthesis of fine chemicals.[193–195] Furthermore, the pentadecyl moiety is interesting for the design of functional materials where lipophilicity is desired.

Based on this idea and the surface-activity of sodium anacardate already discovered in 1958,[196] various surface-active compounds have been derived from cardanol (**92**). Five decades later, the groups of Bullón and Roengsumran synthesised anionic surfactants in the form of sodium 2-O-cardanyl acetate (**94**)[197] and sodium cardanol sulfonate (**95**),[198] respectively (Scheme 9B). The Gooßen group prepared a variety of 3-pentadecylcyclohexyl-substituted surfactants in the form of betaines, N-oxides and quaternary ammonium salts from technical CNSL in a straightforward, eco-friendly fashion (Scheme 10).[199]

The respective cardanol-derived tertiary amine intermediates (**99–100**) were produced in a one-pot phenol hydrogenation to the corresponding cyclohexanone and a subsequent reductive amination sequence in aqueous solution. Moderate
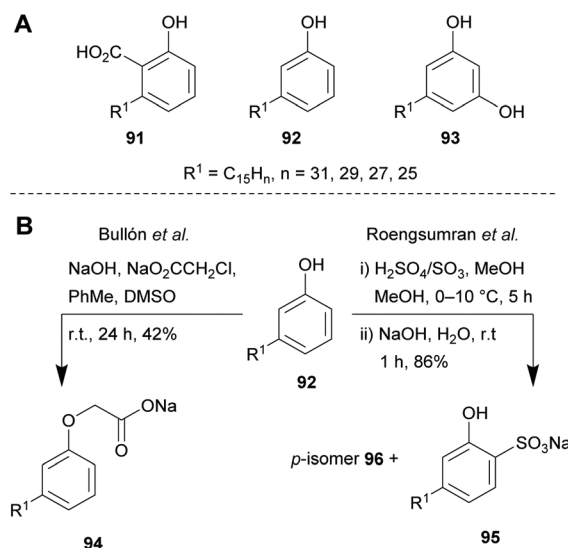
Scheme 9 Constituents of CNSL (A) and syntheses of anionic surfactants **89** and **90** (B).

Scheme 10 Synthesis of cyclohexyl based surfactants from cardanol (**87**) by Gooßen et al.

to high yields with an exceptionally low E-factor of 1.99 (4.84 with water included) in the case of **99** were achieved. The E-factor is specified as the mass ratio of the total waste produced and the product formed.[200,201] The N-oxides **101** and **102** were synthesised in an equally green fashion by reacting **99** and **100** with aqueous hydrogen peroxide at ambient temperature in yields of 94% and 93%, respectively. Furthermore, **101** could also be synthesised in a two-step, one-pot sequence starting from **92** with a yield of 71%. Betaine **103** and quaternary ammonium salt **104** were produced by standard procedures from **99** with moderate yields of 67% and 62%, respectively.

2.5.2. Carbohydrates. The group of Palkovits[202] opted for the synthesis of anionic surfactants from the (hemi)cellulose-derivable dialcohols cyclopentanediol (**105**, CPD),[203] 2,5-bis

(hydroxymethyl)furan (**106**, BHMF), 2,5-bis(hydroxymethyl)-tetrahydrofuran (**107**, BHMTHF)[204] as well as fatty acid-based 1-dodecanol (**108**)[205] and tetradec-1-ene (**109**).[206–208] The key step of this approach was the acid-catalysed etherification of the diols with the respective fatty alcohol and olefin. Subsequently, the second hydroxy group was converted into a sulfate monoester by reaction with pyridine–SO_3 (Scheme 11). Although the yields of the etherification step were low and high temperatures were necessary throughout the sequence, these novel surfactants were constructed entirely from starting materials derived from sustainable carbon sources. This step was conducted under catalytic conditions using either 5 mol% of sulfuric acid or 5 wt% of the cation exchanger Amberlyst® 15 or the zeolite beta H-BEA 150. Furthermore, the reactions could be performed in a favourable solvent or even in a solvent-free fashion.

The presented etherification approach is very eco-friendly as water is the only by-product.

Comparison of the surface-activity properties of the cardanol- and carbohydrate-derived surfactants with sodium dodecylbenzenesulfonate (SDBS, **114**), one of the most widely used and potent surfactants proves the exceptional potential of these biomass-based compounds (Table 3). Their values for

Table 3 Surface-activity properties of cardanol derived surfactants and SDBS (**109**)

Compound	CMC (μmol L^{-1})	Surface tension at CMC (mN m^{-1})
94	830	29.2
95	372 000	32.3
101	28	*ca.* 35
103	10	*ca.* 31
104	5	*ca.* 41
110	349	3.5
112	124	4.0
113	255	4.2
SDBS (**114**)[212]	2000	*ca.* 31

the critical micellar concentration (CMC) as well as for the surface tension at the CMC are highly similar.

