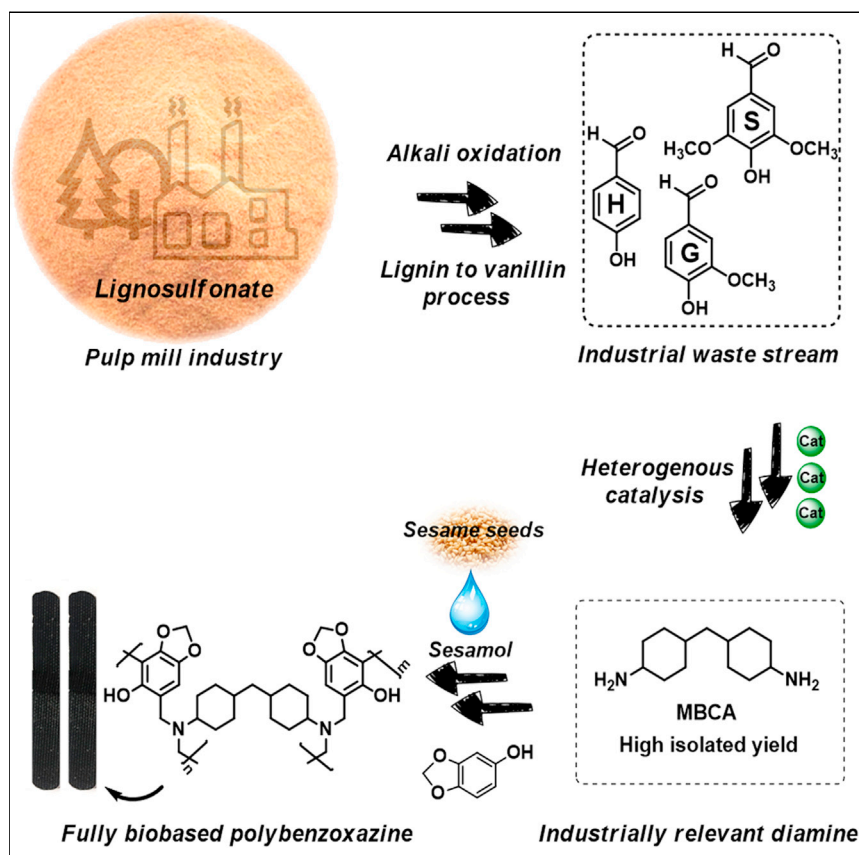CellPress

Article

A well-defined diamine from lignin depolymerization mixtures for constructing bio-based polybenzoxazines

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Highlights

From paper industry side products to industrially relevant diamine MBCA

Catalytic funneling of aldehyde-based bisphenols led to MBC in an excellent yield

Heterogeneous catalysis method for direct amination with ammonia with high selectivity

Bio-based polybenzoxazines with comparable properties to commercial materials

Lignin, generated as a side product in the paper and pulp industry, harbors huge potential to serve as an intriguing raw material for the construction of industrially relevant chemicals and materials. We developed a powerful catalytic downstream processing strategy toward the construction of high-performing, fully bio-based polybenzoxazines, utilizing lignin-derived waste streams. The demand for high-performance and bio-based materials is expected to markedly increase in the coming decades. Therefore, novel waste-to-value chains developed here are a valuable addition to the bio-based economy.

13 CLIMATE ACTION

Article

A well-defined diamine
from lignin depolymerization mixtures
for constructing bio-based polybenzoxazines

Xianyuan Wu,[1] Maxim V. Galkin,[1] and Katalin Barta[1,2,3,*]

SUMMARY

The demand for high-performance materials is increasing, and most of these materials are petrol based. Therefore, the development of highly efficient and selective catalytic methods that allow access to industrially relevant polymer building blocks from complex biomass depolymerization mixtures is essential. Here, we report on a robust catalytic strategy to obtain the industrially relevant 4,4′-methylenebiscyclohexanamine (MBCA) from lignin oxidation mixtures and its use for constructing fully bio-based polybenzoxazines. The strategy consists of two challenging catalytic steps: 1) the funneling of lignin-derived bisphenol mixtures into 4,4′-methylenebiscyclohexanol (MBC) and 2) the highly selective amination of MBC with ammonia to obtain MBCA. The renewable polybenzoxazines were prepared from MBCA and phenolic lignin platform chemicals. The most promising, cured poly (S-MBCA), shows high glass transition temperature T_g of 315°C, outstanding thermal stability ($T_{10\%}$ = 400°C), and good storage modulus ($E'_{25°C}$ = 3.8 GPa), which is competitive with commercial resins.

INTRODUCTION

The demand for high-performance materials in many industries (such as the aviation, automobile, and construction industries) is expected to markedly increase in the coming decades; however, the vast majority of these materials are still petroleum derived.[1,2] There is high demand for renewable alternatives, preferably sourced from biomass waste streams.[3–7] The paper and pulp industry produces approximately 50 Mt lignin annually as a side product.[8] While the alkali oxidation of such lignin by-products is already industrially implemented,[9–11] there is still a large gap between such depolymerization efforts and accessing well-defined industrially relevant products and, consequently, important applications.

Aliphatic diamines are omnipresent in the fine chemicals and polymer industry.[12–14] Thus, the development of sustainable catalytic methodologies to obtain these from renewable resources,[15–17] especially by challenging direct amination with ammonia,[18–22] is an attractive target. It is especially important to establish industrially relevant waste-to-value chains,[23] which enable the efficient conversion of biomass depolymerization mixtures into well-defined chemical building blocks.[24–27]

Due to its unique structural features,[28] 4,4′-methylenebiscyclohexanamine (MBCA) is an interesting diamine building block for the production of high-performance polymers.[29–36] Here, we describe a robust catalytic strategy suitable to transform crude, pre-purified lignin depolymerization mixtures typically produced by the paper and pulp industry,[9–11,37–40] into MBCA in high overall yield. The approach

