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ARTICLE

Molecular design of sulfonated hyperbranched poly(arylene oxindole)s for efficient cellulose conversion to levulinic acid†

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This contribution is about the design and synthesis of various sulfonated hyperbranched poly(arylene oxindole)s (SHPAOs) with different substituents via a convenient $A_2 + B_3$ polycondensation and subsequent sulfonation as water-soluble and recyclable acid catalysts for the conversion of cellulose to levulinic acid (LA). Whereas their molecular weight (from 2.7×10^3 to 20.2×10^3) and acid density (from 3.4 to 4.8 mmol H^+g^{-1}) as well as the polymer structure, *viz.* hyperbranched or linear analogues, only slightly affect the catalytic performance, the presence of electron-withdrawing substituents on the isatin polymer building block are key to the catalytic efficiency. Among all polymer catalyst designs studied, use of 5-Cl-SHPAOs provided the highest LA yield of almost 50%, directly obtained from ball-milled cellulose in aqueous medium at 165°C, being twice the LA yield of that of unsubstituted SHPAOs. The presence of the 5-chloro-substituent substantially facilitates the hydrolysis of the glycoside bonds. The close vicinity of the oxindole functionality to the sulfonic acid group seems essential to realize such high hydrolysis rates, as chemical protection of the NH group or sulfonation at other positions led to substantially lower LA yields. The presence of the 5-chlorine substituent also retards the glucose isomerisation rate, while slightly increasing the HMF conversion rate to LA. As a result, the catalytic reaction progresses in conditions of low concentration of the most reactive intermediates, fructose and HMF, that otherwise could lead to considerable humin formation. Though hydrophobic interactions are usually invoked to explain such catalytic effects, this contribution suggests also a significant role of the steric proximity of the sulfonic acid group to the oxindole NH group, enabling a kinetic optimization of the reaction cascade through molecular design of the catalytically active acid site.

Introduction

Lignocellulosic feedstock as the major component of plant biomass and inedible feedstock is extensively considered as an ideal raw material for the sustainable supply of biofuels and chemicals in the future.[1-14] Cellulose consists of glucose monomer units connected through β-1,4-glycosidic linkages, leading to a fibrous and crystalline structure with large amounts of intra- and intermolecular hydrogen bonds that render it recalcitrant to hydrolysis.[15-18] So far, various catalytic systems have been developed to transform cellulose into profitable chemicals,[19,20] including sugar alcohols,[21-28] glucose,[29-32] lactic acid,[33-37] 5-hydroxymethylfurfural (HMF),[38,39] levulinic acid (LA),[40-47] ethylene glycol,[48-53] propylene glycol and alkanes.[54,55] Among those attractive approaches, production of LA from cellulose has received significant attention because LA is a unique versatile building block with high chemical reactivity, which makes it useful as an intermediate for the preparation of a number of value-added organic chemicals and products in the biorefinery and polymer industries. For instance, LA can be esterified into levulinate esters such as methyl and ethyl levulinate, which can be used as fuel additives and flavouring agents.[56,57] Additionally, α-angelicalactone and γ-valerolactone (GVL), which are synthesized from LA by hydrogenation, can be used as perfume material, food additive and petroleum blender.[58-64] Furthermore, bioactive chemicals such as 5-bromolevulinic acid[65,66] and 5-aminolevulinic acid[64,67] and plasticizers including diphenolic acid, [64,68-71] 1,4-butanediol, 1,4-pentanediol[72-74] and succinic acid[75-77], can be synthesized from LA.

Mineral acids, such as H_2SO_4,[40,78-86] HCl[87-90] and HBr,[91] are widely utilized as homogeneous catalysts to synthesize LA from cellulosic biomass feedstock. Although these catalytic hydrolysis processes are effective, the mineral acids cause serious environmental pollution, corrosion of equipment, and difficulties in the separation of products and recovery of the catalyst.