Zhou *et al.* used glucose or lactose (obtained from cheese whey, a by-product of the dairy industry) with canola oil to produce enzyme-catalysed sophorose lipids (up to 160 g L^{-1}) as biosurfactants.[209]
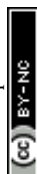
2.6. UV-absorbers

The phenolic hydroxy group of the CNSL constituents not only allows synthetic modification but also serves as a hydrogen bond donor. This permits the synthesis of photostable organic UV-filters which rely on the excited state intramolecular proton transfer (ESIPT) mechanism, for which O–H···H and O–H···N hydrogen bonds play a crucial role.[210,211] Since those compounds usually find application in lipophilic formulations like sunscreens, finishes, coatings or polymers, the nonpolar pentadecyl chain of the CNSL ingredients was assumed to be beneficial for the solubility in these formulations. The groups of de Koning and Opatz opted for the syntheses of cardanol (**92**) as well as anacardic acid (**91**) derived UV-absorbers as potential protectants.[213,214]
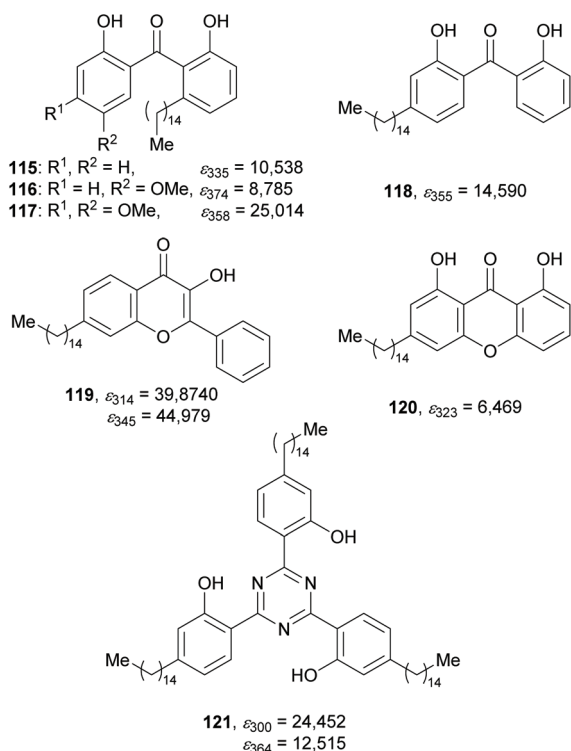
A variety of different compound classes exhibiting hydrogen–oxygen or hydrogen–nitrogen bonds like 2,2′-dihydroxybenzophenones **115–118**, 3-hydroxyflavone **119**, 1,8-dihydroxyxanthones **120**, or *s*-triazines **121** were synthesised by simple transformations (Scheme 12). Throughout these syntheses, the saturated derivatives of the CNSL constituents were used in order to obtain pure single compounds. Besides **91** and **92** as biomass-derived starting materials, all other organic reagents were selected to be accessible from renewable resources to further improve the eco-friendliness in this approach. Benzophenones **115–117** were synthesised from anacardic acid (**91**), whereas the all other presented compounds were produced from the hydrogenation product of **92**.

Comparison of the molar extinction coefficients (ε) of these compounds with the values of commercially available state-of-the-art UV-protectants like oxybenzone (OB, ε_{287} = 15 150 L mol^{-1} cm^{-1}), 2-ethylhexyl 4-methoxycinnamate (OMC, ε_{356} = 39 470 L mol^{-1} cm^{-1}) and avobenzone (ε_{310} = 31 670 L mol^{-1} cm^{-1})[215] displays the potential of the CNSL-derived compounds as UV-filters. In particular, flavone **119** and *s*-triazine **121** show remarkable properties regarding the UV absorption
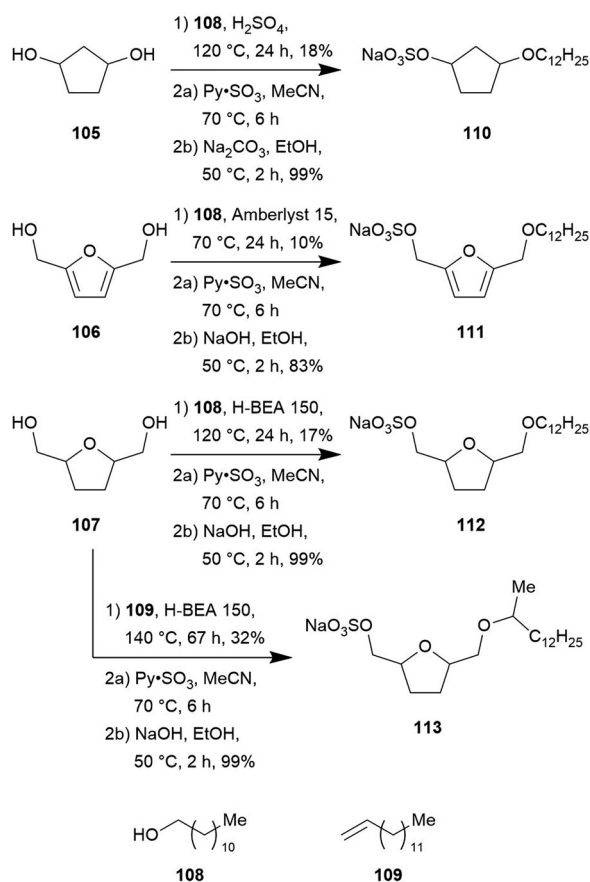
Scheme 11 Synthesis of cellulose based surfactants by Palkovits *et al.* (Amberlyst® 15 and zeolite H-BEA 150 are commercially available catalysts).

115: R^1, R^2 = H, ε_{335} = 10,538
116: R^1 = H, R^2 = OMe, ε_{374} = 8,785
117: R^1, R^2 = OMe, ε_{358} = 25,014

118, ε_{355} = 14,590

119, ε_{314} = 39,8740
ε_{345} = 44,979

120, ε_{323} = 6,469

121, ε_{300} = 24,452
ε_{364} = 12,515

Scheme 12 Examples of the synthesised UV-absorbing compounds by Opatz *et al.* and their respective ε values (in L mol^{-1} cm^{-1}).

spectra as well as the ε values which parallel those of commercial products. Building on these promising results, the implementation of a scalable synthesis could lead to a potential substitution of conventional UV-filters by these eco-friendly alternatives.