The bigger picture

The paper and pulp industry produces up to 50 Mt lignin by-products annually, yet these material streams are still being used as low-value fuel. While the lignin to vanillin process is already industrially implemented, there is a significant gap regarding the catalytic valorization of such depolymerization mixtures to well-defined, industrially relevant products and, consequently, important applications. Here, we show a robust catalytic strategy that allows conversion of lignin oxidation mixtures to an industrially highly relevant diamine, 4,4′-methylenebiscyclohexanamine (MBCA), and describe high-performing and fully bio-based polybenzoxazines with properties competitive with the already industrially utilized high-performance resins (e.g., by Huntsman) based on this diamine. The demand for high-performance and bio-based materials is expected to markedly increase. Therefore, novel waste-to-value chains such as those presented in this work will be of interest for a future bio-based economy.
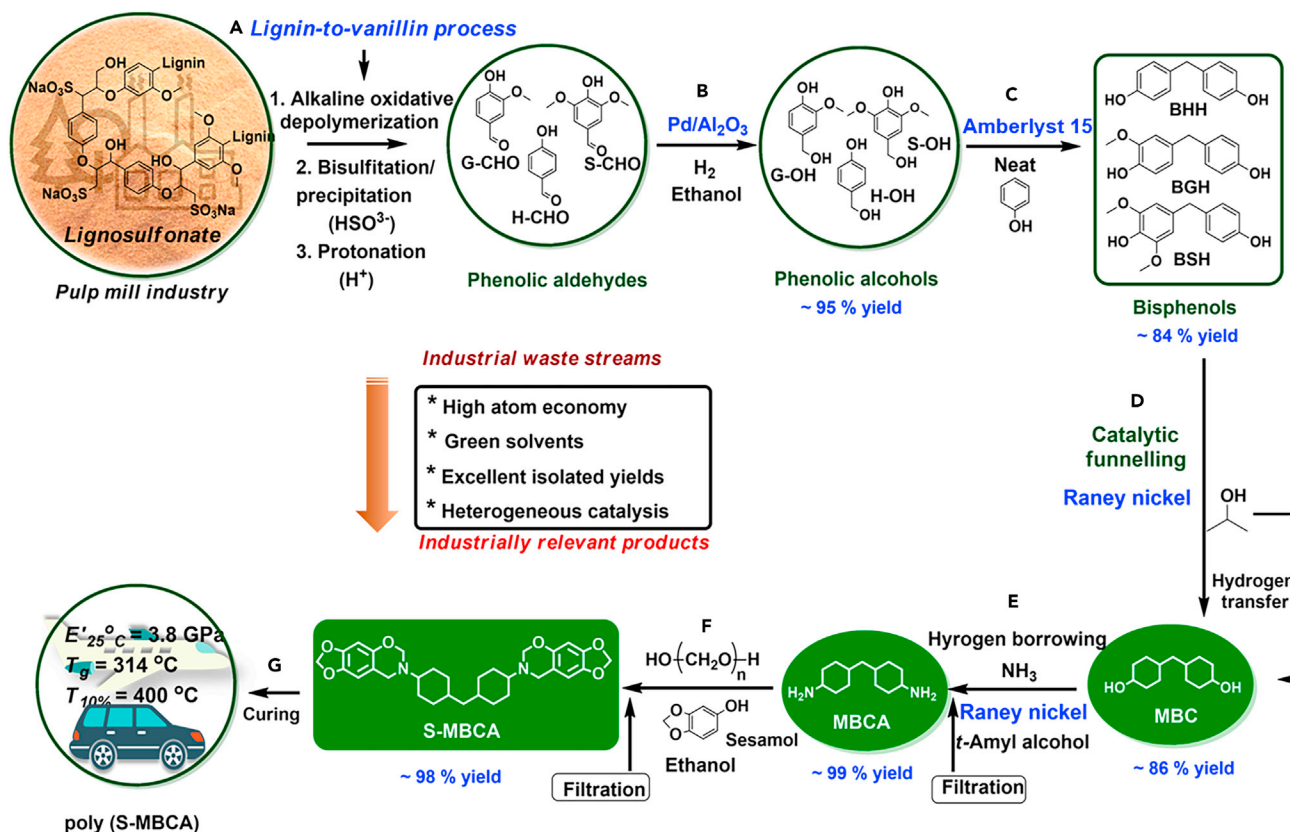
Figure 1. From lignin oxidation mixtures to industrially relevant diamine and high-performance polybenzoxazine resin
(A) A well-known process for the production and purification of aldehydes (lignin to vanillin process).
(B) The reduction of model phenolic S, G, H aldehydes to corresponding S, G, H phenolic alcohols mixture over Pd/Al$_2$O$_3$ catalyst.
(C) Acid catalyzed coupling of S, G, H phenolic alcohols with phenol to deliver a mixture of BHH, BGH, and BSH over Amberlyst 15 catalyst.
(D) Catalytic funneling of BHH, BGH, and BSH bisphenols mixture to single MBC diol over Raney nickel catalyst.
(E) Catalytic direct amination of MBC diol into MBCA diamine over Raney nickel catalyst.
(F) Mannich condensation of MBCA, sesamol, and paraformaldehyde to give benzoxazine monomer S-MBCA.
(G) Thermally induced ring-opening polymerizations to provide fully bio-based poly (S-MBCA).

described here allows for converting mixtures of aldehydes into a single aliphatic diol MBC, and subsequently diamine MBCA, using commercially available catalysts and widely accessible and/or potentially bio-derived reagents, such as phenol[24] and ammonia, without the need for extensive purification procedures (Figure 1). The developed sequence consists of (1) hydrogenation using Pd/Al$_2$O$_3$ as catalyst;[41] (2) electrophilic aromatic substitution promoted by Amberlyst 15;[42] (3) selective Raney nickel-catalyzed funneling via demethoxylation/hydrogenation to methylene-biscyclohexanol (MBC); and (4) the direct amination of MBC with ammonia via the hydrogen-borrowing strategy, in near-perfect MBCA selectivity.

Starting from MBCA and potentially lignin-derived[16,43,44] or naturally occurring[45–47] phenol derivatives, fully bio-based high-performance polybenzoxazines of novel compositions were synthesized. The use of sesamol (S) has proven to be the most promising, as the cured S-MBCA afforded outstanding thermal performance (T_g of 315°C and $T_{10\%}$ of >400°C) and good mechanical strength (E' = 3.8 GPa at 25°C), which is competitive or better than currently developed petrol-based or other bio-based polybenzoxazine resins using vanillin-,[48] guaiacol (G)-,[49,50] eugenol (E)-,[51,52] cardanol-,[53,54] and cellulose-derived furfuryl amine[50,55–57] as building blocks.