Recently, a multitude of solid acid catalysts have been developed for the production of LA from hydrolysis of cellulose as to overcome the disadvantages brought by the use of mineral acids.[8,19,20,92] In 2010, Lucht *et al.* were first to report

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† Electronic Supplementary Information (ESI) available: Synthesis of methylated 5-Cl-SHPAOs, sulfonated linear polymer and other additional synthesis details, characterization data (^1H and ^{13}C NMR, GPC, FTIR etc.) of hyperbranched and linear polymers, additional analytical information and catalysis results. See DOI: 10.1039/x0xx00000x

the application of the heterogeneous acid catalyst Nafion SAC 13 in the catalytic degradation of cellulose to LA in water,[93] but only a few percent of LA were obtained at different temperatures, going up to 190 °C, even after prolonging the reaction time to 3 days. Almost at the same time, sulfonated TiO_2 acid catalyst was prepared and used in the production of LA from cellulose in aqueous media by Wang *et al.*, achieving a 38% yield of LA at 240 °C in 15 min.[94] By grafting the acidic SO_3H groups onto a composite of mesoporous silica and magnetic iron oxide, Fu *et al.* developed a new type of Fe_3O_4-SBA-SO_3H solid catalyst, which can be recycled with the use of a magnet, for the transformation of cellulose into LA, providing a 45% yield of LA at 150 °C after 12 h.[95] In addition, a two-step process to produce LA from cellulose with the use of the heterogeneous catalyst Amberlyst 70 was introduced by Huber *et al.* and gave maximum 28 % yield of LA.[44] The two reaction steps include non-catalytic hydrothermal decomposition of cellulose at 190–270 °C to produce organic water-soluble compounds, including glucose and HMF, and the further reaction with a solid acid catalyst at 160 °C to produce LA and formic acid. Lin and co-workers developed a one-pot catalytic aqueous phase partial oxidation process to produce LA from cellulose over a ZrO_2 catalyst, affording a high yield of LA 52 % at 240 °C in 25 min under 24 bar pressure from 97.2 % N_2 and 2.8 % O_2.[42] Apart from being used in the partial oxidation of cellulose, ZrO_2 was also directly used as a solid acid catalyst to efficiently convert cellulose into LA.[96] Besides, several other heterogeneous catalysts, including $S_2O_8^{2-}/ZrO_2$-SiO_2-Sm_2O_3,[97] HY zeolite,[98] Ru-Al-SBA-15,[99] Al-$NbOPO_4$,[46] Fe-resin,[100] CP-SO_3H-1.69[47] and Amberlyst 70[101] were also utilized to produce LA from cellulose.

Although the ease of catalyst separation and its reusability make heterogeneous catalysis preferable over homogeneous catalysis, the formation of undesired side products in the catalytic processes, such as soluble and insoluble humins, which can deposit on the catalyst surface or in the catalyst pores, requires cumbersome catalyst regeneration. This issue suggests a need to design and develop a new type of catalyst, combining both advantages of homogeneous and heterogeneous catalysts, for the LA production from degradation of carbohydrates in aqueous media.

We previously reported the synthesis of hyperbranched poly(arylene oxindole)s (HPAOs) in a one-step A_2 + B_3 polycondensation via superelectrophilic arylation of isatin, which is a more attractive synthesis strategy than the classical AB_x polycondensation as the required monomers are usually more conveniently obtained.[102,103] The macromolecular architecture of the resulting hyperbranched polymers gives rise to some attractive features, such as potentially high functional group densities, high solubility and low viscosity, for catalytic application.[104-110] We furthermore functionalized this HPAOs by controlled sulfonation in oleum affording a new class of water-soluble acid catalyst–sulfonated hyperbranched poly(arlene oxindole)s (SHPAOs). This acid material was then successfully used in the catalytic conversion of cellulose and other biomass-derived carbohydrates to LA in water at mild temperature and exhibited comparable catalytic performance to H_2SO_4 (29.5% LA yield) with the significant advantage of recyclability.[45] Moreover, SHPAOs also found their efficient utilization in acid-catalysed condensation between LA and phenol to form diphenolic acid.[70,71]