3. Conclusions

In addition to the conversion of lignin in the production of syngas[216] or biofuels,[217,218] technical grade lignin has found application as a replacement for chemically defined phenols and polyols in the manufacturing of resins, polyurethane foams, carbon fibres or additives in bitumen.[219–222] However, the valorisation of lignin needs to be cost-competitive and is ideally integrated in high-value commercial applications.[223,224] The catalysts employed in production and transformations of xylochemicals need to be improved with the aim of operating under mild conditions and possessing a long lifetime as well as a high selectivity while being tolerant towards the inevitable impurities contained. Furthermore, an efficient purification process (*e.g.* membrane processes such as organic solvent nanofiltration)[225,226] as well as by-product and waste management are crucial to the sustainability of the whole process, while conventional methods of purification (*e.g.* chromatography and distillation) are material and energy inefficient and should be avoided.[227,228]

A main goal of this review was to showcase possible benefits of the use of xylochemicals and how they can be employed in total syntheses or the manufacturing of products with an industrial application. To this end, a variety of platform chemicals and the procedures to obtain them from woody biomass were presented.

These technical possibilities are particularly important in the light of increasing atmospheric CO_2 levels and the depletion of formerly rich underground deposits of fossil carbon sources. There is a growing need to switch from fossil resources to renewable starting materials available from biomass which do not compete with agricultural food production. In some cases, the obtained materials and products can even provide superior properties relative to petroleum-based commodities, as in the case of biodegradable polymers or promising absorption characteristics as in the case of UV-absorbers. This scenario should provide a formidable challenge and motivation for today's chemists to develop renewable alternatives which ideally require no further replacement at any point. Future challenges lie instead in the exploitation of new renewable feedstocks for accessing additional platform chemicals and to broaden the product scope while maintaining a favourable ecological profile. Also, further side- or waste-streams should be reconsidered as possible raw materials in the light of new technologies and of the true cost of the use of fossil resources.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 D. Stubba, G. Lahm, M. Geffe, J. W. Runyon, A. J. Arduengo III and T. Opatz, *Angew. Chem., Int. Ed.*, 2015, **54**, 14187–14189.
2 D. Stubba, G. Lahm, M. Geffe, J. W. Runyon, A. J. Arduengo III and T. Opatz, *Angew. Chem.*, 2015, **127**, 14394–14396.
3 L. Wu, T. Moteki, A. A. Gokhale, D. W. Flaherty and F. D. Toste, *Chem*, 2016, **1**, 32–58.
4 R. L. Braun and A. K. Burnham, *Chemical reaction model for oil and gas generation from type 1 and type 2 kerogen*, Lawrence Livermore National Lab., CA (United States), 1993.

5   R. A. Sheldon, *Curr. Opin. Green Sustainable Chem.*, 2019, **18**, 13–19.

6   R. A. Sheldon and J. M. Woodley, *Chem. Rev.*, 2018, **118**, 801–838.

7   S. Chu and A. Majumdar, *Nature*, 2012, **488**, 294–303.

8   D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.

9   I. Parmar and H. V. Rupasinghe, *Bioresour. Technol.*, 2013, **130**, 613–620.

10 R. Liguori, C. R. Soccol, L. Porto de Souza Vandenberghe, A. L. Woiciechowski and V. Faraco, *Energies*, 2015, **8**, 2575–2586.

11 R. A. Verlinden, D. J. Hill, M. A. Kenward, C. D. Williams, Z. Piotrowska-Seget and I. K. Radecka, *AMB Express*, 2011, **1**, 11.

12 V. L. Budarin, P. S. Shuttleworth, J. R. Dodson, A. J. Hunt, B. Lanigan, R. Marriott, K. J. Milkowski, A. J. Wilson, S. W. Breeden and J. Fan, *Energy Environ. Sci.*, 2011, **4**, 471–479.

13 J. H. Clark and F. Deswarte, *Introduction to chemicals from biomass*, Wiley-VCH, 2014.

14 H. Alizadeh, F. Teymouri, T. I. Gilbert and B. E. Dale, *Appl. Biochem. Biotechnol.*, 2005, **124**, 1133–1141.

15 R. Ravindran and A. K. Jaiswal, *Trends Biotechnol.*, 2016, **34**, 58–69.

16 O. M. Adeniyi, U. Azimov and A. Burluka, *Renewable Sustainable Energy Rev.*, 2018, **90**, 316–335.

17 S. Prasad and A. P. Ingle, in *Sustainable Bioenergy*, ed. M. Rai and A. P. Ingle, Elsevier, 2019, pp. 327–346.

18 A. Ajanovic, *Energy*, 2011, **36**, 2070–2076.

19 D. Graham-Rowe, *Nature*, 2011, **474**, S6–S8.

20 B. Kamm, *Angew. Chem., Int. Ed.*, 2007, **46**, 5056–5058.

21 R. A. Sheldon, *Green Chem.*, 2014, **16**, 950–963.

22 A. J. J. Straathof, *Chem. Rev.*, 2014, **114**, 1871–1908.

23 D. J. Hayes, S. Fitzpatrick, M. H. Hayes and J. R. Ross, in *Biorefineries–Industrial Processes and Product*, Wiley-VCH, Weinheim, 2006, vol. 1, pp. 139–164.

24 V. Menon and M. Rao, *Prog. Energy Combust. Sci.*, 2012, **38**, 522–550.

25 K. Zhang, Z. Pei and D. Wang, *Bioresour. Technol.*, 2016, **199**, 21–33.

26 F. Stecker, I. M. Malkowsky, A. Fischer, S. R. Waldvogel and C. Regenbrecht, *US Pat*, US20140034508, 2014.

27 D. Schmitt, C. Regenbrecht, M. Hartmer, F. Stecker and S. R. Waldvogel, *Beilstein J. Org. Chem.*, 2015, **11**, 473–480.