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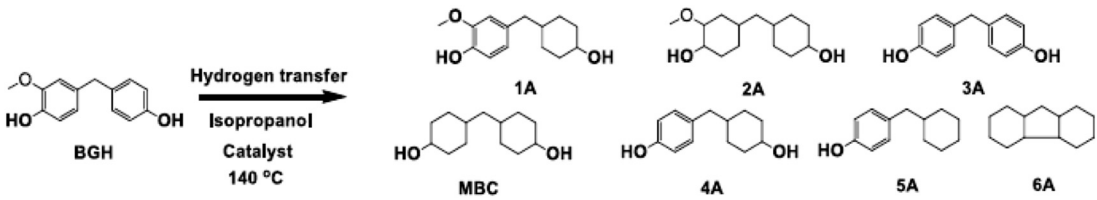*Correspondence: katalin.barta@uni-graz.at

RESULTS AND DISCUSSION

The alkaline oxidation of softwood lignosulfonate to vanillin, industrially implemented by Borregaard,[9–11] gives a product mixture consisting of predominately phenolic vanillin up to 7.2 wt % yield based on lignin[58,59] and smaller amounts of syringaldehyde, 4-hydroxybenzaldehyde, ketones, and carboxylic acids depending on the use of oxidants, pH, catalysts, temperature, and lignin natural origin.[59] When hardwood lignosulfonate is used instead of softwood, for example, *Eucalyptus* (manufactured by Borregaard and Sappi),[9–11] the aldehyde yield increases at the expense of vanillin selectivity, and a more complex mixture of phenolic aldehydes (syringaldehyde: 16.1 wt %, vanillin 4.5 wt %, and a small amount of 4-hydroxybenzaldehyde) is obtained.[60] These aldehyde mixtures can be isolated from the crude lignin depolymerization oil by bisulfitation with $NaHSO_3$[40,61] and subsequent precipitation. However, further separation of the individual components would be very tedious and economically unfeasible, due to similar chemical-physical properties.[40] Nonetheless, either vanillin or aldehyde mixtures should serve as excellent starting material for the production of value-added industrially relevant chemicals, especially for input into the fine chemicals[16,62] and polymer sectors.[63]

Here, we have aimed to develop a strategy to access single symmetric diol and diamine from vanillin or phenolic aldehyde mixtures (shown in Figure 1). This strategy builds upon the knowledge that benzyl alcohols are prone to rapid dehydration and subsequent aromatic electrophilic substitution reactions with phenol.[42] Thus, the crude aldehyde mixtures from lignin oxidation could be turned into a mixture of benzyl alcohols upon a simple hydrogenation step, and subsequently produce a mixture of functionalized bisphenols upon coupling with phenol. Based on our earlier investigations,[64] our assumption was that the catalytic funneling of such bisphenol mixtures to the single aliphatic diol MBC would be highly efficient. Moreover, MBC may serve as a precursor for the industrially important diamine MBCA if an appropriate catalytic strategy for direct coupling with ammonia can be found.

Thus, the two most challenging steps in the proposed strategy depicted in Figure 1 are the catalytic funneling of the mixture of bisphenol derivatives into the single aliphatic diol MBC and its subsequent amination. Therefore, these two steps were more extensively studied, as detailed below.

Catalytic funneling of functionalized bisphenols

Firstly, the catalytic defunctionalization/funneling methodology was established, using the model compound 4-(4-hydroxybenzyl)-2-methoxyphenol (BGH) obtained by acid-mediated coupling of vanillyl alcohol and phenol, following literature procedures[42] (see supplemental information 1.1). Inspired by the pioneering work of Rinaldi, on highly efficient transfer hydrogenation of biomass-derived phenolic substrates[65–67] and our previous investigation regarding the catalytic funneling of lignin-derived phenols to aliphatic diols,[64] we investigated the demethoxylation/hydrogenation of BGH under transfer hydrogenation conditions using isopropanol at 140°C for 3 h (Table 1). Isopropanol, in combination with Raney nickel has shown superior catalytic activity in hydrogen transfer reactions, compared with other simpler alcohols, methanol or ethanol, which may be easily sourced from renewables (see Notes S1 and S2).[64–67] Indeed, among the tested catalysts, Raney nickel exhibited excellent hydrogen transfer ability, with full conversion of BGH and close to 80% selectivity of MBC obtained as a mixture of isomers of *cis-cis*:*cis-trans*:*trans-trans* (10:43:47), characterized by ^{1}H NMR, ^{13}C NMR, and 2D HSQC (Figures S24–S36).

Table 1. Catalytic demethoxylation and hydrogenation of BGH to MBC over various heterogeneous metal catalysts[a]

Entry	Metal loading (wt %)	Catalyst	Conversion[b] (%)	Selectivity (%) [b]							Yield[c] (%)
				MBC	1A	2A	3A	4A	5A	6A	
1	65	Ni/SiO$_2$-Al$_2$O$_3$	–	–	–	–	–	–	–	–	–
2	5	Pd/Al$_2$O$_3$	19.1	0	44.4	–	–	–	–	–	–
3	5	Ru/Al$_2$O$_3$	49.1	1.9	91.9	–	–	6.1	–	–	0.9
4	5	Ru/C	36.7	7.9	92.1	–	–	–	–	–	2.9
5	≥89	Raney Ni	100	79.2	2.6	4.9	–	3.8	3.8	5.6	79.2 (76.4) [c]

Note: no side products produced by aldol condensation of acetone were observed.

[a]Reaction conditions: 0.5 mmol BGH, 100 mg catalyst, 15 mL isopropanol, 140°C, 3 h, 10 mg dodecane.

[b]Conversion, selectivity and yield was determined by GC-FID.

[c]GC yield in parentheses was determined by calibration curve using dodecane as internal standard. MBC was obtained as mixture of isomers (*cis-cis:cis-trans:trans-trans*) with the ratio of 10:43:47, quantified by ^{1}H-NMR (Figure S33).

In addition to the target product MBC, other partly defunctionalized intermediates 1A, 2A, 3A, and 4A, or fully defunctionalized side products 5A and 6A, were detected. Noble metal catalyst Pd/Al$_2$O$_3$ showed only 20% BGH conversion and 44% selectivity to 1A, while Ru catalysts displayed more than 90% 1A selectivity using Ru/Al$_2$O$_3$ and Ru/C as catalyst, at moderate conversions and minimal MBC yield.