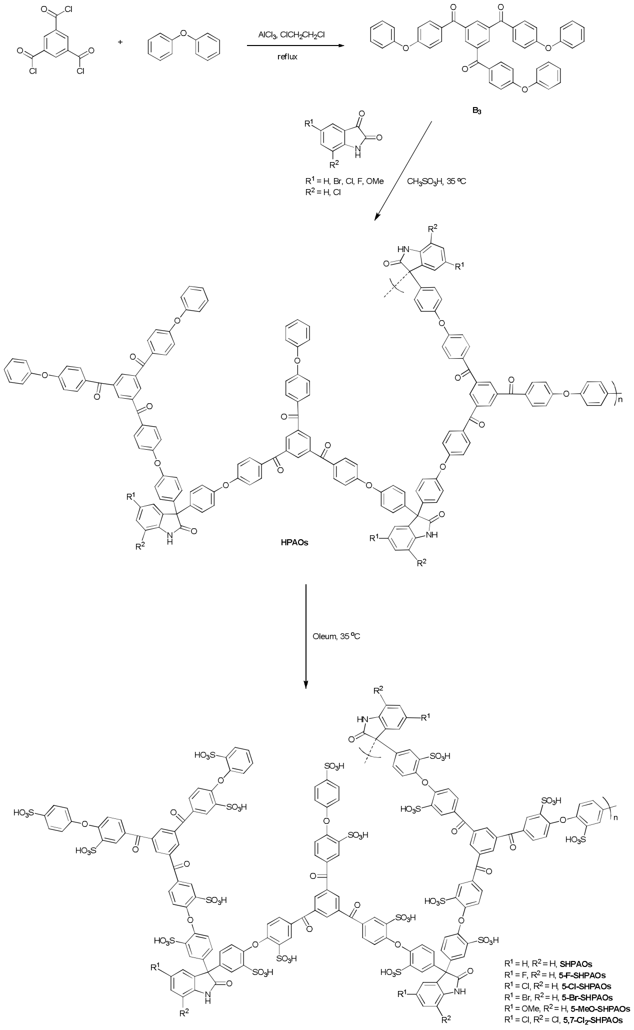
In this study, a series of new SHPAOs with different substituent groups to adjust the catalytic acid properties were prepared and studied in the catalytic conversion of cellulose and other biomass-derived carbohydrates into LA in water. The substituent modification on the hyperbranched polymer catalyst significantly affects its catalytic efficiency of producing LA from carbohydrates.

Results and discussion

Synthesis of sulfonated hyperbranched poly(arylene oxindole)s

Following our previously reported A_2 + B_3 polymerization approach, a series of hyperbranched poly(arylene oxindole)s were prepared via superelectrophilic arylation of various substituted isatins with a B_3 partner. As shown in scheme 1, B_3 monomer 1,3,5-tri-(4-phenoxylbenzoyl)benzene was first synthesized by a typical Friedel-Crafts acylation of benzene-1,3,5-tricarbonyl trichloride with diphenyl ether. In a superacidic environment, B_3 monomer was then condensed readily with doubly protonated substituted isatin, acting as the A_2 monomer, to give hyperbranched poly(arylene oxindole)s in high yield. The absence of resonance signals from the starting isatin in the ^1H NMR spectrum of the resulting polymer, as well as the occurrence of a ^{13}C NMR signal at around 62, indicates complete integration of the A_2 units in the macromolecular structure during polymerization (see ESI). As shown in Scheme. S1, the methylation of hyperbranched poly(arylene oxindole)s was achieved by treatment with methyl iodide in basic reaction media. In the ^1H NMR spectrum, the occurrence of the single peak at around 3.21 and the disappearance of the resonance signal from the NH group at around 11.0 revealed that the hyperbranched polymer was fully methylated. The average molecular weight $\overline{M}_n$ and the polydispersity index of the resulting polymer were evaluated by GPC and can be found in the ESI.

Compared to dendrimers, the hyperbranched poly(arylene oxindole)s may contain more branching defects. However, the remarkably easy one-step synthesis procedure and the large potential for further functionalization at the free *ortho-* and *para* positions with respect to the ether groups and even at the reactive position on the oxindole groups make them more attractive for practical applications. The polymer was functionalized into an acid catalyst through sulfonation in oleum. By adjusting the SO_3 concentration of oleum used in the sulfonation treatment, the density of sulfonic acid groups in the hyperbranched structures can be regulated. In the ^1H NMR spectrum of the resulting hyperbranched polymer acid, the typical shift of the characteristic signals for the aromatic ether moieties evidences successful functionalization (see ESI). In addition, the sulfonation of the polymer upon oleum treatment is also evident from the corresponding FT-IR spectra. For instance, in the FT-IR spectrum of 5-Cl-SHPAOs, the appearance of two intense vibrational signals at around 1017 and 1081 cm^{-1} are attributed to asymmetric and symmetric SO_3 stretching vibrations, respectively. Elemental analysis of the sulfonated polymer shows an approximate sulfur content of 16.4 % in the polymer, revealing the presence of *ca.* 1.0 sulfonyl group per aromatic ring. Additionally, the acid density of the sulfonated polymers were measured by back titration with a 2 M NaCl and 0.001 M NaOH solution using a Metrohm 808 Titrando antotitrator & 801 stirrer. The titration experiments were performed in duplicate and values were confirmed in the range of 3.4–4.8 mmol H$^+$ g^{-1}.