28 M. Zirbes and S. R. Waldvogel, *Curr. Opin. Green Sustainable Chem.*, 2018, **14**, 19–25.

29 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.

30 K. J. Zeitsch, *The chemistry and technology of furfural and its many by-products*, Elsevier, 2000.

31 S. W. Fitzpatrick, *US Pat*, US4897497A, 1990.

32 S. W. Fitzpatrick, *US Pat*, US5608105A, 1997.

33 P. Saling, P. Spicher, R. Schröder, M. Kaltschmitt, E. Dinjus, F. Seyfried, K. Hill, C. Estéves, A. Gozzo and M. Kunz, *Sustainable solutions for modern economies*, RCS Publishing, 2009.

34 J. Akhtar, A. Idris and R. Abd. Aziz, *Appl. Microbiol. Biotechnol.*, 2014, **98**, 987–1000.

35 H. Choudhary, S. Nishimura and K. Ebitani, *Appl. Catal., A*, 2013, **458**, 55–62.

36 F. Cherubini and A. H. Strømman, *Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems*, Wiley-VCH, Weinheim, 2011.

37 M. Rose and R. Palkovits, *Macromol. Rapid Commun.*, 2011, **32**, 1299–1311.

38 M. Mascal and E. B. Nikitin, *Green Chem.*, 2010, **12**, 370–373.

39 T. Werpy and G. Petersen, *Top value added chemicals from biomass: volume I–results of screening for potential candidates from sugars and synthesis gas*, National Renewable Energy Lab., Golden, CO (US), 2004.

40 B. Kamm, P. R. Gruber and M. Kamm, *Biorefineries-industrial processes and products*, Wiley-VCH, Weinheim, 2006.

41 X. Qi, M. Watanabe, T. M. Aida and R. L. Smith Jr., *Green Chem.*, 2010, **12**, 1855–1860.

42 E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner and J. A. Dumesic, *Science*, 2008, **322**, 417.

43 L. E. Manzer, *EPO*, EP1368333A1, 2003.

44 F. Jin and H. Enomoto, *BioResources*, 2009, **4**, 704–713.

45 P. L. Rivilli, G. I. Yranzo and J. D. Pérez, *BioResources*, 2011, **6**, 2703–2710.

46 A. Deneyer, T. Renders, J. Van Aelst, S. Van den Bosch, D. Gabriëls and B. F. Sels, *Curr. Opin. Chem. Biol.*, 2015, **29**, 40–48.

47 J. S. Luterbacher, D. Martin Alonso and J. A. Dumesic, *Green Chem.*, 2014, **16**, 4816–4838.

48 J. C. Serrano-Ruiz, R. M. West and J. A. Dumesic, *Annu. Rev. Chem. Biomol. Eng.*, 2010, **1**, 79–100.

49 J. Q. Bond, D. Martin Alonso, R. M. West and J. A. Dumesic, *Langmuir*, 2010, **26**, 16291–16298.

50 J. Kühlborn, J. Groß and T. Opatz, *Nat. Prod. Rep.*, 2020, **37**, 380–424.

51 S. Van den Bosch, S.-F. Koelewijn, T. Renders, G. Van den Bossche, T. Vangeel, W. Schutyser and B. Sels, *Top. Curr. Chem.*, 2018, **376**, 36.

52 A. Lipp, D. Ferenc, C. Gütz, M. Geffe, N. Vierengel, D. Schollmeyer, H. J. Schäfer, S. R. Waldvogel and T. Opatz, *Angew. Chem., Int. Ed.*, 2018, **57**, 11055–11059.

53 A. Lipp, D. Ferenc, C. Gütz, M. Geffe, N. Vierengel, D. Schollmeyer, H. J. Schäfer, S. R. Waldvogel and T. Opatz, *Angew. Chem.*, 2018, **130**, 11221–11225.

54 B. Pfundstein, S. K. El Desouky, W. E. Hull, R. Haubner, G. Erben and R. W. Owen, *Phytochemistry*, 2010, **71**, 1132–1148.

55 I. W. Southon and J. Buckingham, *Dictionary of Alkaloids, with CD-ROM*, CRC Press, 1989.

56 S. Ghosal and R. S. Srivastava, *Phytochemistry*, 1973, **12**, 193–197.

57 M. A. Schwartz, *Synth. Commun.*, 1973, **3**, 33–35.

58 M. A. Schwartz and I. S. Mami, *J. Am. Chem. Soc.*, 1975, **97**, 1239–1240.

59 B. Franck, G. Dunkelmann and H. Lubs, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 1075–1076.

60 D. H. R. Barton, D. S. Bhakuni, R. James and G. W. Kirby, *J. Chem. Soc. C*, 1967, 128–132.

61 T. Kametani, T. Sugahara, H. Yagi and K. Fukumoto, *Tetrahedron*, 1969, **25**, 3667–3673.

62 G. Lahm, J.-G. Deichmann, A. L. Rauen and T. Opatz, *J. Org. Chem.*, 2015, **80**, 2010–2016.

63 J. C. Orejarena Pacheco, G. Lahm and T. Opatz, *J. Org. Chem.*, 2013, **78**, 4985–4992.

64 J. C. Liermann and T. Opatz, *J. Org. Chem.*, 2008, **73**, 4526–4531.

65 S. M. Klein, C. Zhang and Y. L. Jiang, *Tetrahedron Lett.*, 2008, **49**, 2638–2641.

66 T. R. Nunn, J. B. Howard, J. P. Longwell and W. A. Peters, *Ind. Eng. Chem. Process Des. Dev.*, 1985, **24**, 844–852.