Experiments at lower temperature 110°C–130°C (Figure 2A) or shorter reaction time (Figure 2B) revealed the dominance of the two earlier products 1A and 4A, originating from the partial hydrogenation of BGH to 1A, followed by demethoxylation of 1A to 4A and its subsequent hydrogenation to target MBC. This demethoxylation prior to the aromatic ring hydrogenation sequence is in line with our earlier investigations.[64] Intermediate 3A was present in very small quantities, revealing a rapid demethoxylation step. The relatively small quantities of 5A and 6A[68,69] have shown that total deoxygenation is not a major concern in this system (Figure 2C); nonetheless, the existence of these side products is reason for lower product yield at all reaction temperatures. Further increasing the reaction temperature has seen a sharp decrease of the intermediates 1A, 4A, and 3A, while the amount of 2A remained relatively constant, suggesting a very slow demethoxylation once the aromatic ring is saturated, thereby pointing toward another hurdle to achieving full product selectivity. Hence, the highest MBC yield was identified as 85% at 150°C for 3 h.

Due to its magnetic properties, Raney nickel can be easily isolated by means of a magnet, as reported earlier.[65–67] Thus, a series of recycling experiments (Figure S55) were performed at 150°C for 3 h, showing good reusability, and ICP measurements indicated no obvious Ni leaching (Table S3).

Further work focused on investigating the reactivity of other bisphenols, featuring one to four methoxy groups (Figure 3; Table S3). This provides a good orientation for the selection of an appropriate reaction partner when using benzyl alcohol mixtures for making
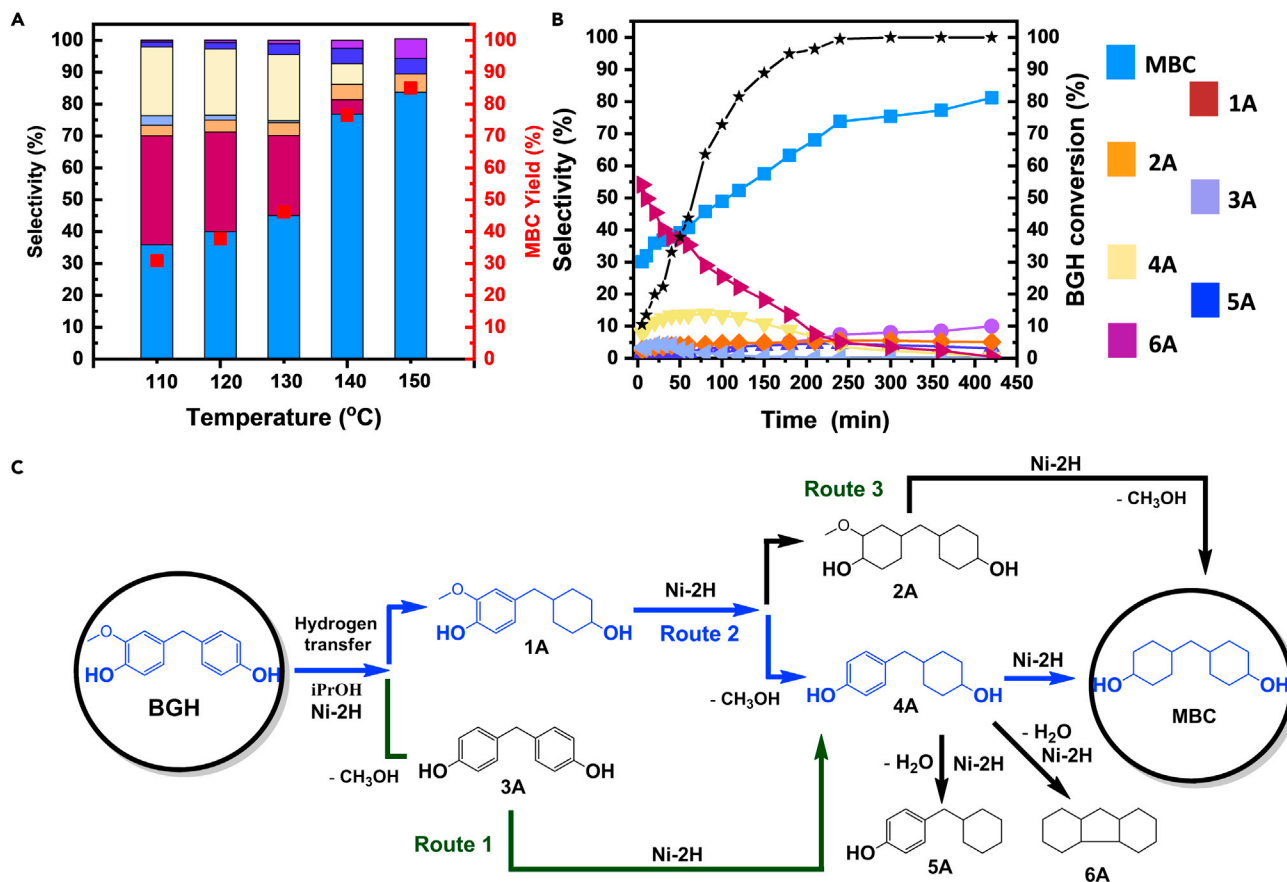
Figure 2. Catalytic demethoxylation/hydrogenation of BGH to MBC over Raney nickel catalyst

Reaction conditions: (A) 0.5 mmol BGH, 100 mg wet Raney nickel catalyst, 15 mL isopropanol, 110°C–150°C, 3 h, 10 mg dodecane.

(B) 0.5 mmol BGH, 100 mg wet Raney nickel catalyst, 15 mL isopropanol, 150°C, 0–450 min, 10 mg dodecane. Red square symbol stands for MBC yield. Black star symbol stands for BGH conversion. Selectivity and conversion were determined by GC-FID. Yield was determined by calibration curve using dodecane as internal standard.

(C) Proposed reaction network for defunctionalization of BGH.

the desired bisphenol derivatives. As expected, the MBC yield depended on the degree of methoxylation of the bisphenols, with 4,4′-methylenediphenol (BHH) showing highest MBC yield and 4,4′-methylenebis(2,6-dimethoxyphenol) (BSS) lowest (95% versus 65%). Furthermore, interestingly, a higher reactivity was achieved starting from 4-(4-hydroxy-benzyl)-2,6-dimethoxyphenol (BSH) (84%) as opposed to 4,4′-methylenebis(2-methoxy-phenol) (BGG) (73.3%). Interestingly, two types of lignin-derived building blocks β-1 and β-β were also converted into the corresponding diols, with the isolated yields of 72.7% and 68.9%, respectively (Figures S56–S63).