67 A. Lipp, M. Selt, D. Ferenc, D. Schollmeyer, S. R. Waldvogel and T. Opatz, *Org. Lett.*, 2019, **21**, 1828–1831.

68 M. A. A. Endoma-Arias, M. Makarova, H. E. Dela Paz and T. Hudlicky, *Synthesis*, 2019, 225–232.

69 V. Fajardo, C. Cárcamo and B. Moreno, *Heterocycles*, 1996, **5**, 949–951.

70 J. Rowe and A. Conner, *General Technical Report FPL-United States*, 1979.

71 T. Fedorova, S. Fedorov and V. Babkin, *Russ. J. Bioorg. Chem.*, 2019, **45**, 927–932.

72 M. Z. M. Salem and M. Böhm, *BioResources*, 2013, **8**, 4775–4790.

73 J. Guyot and L. J. Simon, *C. R. Hebd. Seances Acad. Sci.*, 1919, **169**, 795–797.

74 R. A. Sheldon, *Chem. Soc. Rev.*, 2012, **41**, 1437–1451.

75 C.-J. Chen, W.-S. Lee and A. Bhan, *Appl. Catal., A*, 2016, **510**, 42–48.

76 C. Grundke and T. Opatz, *Green Chem.*, 2019, **21**, 2362–2366.

77 A. M. Nauth, N. Otto and T. Opatz, *Adv. Synth. Catal.*, 2015, **357**, 3424–3428.

78 J. Kühlborn, M. Konhäuser, J. Groß, P. R. Wich and T. Opatz, *ACS Sustainable Chem. Eng.*, 2019, 4414–4419.

79 M. Melián-Rodríguez, S. Saravanamurugan, S. Kegnæs and A. Riisager, *Top. Catal.*, 2015, **58**, 1036–1042.

80 A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415–6418.

81 L. Gavara, T. Boisse, J.-P. Hénichart, A. Daïch, B. Rigo and P. Gautret, *Tetrahedron*, 2010, **66**, 7544–7561.

82 D. Orphanos and A. Taurins, *Can. J. Chem.*, 1966, **44**, 1875–1879.

83 W. H. Perkin, *Proc. R. Soc. London*, 1862, **12**, 713–715.

84 A. von Baeyer and V. Drewsen, *Ber. Dtsch. Chem. Ges.*, 1882, **15**, 2856–2864.

85 A. von Baeyer and V. Drewsen, *Ber. Dtsch. Chem. Ges.*, 1883, **16**, 2205–2208.

86 A. von Baeyer and A. Emmerling, *Ber. Dtsch. Chem. Ges.*, 1870, **3**, 514–517.

87 P. Rys and H. Zollinger, *Farbstoffchemie: ein Leitfaden*, Verlag Chemie, Weinheim, 3 edn, 1982.

88 N. Welsch and C. C. Liebmann, *Farben: Natur, Technik, Kunst*, Spektrum Akademischer Verlag, Heidelberg, 3rd edn, 2012.

89 J. Kühlborn, A.-K. Danner, H. Frey, R. Iyer, A. J. Arduengo and T. Opatz, *Green Chem.*, 2017, **19**, 3780–3786.

90 J. Liu, *Liquid Explosives*, Springer, Berlin, Heidelberg, 2015.

91 J. Saska, Z. Li, A. L. Otsuki, J. Wei, J. C. Fettinger and M. Mascal, *Angew. Chem.*, 2019, **58**, 17293–17296.

92 Q. Girka, B. Estrine, N. Hoffmann, J. Le Bras, S. Marinković and J. Muzart, *React. Chem. Eng.*, 2016, **1**, 176–182.

93 M. Zirbes, D. Schmitt, N. Beiser, D. Pitton, T. Hoffmann and S. R. Waldvogel, *ChemElectroChem*, 2019, **6**, 155–161.

94 M. D. Kärkäs, B. S. Matsuura, T. M. Monos, G. Magallanes and C. R. J. Stephenson, *Org. Biomol. Chem.*, 2016, **14**, 1853–1914.

95 M. Fache, B. Boutevin and S. Caillol, *ACS Sustainable Chem. Eng.*, 2016, **4**, 35–46.

96 F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. Robert McElroy and J. Sherwood, *Sustainable Chem. Processes*, 2016, **4**, 7.

97 K. Galyan and J. Reilly, *Curr. Opin. Green Sustainable Chem.*, 2018, **11**, 76–80.

98 A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna and M. Keller, *Science*, 2014, **344**, 1246843.

99 B. M. Upton and A. M. Kasko, *Chem. Rev.*, 2016, **116**, 2275–2306.

100 S. Sen, S. Patil and D. S. Argyropoulos, *Green Chem.*, 2015, **17**, 4862–4887.

101 D. M. Alonso, S. H. Hakim, S. Zhou, W. Won, O. Hosseinaei, J. Tao, V. Garcia-Negron, A. H. Motagamwala, M. A. Mellmer and K. Huang, *Sci. Adv.*, 2017, **3**, e1603301.

102 J. Artz and R. Palkovits, *Curr. Opin. Green Sustainable Chem.*, 2018, **14**, 14–18.

103 E. E. Harris, J. D'Ianni and H. Adkins, *J. Am. Chem. Soc.*, 1938, **60**, 1467–1470.

104 H. Danner and R. Braun, *Chem. Soc. Rev.*, 1999, **28**, 395–405.

105 Y. Jiang, D. Maniar, A. J. J. Woortman, G. O. R. Alberda van Ekenstein and K. Loos, *Biomacromolecules*, 2015, **16**, 3674–3685.

106 M. Winnacker, M. Neumeier, X. Zhang, C. M. Papadakis and B. Rieger, *Macromol. Rapid Commun.*, 2016, **37**, 851–857.

107 M. Winnacker and B. Rieger, *Macromol. Rapid Commun.*, 2016, **37**, 1391–1413.

108 M. Winnacker and J. Sag, *Chem. Commun.*, 2018, **54**, 841–844.

109 P. Zierdt, T. Theumer, G. Kulkarni, V. Däumlich, J. Klehm, U. Hirsch and A. Weber, *Sustainable Mater. Technol.*, 2015, **6**, 6–14.

110 J. R. Cabrero-Antonino, E. Alberico, K. Junge, H. Junge and M. Beller, *Chem. Sci.*, 2016, **7**, 3432–3442.

111 M. Okada, *Prog. Polym. Sci.*, 2002, **27**, 87–133.

112 R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807.

113 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841–1846.

114 I. Vroman and L. Tighzert, *Materials*, 2009, **2**, 307–344.

115 A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardini and R. M. Filho, *Biotechnol. Adv.*, 2012, **30**, 321–328.

116 K. Fukushima and Y. Kimura, *Polym. Int.*, 2006, **55**, 626–642.

117 C. M. Thomas, *Chem. Soc. Rev.*, 2010, **39**, 165–173.

118 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.

119 Z. Zheng, G. Zhao, R. Fablet, M. Bouyahyi, C. M. Thomas, T. Roisnel, O. Casagrande Jr. and J.-F. Carpentier, *New J. Chem.*, 2008, **32**, 2279–2291.

120 B. Lian, C. M. Thomas, O. L. Casagrande Jr., T. Roisnel and J.-F. Carpentier, *Polyhedron*, 2007, **26**, 3817–3824.

121 M. J.-L. Tschan, E. Brulé, P. Haquette and C. M. Thomas, *Polym. Chem.*, 2012, **3**, 836–851.

122 The manufacturing facility is located in Blair, Nebraska, USA.

123 E. T. Vink, S. Davies and J. J. Kolstad, *Ind. Biotechnol.*, 2010, **6**, 212–224.

124 E. T. Vink and S. Davies, *Ind. Biotechnol.*, 2015, **11**, 167–180.

125 R. M. Saville, S. Lee, D. D. REGITSKY, S. M. Resnick and J. Silverman, *WIPO (PCT)*, WO2014205146A1, 2014.

126 NatureWorks, https://www.natureworksllc.com/News-and-Events/Press-Releases/2016/03-09-16-NatureWorks-Methane-to-Lactic-Acid-Fermentation-Lab and https://www.natureworksllc.com/What-is-Ingeo/Where-Ingeo-Comes-From, (accessed 20.04.2020).

127 M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1704302.

128 C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032–2038.

129 M. Poliakoff, W. Leitner and E. S. Streng, *Faraday Discuss.*, 2015, **183**, 9–17.

130 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082.

131 A. A. Olajire, *Energy*, 2010, **35**, 2610–2628.

132 S. Inoue, H. Koinuma and T. Tsuruta, *Macromol. Chem. Phys.*, 1969, **130**, 210–220.

133 S. Fukuoka, I. Fukawa, T. Adachi, H. Fujita, N. Sugiyama and T. Sawa, *Org. Process Res. Dev.*, 2019, **23**, 145–169.

134 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405.

135 G. A. Burdock, *Fenaroli's handbook of flavor ingredients*, CRC press, 2016.

136 F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro and R. Ciriminna, *ACS Omega*, 2018, **3**, 4884–4890.

137 N. Kindermann, À. Cristòfol and A. W. Kleij, *ACS Catal.*, 2017, **7**, 3860–3863.

138 G. Fiorani, M. Stuck, C. Martín, M. M. Belmonte, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *ChemSusChem*, 2016, **9**, 1304–1311.

139 J. E. Gómez and A. W. Kleij, in *Adv. Organomet. Chem*, ed. P. J. Pérez, Academic Press, 2019, vol. 71, pp. 175–226.

140 L. E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.

141 M. W. P. C. van Rossum, M. Alberda and L. H. W. van der Plas, *Phytochemistry*, 1998, **49**, 723–729.

142 Y. Kato, H. Yoshida, K. Shoji, Y. Sato, N. Nakajima and S. Ogita, *Tetrahedron Lett.*, 2009, **50**, 4751–4753.

143 U. Ali, K. J. B. A. Karim and N. A. Buang, *Polym. Rev.*, 2015, **55**, 678–705.

144 M. M. Demir, M. Memesa, P. Castignolles and G. Wegner, *Macromol. Rapid Commun.*, 2006, **27**, 763–770.

145 Z. J. A. Amer, J. K. Ahmed and S. F. Abbas, *Int. J. Eng. Technol.*, 2014, **4**, 1–6.

146 H. Lu, W. M. Huang, X. L. Wu, Y. C. Ge, F. Zhang, Y. Zhao and J. Geng, *Smart Mater. Struct.*, 2014, **23**, 067002.

147 X. Wang, P. Wang, Y. Jiang, Q. Su and J. Zheng, *Compos. Sci. Technol.*, 2014, **104**, 1–8.

148 J. Mosnáček, J. A. Yoon, A. Juhari, K. Koynov and K. Matyjaszewski, *Polymer*, 2009, **50**, 2087–2094.

149 J. Suenaga, D. M. Sutherlin and J. K. Stille, *Macromolecules*, 1984, **17**, 2913–2916.

150 G. M. Miyake, Y. Zhang and E. Y. X. Chen, *Macromolecules*, 2010, **43**, 4902–4908.

151 I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky and A. Springer, *Chem. Eng. Technol.*, 2008, **31**, 647–654.