Next, the demethoxylation/hydrogenation of a model mixture of BHH, BGH, and BSH with a molar ratio of 2:2:1 was investigated under optimized reaction conditions. All three bisphenols were successfully converted into a single product, MBC diol, in 87.4% yield, showing highly successful chemical funneling.

Conversion of an aldehyde mixture to a single MBC diol

Next, we explored the possibility to get MBC from aldehyde mixtures, mimicking those originating from alkali lignin oxidation, based on the reaction sequence shown in Figures 1 and 4. Beside the catalytic funneling step investigated above, an
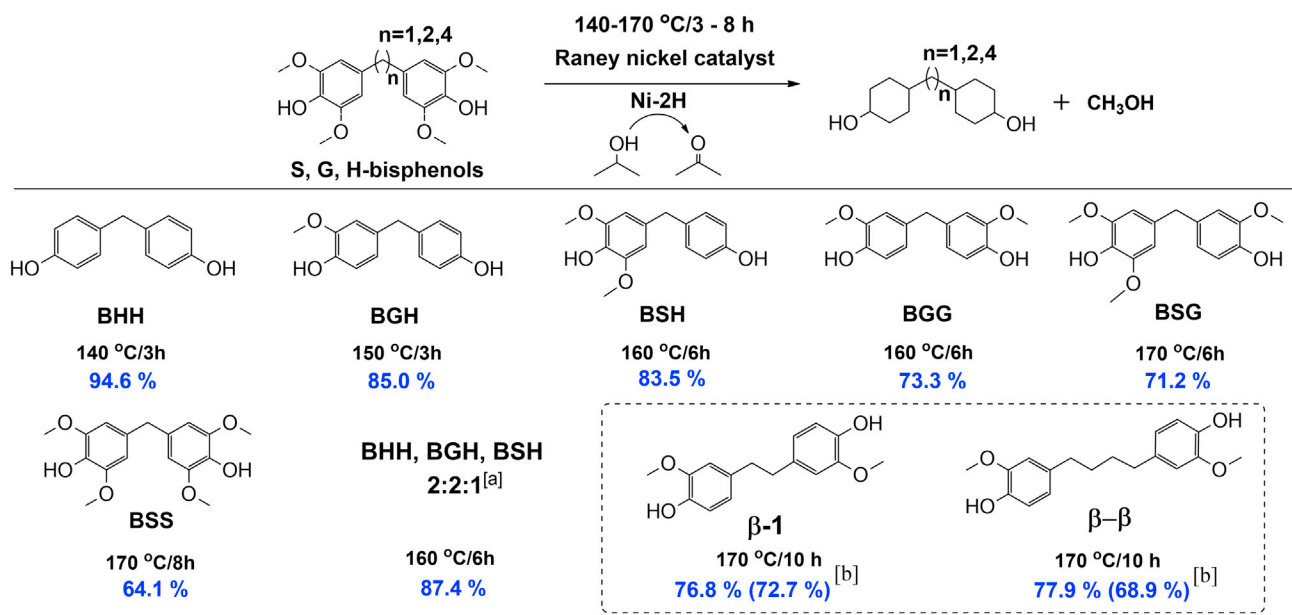
Figure 3. Catalytic demethoxylation and hydrogenation of lignin-derived bisphenols over Raney nickel catalyst
Reaction conditions: 0.5 mmol substrate, 100 mg Raney nickel catalyst, 15 mL isopropanol, 10 mg dodecane.
(a) Molar ratio; GC yield was determined using calibration curve and dodecane as internal standard. (b) Yield was determined by GC-FID. Isolated yield in parentheses.