152 P. Lee, S. Lee, S. Hong, H. N. Chang and S. Park, *Biotechnol. Lett.*, 2003, **25**, 111–114.

153 P. C. Lee, W. G. Lee, S. Y. Lee, H. N. Chang and Y. K. Chang, *Biotechnol. Bioprocess Eng.*, 2000, **5**, 379–381.

154 C. Delhomme, D. Weuster-Botz and F. E. Kühn, *Green Chem.*, 2009, **11**, 13–26.

155 C. Gioia, M. Vannini, P. Marchese, A. Minesso, R. Cavalieri, M. Colonna and A. Celli, *Green Chem.*, 2014, **16**, 1807–1815.

156 I. Villuendas, J. J. Bou, A. Rodríguez-Galán and S. Muñoz-Guerra, *Macromol. Chem. Phys.*, 2001, **202**, 236–244.

157 A. Cukalovic and C. V. Stevens, *Biofuels, Bioprod. Biorefin.*, 2008, **2**, 505–529.

158 G. Soula and P. Duteurtre, *US Pat*, US4199462A, 1978.

159 R. H. Wollenberg and F. Plavac, *US Pat*, US4747850A, 1988.

160 Y. Lu and R. C. Larock, *Biomacromolecules*, 2006, **7**, 2692–2700.

161 S. Matsumura and J. Takahashi, *Macromol. Rapid Commun.*, 1986, **7**, 369–373.

162 D. Teomim, A. Nyska and A. J. Domb, *J. Biomed. Mater. Res.*, 1999, **45**, 258–267.

163 U. Biermann, U. Bornscheuer, M. A. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 3854–3871.

164 U. Biermann and J. O. Metzger, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 805–811.

165 S. S. Gupta, T. P. Hilditch and J. P. Riley, *J. Sci. Food Agric.*, 1951, **2**, 245–251.

166 A. Köckritz and A. Martin, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 812–824.

167 G. Knothe, J. Kenar and F. Gunstone, *The Lipid Handbook*, CRC Press, Boca Raton, FL, 2007.

168 U. Biermann, W. Butte, T. Eren, D. Haase and J. O. Metzger, *Eur. J. Org. Chem.*, 2007, 3859–3862.

169 U. Biermann and J. O. Metzger, *J. Am. Chem. Soc.*, 2004, **126**, 10319–10330.

170 J. G. O. Metzger and U. Riedner, *Lipid/Fett*, 1989, **91**, 18–23.

171 G. B. Bantchev, J. A. Kenar, G. Biresaw and M. G. Han, *J. Agric. Food Chem.*, 2009, **57**, 1282–1290.

172 P. Van Dam, M. Mittelmeijer and C. Boelhouwer, *J. Chem. Soc., Chem. Commun.*, 1972, 1221–1222.

173 M. A. R. Meier, *Macromol. Chem. Phys.*, 2009, **210**, 1073–1079.

174 A. Rybak, P. A. Fokou and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 797–804.

175 D. M. Ohlmann, N. Tschauder, J.-P. Stockis, K. Gooßen, M. Dierker and L. J. Gooßen, *J. Am. Chem. Soc.*, 2012, **134**, 13716–13729.

176 R. E. Montenegro and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2012, **114**, 55–62.

177 G. Heublein, H. Hartung, M. Helbig and D. Stadermann, *J. Macromol. Sci., Chem.*, 1982, **17**, 821–845.

178 S. Huf, S. Krügener, T. Hirth, S. Rupp and S. Zibek, *Eur. J. Lipid Sci. Technol.*, 2011, **113**, 548–561.

179 U. Biermann, W. Butte, R. Holtgrefe, W. Feder and J. O. Metzger, *Eur. J. Lipid Sci. Technol.*, 2010, **112**, 103–109.

180 J. T. P. Derksen, F. Petrus Cuperus and P. Kolster, *Prog. Org. Coat.*, 1996, **27**, 45–53.

181 M. Eissen, J. O. Metzger, E. Schmidt and U. Schneidewind, *Angew. Chem., Int. Ed.*, 2002, **41**, 414–436.

182 M. G. Kulkarni, A. K. Dalai and N. N. Bakhshi, *Bioresour. Technol.*, 2007, **98**, 2027–2033.

183 https://www.statista.com/statistics/967702/global-cashew-nut-production/, (accessed March 23, 2020).

184 J. Mgaya, G. B. Shombe, S. C. Masikane, S. Mlowe, E. B. Mubofu and N. Revaprasadu, *Green Chem.*, 2019, **21**, 1186–1201.

185 E. B. Mubofu, *Pure Appl. Chem.*, 2016, **88**, 17–27.

186 C. N. Subbarao, K. Krishna Prasad and V. Prasad, *Pharm. Res. J.*, 2011, **6**, 21–41.

187 E. A. Taiwo, in *Advances in Petrochemicals*, Intech, Ile-Ife, 2015.

188 M. L. D. Santos and G. C. D. Magalhães, *J. Braz. Chem. Soc.*, 1999, **10**, 13–20.

189 S. Kumar, P. Dinesha and M. A. Rosen, *Energy Fuels*, 2018, **32**, 7237–7244.

190 M. C. Lubi and E. T. Thachil, *Des. Monomers Polym.*, 2000, **3**, 123–153.

191 A. S. Trita, L. C. Over, J. Pollini, S. Baader, S. Riegsinger, M. A. R. Meier and L. J. Gooßen, *Green Chem.*, 2017, **19**, 3051–3060.

192 C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142–3162.

193 L. Kisula, S. J. M. Mdachi, C. B. de Koning and Q. A. Mgani, *Tanzania J. Sci.*, 2015, **41**, 27–37.

194 J. E. Mgaya, E. B. Mubofu, Q. A. Mgani, D. B. Cordes, A. M. Slawin and D. J. Cole-Hamilton, *Eur. J. Lipid Sci. Technol.*, 2015, **117**, 190–199.

195 J. A. Mmongoyo, Q. A. Mgani, S. J. M. Mdachi, P. J. Pogorzelec and D. J. Cole-Hamilton, *Eur. J. Lipid Sci. Technol.*, 2012, **114**, 1183–1192.

196 A. K. Biswas and A. B. Roy, *Nature*, 1958, **182**, 1299–1300.

197 C. Scorzza, J. Nieves, F. Vejar and J. Bullón, *J. Surfactants Deterg.*, 2009, **13**, 27.

198 P. Peungjitton, P. Sangvanich, S. Pornpakakul, A. Petsom and S. Roengsumran, *J. Surfactants Deterg.*, 2009, **12**, 85–89.

199 V. Bragoni, R. K. Rit, R. Kirchmann, A. S. Trita and L. J. Gooßen, *Green Chem.*, 2018, **20**, 3210–3213.

200 R. A. Sheldon, *Chem. Ind.*, 1992, 903–906.

201 R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273–1283.

202 L. Kipshagen, L. T. Vömel, M. A. Liauw, A. Klemmer, A. Schulz, C. Kropf, P. J. C. Hausoul and R. Palkovits, *Green Chem.*, 2019, **21**, 3882–3890.

203 G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 3607–3613.

204 J. Ohyama, Y. Ohira and A. Satsuma, *Catal. Sci. Technol.*, 2017, **7**, 2947–2953.

205 K. Noweck and W. Grafahrend, *in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2006.

206 F. Krafft, *Ber. Dtsch. Chem. Ges.*, 1883, **16**, 3018–3024.

207 S. Warwel, P. Bavaj and M. Rüsch, gen. Klaas and B. Wolff, in *Perspektiven nachwachsender Rohstoffe in der Chemie*, ed. H. Eierdanz, Wiley-VCH, Weinheim, 1996, pp. 119–135.

208 S. Warwel, F. Brüse, C. Demes, M. Kunz and M. Rüsch, gen. Klaas, *Chemosphere*, 2001, **43**, 39–48.

209 Q.-H. Zhou and N. Kosaric, *J. Am. Oil Chem. Soc.*, 1995, **72**, 67–71.

210 A. Maliakal, G. Lem, N. J. Turro, R. Ravichandran, J. C. Suhadolnik, A. D. DeBellis, M. G. Wood and J. Lau, *J. Phys. Chem. A*, 2002, **106**, 7680–7689.

211 P. F. McGarry, S. Jockusch, Y. Fujiwara, N. A. Kaprinidis and N. J. Turro, *J. Phys. Chem. A*, 1997, **101**, 764–767.

212 G. Basu Ray, I. Chakraborty, S. Ghosh and S. P. Moulik, *Colloid Polym. Sci.*, 2007, **285**, 457–469.

213 K. J. Ngwira, J. Kühlborn, Q. A. Mgani, C. B. de Koning and T. Opatz, *Eur. J. Org. Chem.*, 2019, 4778–4790.

214 T. Opatz, J. Kühlborn, C. B. de Koning, K. J. Ngwira and Q. A. Mgani, *South African provisional patent*, ZA2019/01514, 2019.

215 H. M. Chawla, N. Pant, S. Kumar, S. Mrig, B. Srivastava, N. Kumar and D. S. Black, *J. Photochem. Photobiol., B*, 2011, **105**, 25–33.

216 M. P. Pandey and C. S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29–41.

217 F. Chen and R. A. Dixon, *Nat. Biotechnol.*, 2007, **25**, 759–761.

218 J.-K. Weng, X. Li, N. D. Bonawitz and C. Chapple, *Curr. Opin. Biotechnol.*, 2008, **19**, 166–172.

219 N. Smolarski, *High-value opportunities for lignin: unlocking its potential*, Frost & Sullivan, 2012, vol. 1.

220 R. Behling, S. Valange and G. Chatel, *Green Chem.*, 2016, **18**, 1839–1854.

221 V. E. Tarabanko and N. Tarabanko, *Int. J. Mol. Sci.*, 2017, **18**, 2421.

222 L. Dessbesell, M. Paleologou, M. Leitch, R. Pulkki and C. Xu, *Renewable Sustainable Energy Rev.*, 2020, 109768.

223 L. P. Dansereau, M. El-Halwagi, B. Mansoornejad and P. Stuart, *Comput. Chem. Eng.*, 2014, **63**, 34–50.

224 L. Dessbesell, C. Xu, R. Pulkki, M. Leitch and N. Mahmood, *Can. J. For. Res.*, 2016, **47**, 277–288.

225 J. F. Kim, G. Székely, I. B. Valtcheva and A. G. Livingston, *Green Chem.*, 2014, **16**, 133–145.

226 P. Vandezande, L. E. M. Gevers and I. F. J. Vankelecom, *Chem. Soc. Rev.*, 2008, **37**, 365–405.

227 R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 32–48.

228 J. F. Jenck, F. Agterberg and M. J. Droescher, *Green Chem.*, 2004, **6**, 544–556.