appropriate method to access the desired bisphenol derivatives by electrophilic aromatic substitution was developed. Given the results of catalytic funneling in Figure 3, phenol was chosen as appropriate coupling partner because it can be sustainably produced from birch lignocellulose in 20 wt % yield (based on lignin content),[24] and the reaction results in bisphenol derivatives with at least one phenol moiety lacking further -OCH₃ substitution. First, the reactivity of vanillyl alcohol (G-OH), syringic alcohol (S-OH), and 4-hydroxybenzylalcohol (H-OH) in neat phenol was assessed and the reaction conditions optimized (see supplemental information and Table S1 for more details). Next, a mixture comprising 1 mmol vanillin (152 mg), 0.5 mmol syringaldehyde (91 mg), and 0.5 mmol 4-hydroxybenzaldehyde (61 mg) was subjected to hydrogenation (5 bar H_2, 30 mL ethanol, overnight) over 30 mg of Pd/Al₂O₃ to smoothly deliver a mixture of vanillyl alcohol (G-OH), syringic alcohol (S-OH), and 4-hydroxybenzylalcohol (H-OH), in an excellent, 94.8% yield (292 mg) (Figures S64A and S64B). Subsequently, the benzyl alcohol mixture was subjected to reaction in neat phenol over Amberlyst 15. During optimizations, it was found that at least 10 equivalents of phenol are necessary to achieve excellent selectivity and avoid the formation of trimers and oligomers, as evident from GPC (Figure S53). As a result, a mixture of p-p'/m-p'-bisphenols (BHH, BGH, and BSH, total 363 mg) was obtained in a high, 78.9% yield (Table S1; Figure S64C). After recycling of residual phenol (1.54 g) by distillation in vacuum (105°C at 1 mPa for 1 h), the mixture was subjected to the Raney nickel-catalyzed demethoxylation/hydrogenation protocol at 160°C for 6 h, to give m-p'/p-p'-MBC isomers (264 mg) (m-p':p-p' = 15:85), in an overall yield of 62.3% based on the aldehyde mixture. In addition, 44 mg of 6A (dodecahydro-1H-fluorene), a C13 cyclic hydrocarbon (Figure S64D), was obtained as a side product, which has favorable properties (density, 0.96 g/mL; freezing point, 258.0 K) to serve as jet fuel.[68,69] To provide a clear overview regarding the amount of lignin and phenol required for the production of desired amount of MBC, starting from various lignin and wood species, please refer to Notes S3 and S4.
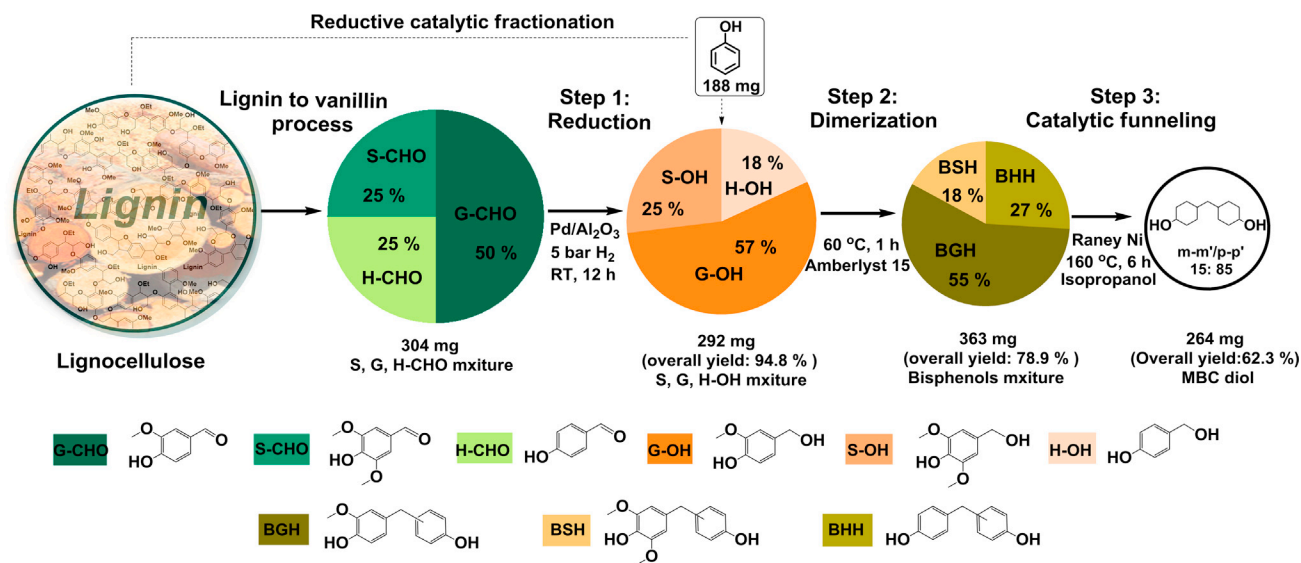
Figure 4. A catalytic strategy for the production of MBC from aldehyde mixture (modeling the lignin to vanillin process)
Step 1: 0.5 mmol 4-hydroxybenzaldehyde, 0.5 mmol syringaldehyde, and 1 mmol vanillin, 30 mg Pd/Al$_2$O$_3$, 5 bar H$_2$, 30 mL ethanol, RT, overnight.
Step 2: 150 mg Amberlyst 15 catalyst, 1.8 g phenol (188 mg, theoretical amount), 60°C, 1 h.
Step 3: 500 mg Raney nickel catalyst, 30 mL isopropanol, 160°C, 6 h.
Yields were quantified based on original aldehydes mixture by parallel experiments under the same reaction conditions (overall yield [%] = mass of the obtained products/theoretical mass of obtained products by complete conversion of original aldehydes mixtures).

Highly selective catalytic amination of the diol MBC to diamine MBCA

The direct coupling of aliphatic alcohols with ammonia is an attractive prospect to produce primary amines.[70–73] Here, we set out to realize the catalytic diamination of MBC directly to MBCA via the waste-free hydrogen-borrowing methodology. The reaction in question is particularly challenging, since excellent selectivity should be achieved for both of the alcohol moieties and the symmetric diol may also undergo dimerization via secondary amine formation. t-Amyl alcohol, in this case, was selected because it has been successfully used as a solvent for amination reactions, especially toward primary amines.[70,74–75] In addition, in our previous work, we found this solvent highly suitable in the direct amination of benzyl alcohols with ammonia.[70] Indeed, under the tested reaction conditions (170°C, for 18 h reaction time, 7 bar NH$_3$), summarized in Table 2, these products (7A and 8A) were clearly visible, albeit in smaller quantities. Among the range of commercially available or synthesized metal catalysts evaluated, Ni/PMO and Ni/γ-Al$_2$O$_3$ were completely inactive, while the Ni/SiO$_2$-Al$_2$O$_3$ and Ni/SiO$_2$ catalysts showed near identical catalytic behavior, with 87% conversion of MBC and 50% selectivity to MBCA, while still displaying a substantial amount of the mixed amine-alcohol product 7A. Fortunately, a high selectivity toward the primary amine, MBCA, was achieved in almost all cases, except with Ru/C (0.62%). Likely the increase of the partial pressure of NH$_3$ to 7 bar in our system, facilitated imine formation and suppressed the further N-alkylation of MBCA with MBC.[76]

Excellent 98% conversion of MBC and 75.9% selectivity of MBCA were observed with Ru/C as catalyst, although still displaying incomplete diamination. Gratifyingly, using Raney nickel as catalyst, MBCA was obtained in near-perfect (99%) GC selectivity and 96% isolated yield at 170°C, while other reaction temperatures were tested as well (Figure 5B). We attribute the excellent selectivity to the ability of the catalyst to facilitate the two key steps in the hydrogen-borrowing sequence: (1) high activity

Table 2. Evaluation of commercially available heterogeneous and homemade nickel-based catalysts in the one-pot direct catalytic amination of MBC to MBCA[a]
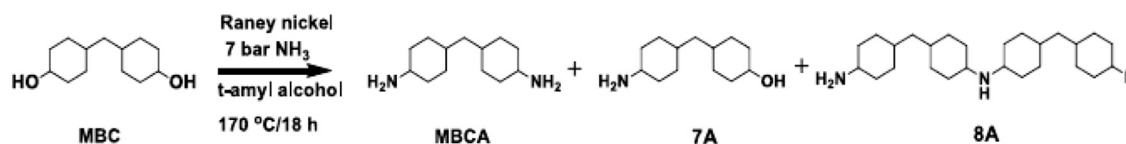
Entry	Metal loading (wt %)	Catalyst	Conversion[b] (%)	Selectivity[b] (%)			Yield[c] (%)
				MBCA	7A	8A	
1	13	Ni/PMO	–	–	–	–	–
2	10	Ni/γ-Al$_2$O$_3$	–	–	–	–	–
3	65	Ni/SiO$_2$-Al$_2$O$_3$	87.9	49.3	50.7	–	40.8
4	64	Ni/SiO$_2$	87.4	50.1	49.9	–	41.2
5	5	Ru/C	98.0	75.9	23.0	0.62	70.5
6	≥89	Raney Ni	100	99.0	–	–	99.0 (96.0)

[a]Reaction conditions: 0.5 mmol MBC (105 mg), 50 mg catalysts, 2.5 mL t-amyl alcohol, 170°C, 18 h, 7 bar NH$_3$, 10 mg dodecane.
[b]Conversion and selectivity were determined by GC-FID.
[c]GC yield was determined using calibration curve and dodecane as internal standard. (isolated yield).

for alcohol dehydrogenation and (2) facile hydrogen transfer to the imine and thereby rapid imine reduction (see also Note S2). After filtration and solvent removal, the obtained crude MBCA was characterized by GC-FID (Figure S65), ^{1}H NMR, ^{13}C NMR, 2D HSQC, and 2D COSY (Figures S66–S69). In addition, no obvious nickel leaching was observed (Table S4) after four cycles, resulting in high reusability (Figure S70).

Synthesis of fully bio-based polybenzoxazine resins from phenolic monomers and MBCA

Next, MBCA was utilized as an aliphatic diamine building block to design fully bio-based polybenzoxazine resins. The novel benzoxazine monomers S-MBCA, PG-MBCA, G-MBCA, and E-MBCA were prepared through Mannich condensation of
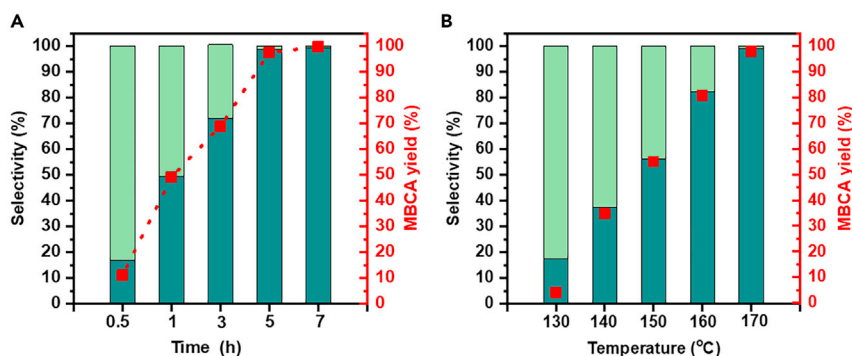
Figure 5. Influence of different parameters on the direct amination of MBC to MBCA
(A) Influence of reaction time; conditions: 0.5 mmol MBC, 50 mg Raney nickel, 2.5 mL t-amyl alcohol, 170°C, 0.5–7 h, 7 bar NH$_3$, 10 mg dodecane; Selectivity was determined by GC-FID
(B) Influence of reaction temperature; conditions: 0.5 mmol MBC, 50 mg Raney nickel, 2.5 mL t-amyl alcohol, 140°C–170°C, 5 h, 7 bar NH$_3$, 10 mg dodecane. Selectivity was determined by GC-FID. Yield was determined by calibration curve using dodecane as internal standard. The red square symbol stands for MBCA yield determined by calibration curve using dodecane as internal standard. The dark green color stands for selectivity to MBCA. The light green color stands for selectivity to 7A.
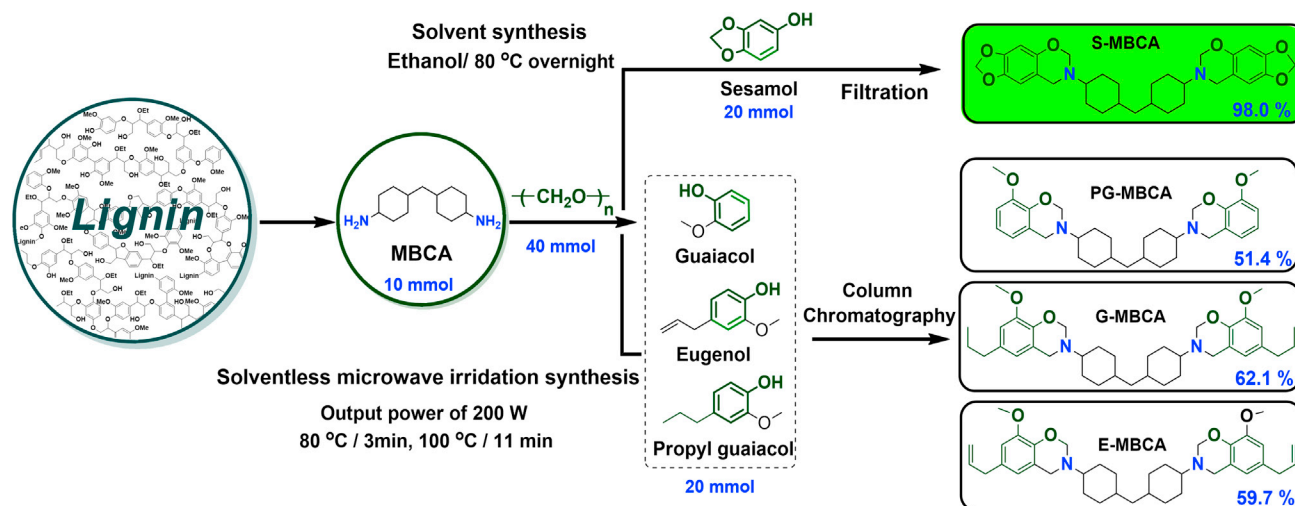
Figure 6. Proposed reaction pathways toward fully biobased polybenzoxazines using lignin-derived monomers
Synthesis of fully bio-based benzoxazine monomers by coupling of the obtained MBCA with guaiacol, propyl guaiacol, or naturally occurring sesamol and eugenol. Synthesis procedure performed either in ethanol as solvent or by solventless microwave irradiation.

MBCA with formaldehyde and four different lignin-derived monophenols: S, propyl guaiacol (PG),[77] G-,[78] and E,[79] as shown in Figure 6. Detailed information on possible sustainable sources of S being vanillin or HMF-derived 1,2,4-benzenetriol, can be found in Note S5. Benzoxazines PG-MBCA, G-MBCA, and E-MBCA were obtained by solventless microwave irradiation (output power of 200 W) at 80°C–100°C for totally 15 min lead, followed by column chromatography, in 51.4%, 62.1%, and 59.7% isolated yield, respectively. Interestingly, S-MBCA could be obtained after a simple filtration in an excellent isolated yield (98%) upon performing the synthesis in ethanol. The obtained S-MBCA, PG-MBCA, G-MBCA, and E-MBCA were structurally characterized by ^{1}H NMR, ^{13}C NMR, 2D HSQC, 2D COSY (Figures 7 and S37–S52), and FTIR (Figure S74). For example, the ^{1}H NMR spectrum (Figure S37) of S-MBCA showed the characteristic signals of O-CH$_2$-N and Ph-CH$_2$-N,[57] characteristic for the benzoxazine ring at 4.89 and 3.96 ppm, respectively. The FTIR characterization further confirmed the formation of the benzoxazine ring by the absorbance bands observed at 930 cm^{-1} (oxazine ring stretching),[80] at 1,147 cm^{-1} (C-N-C stretching),[81] at 1,230 cm^{-1} (C-O-C stretching),[81] and at 1,488 cm^{-1} (-CH$_2$- bending of the methylenedioxy benzene of S.[82]

Secondly, these benzoxazine monomers were subjected to ring-opening polymerization by stepwise curing at 170°C–280°C to give poly (S-MBCA), poly (PG-MBCA), poly (G-MBCA), and poly (E-MBCA). The ring-opening polymerization was confirmed by the disappearance of the characteristic signal at 930 cm^{-1}, which belongs to the benzoxazine ring. The thermal properties of these polybenzoxazines were determined by Differential Scanning Calorimetry (DSC) (Figure S73) and Thermogravimetric Analysis (TGA) (Figure S72); the results are summarized in Table 3. The difference in thermal properties, to a certain extent, depended on the type of lignin-derived phenolic monomers used. Poly (S-MBCA) showed the best thermal stability, with $T_{10\%}$ of 401°C, and its T_g (up to 315°C) was the highest as well, by Dynamic Mechanical Analysis (DMA) characterization. The mechanical properties of poly (S-MBCA) were found to be excellent E' = 3.8 GPa at 25°C, E' = 2.7 GPa at 200°C (Figure S75). These values are comparable with the commercially available polybenzoxazine resins, for example, those produced by Huntsman.[83]
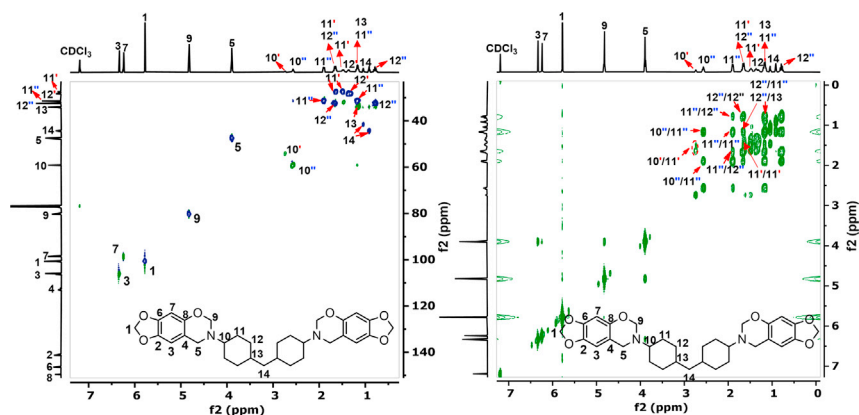
Figure 7. Proposed peak assignments for benzoxazine S-MBCA by 2D HSQC and 2D COSY NMR measurements

10′ stands for 10 *cis-cis*, *cis-trans*, while 10″ stands for 10 *trans-trans*, *cis-trans*.

Conclusion

In conclusion, this work demonstrates the valorization of industrially relevant product mixtures, originating from the lignin to vanillin process, into well-defined chemical building blocks in excellent efficiency. The two, highly selective key catalytic steps of the strategy are the catalytic funneling of bisphenol mixtures into MBC, and the direct amination of MBC with ammonia (96% isolated yield of MBCA from pure MBC). Notably, for both key steps, the commercially available Raney nickel catalyst is most ideal, which underscores industrial relevance. Overall, the strategy enables the efficient conversion of pre-purified mixtures of aldehydes from the lignin to vanillin process, which can be subjected to reduction, coupling with phenol to a mixture of bisphenols (and following the two mentioned catalytic steps), to well-defined molecules in overall high efficiency.

Based on the MBCA building block, a green synthetic approach to obtain high-performance polybenzoxazine resins is presented. These materials display outstanding thermal resistance and good mechanical properties, which is highly relevant in a future bio-refinery context, leading to economic and environmental benefits.

The novel catalytic upgrading method described here, which is capable of converting industrially relevant waste streams to single compounds with minimal purification effort, will contribute to broadening the scope of future bio-refinery methods. Moreover, given their waste- and solvent-free manner of preparation, excellent

Table 3. Mechanical and thermal properties of the prepared polybenzoxazine resins[a]

Entry	Polybenzoxazine	T_m (°C)	T_P[a] (°C)	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield[b] (%)	LOI[c]
1	poly (G-MBCA)	–	246	157	298	336	12.1	22.3
2	poly (E-MBCA)	–	259	144	285	332	19.1	25.1
3	poly (PG-MBCA)	–	263	82	286	304	14.9	23.5
4	poly (S-MBCA)	141	213	315	365	401	12.5	22.5
5	poly (BPA-A)[d]	–	232	173	325	350	29.0	29.1
6	poly (BPF-A)[d]	–	236	162	306	–	46.0	35.9

[a]Polymerization temperature.

[b]Char yield: percentage residual mass left at 800°C.

[c]LOI = 17.5 + 0.4 (char yield).

[d]Commercial bisphenol A and bisphenol F-based polybenzoxazines, cured by aniline (A).[84,85]

thermal and mechanical properties, and industrial relevance, the polybenzoxazines obtained here are attractive examples for emerging bio-based polymers.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact
Further information and requests for the resources and reagents should be directed to and will be fulfilled by the lead contact, Katalin Barta (katalin.barta@uni-graz.at).

Materials availability
All materials generated in this study are available from the lead contact without restriction.

Data and code availability
Full experimental procedures are provided in the supplemental information.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.checat. 2021.10.022.

AUTHOR CONTRIBUTIONS

X.W. and K.B. conceived the project, designed the experiments, and performed data interpretation. X.W. performed all related experiments, collected and analyzed data, performed the synthesis and structural analysis of resins, and provided the first manuscript draft. M.V.G. contributed to data interpretation, resins synthesis, and manuscript revision. K.B. supervised the research and wrote the manuscript. All authors commented on and approved the final manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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