Scheme 1 Synthesis of various sulfonated hyperbranched poly(arylene oxindole)s.

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of the sulfonated hyperbranched polymer. It is worth noting that a dehydrating pretreatment for the sample was employed before TGA measurement concerning high water physisorption of this highly hydrophilic acid catalyst, which was confirmed to be about 20% water content in the polymer on the basis of the mass loss at 373 K for 1 h. Typically, Fig. S3 shows the TGA results from sulfonated hyperbranched polymer catalyst 5-Cl-SHPAOs, indicating that the sample contains 20.4% of water. A marginal weight loss of 3% over a temperature range of 100–250 °C is due to the further loss of a small amount of remaining water in the catalyst. Furthermore, the TGA results reveal that the sulfonated polymer is rapidly decomposed when the temperature reaches above 270 °C.

Catalytic conversion of cellulose into LA

Initially, acid-catalysed hydrolysis of microcrystalline cellulose (Avicel PH-101 type), pretreated by ball-milling, was explored using a series of sulfonated hyperbranched poly(arylene oxindole)s as catalysts. In the presence of an equivalent catalyst loading (based on 0.17 mmol H$^+$), the catalytic reaction of cellulose to LA was carried out at 165 °C for 5 h in water with 2 wt% of cellulose content. The results from the reactions are summarized in Table 1.

Of all sulfonated hyperbranched polymers, 5-Cl-SHPAOs gave the highest yield of 48% LA, with one equivalent of formic acid, along with a little amount of intermediate degradation products, such as 1.2% of HMF and 1.8% of levoglucosan, and ignorable quantities (<1%) of glucose, fructose and furfural (Table 1, entry 2). Besides 5-Cl-SHPAOs, all other sulfonated hyperbranched polymers such as 5-Br-SHPAOs, 5-F-SHPAOs and 5,7-Cl$_2$-SHPAOs, with electronegative halogen substituents, afforded higher than 40% yields of LA, among them 5-F-SHPAOs showed an as high as 47% LA yield (Table 1, entries 1, 3 and 5). The overall superior results from these polymers catalysts with halide substituents imply that properly increasing the acid strength of the polymer catalyst is beneficial to enhance its catalytic efficiency for the conversion of cellulose into LA. Indeed, the sulfonated hyperbranched polymer 5-MeO-SHPAOs, with an electron-donating substituent MeO at 5 position in oxindole structure, only gave a 38% yield of LA, which represented the lowest catalytic efficiency in all sulfonated hyperbranched polymers shown in Table1

Notwithstanding the electron-withdrawing groups, a significant drop in LA yield was observed in presence of the doubly halogenated sulfonated polymer, 5,7-Cl$_2$-SHPAOs, with two chlorine groups substituted on the 5 and 7 positions of the oxindoles (Table1, entries 2 and 5). A similar drop in LA yield was also found with oxindole-protected methylated 5-Cl-SHPAOs (Table1, entry 6), which showed lower catalytic efficiency (41%) in the production of LA, compared to the non-methylated 5-Cl-SHPAOs, therefore implying an important role of the free oxindole NH group in the catalytic system.

For comparison, H_2SO_4 and HCl, two most common mineral acids utilized in biomass conversion, were also used as reference acid catalyst for the conversion of cellulose to LA, and gave 29% and 32% yields of LA, respectively (Table1, entries 7 and 8). Compared to H_2SO_4, a slight increase in LA yield from HCl was observed, which is consistent with the previous report,[111] probably resulting from the more beneficial effect of Cl^- on cellulose conversion than that of SO_4^{2-} and HSO_4^-.

It is worth noting that, although the synthesized sulfonated hyperbranched poly(arylene oxindole)s possess a range of average molecular weight and acid density of sulfonic acid groups, the effect from these variations on the catalytic performance in the degradation of cellulose into LA is negligible. The control experiments for non-substituted hyperbranched polymer SHPAOs with different average molecular weight and acid density are found in the supporting information (see Fig. S2). In the study, SHPAOs with the average molecular weight ranging from 2.7 × 10^3 to 20.2 × 10^3 and the acid density ranging from 3.4 to 4.8 mmol H^+g^{-1} were compared in the catalytic hydrolysis of cellulose into LA at 165°C in water in presence of the same amount of catalyst based on sulfonic acid groups quantity. After 5 h reaction, the yields of LA from all these polymer catalysts showed to be very close, fluctuating in a very short range from 30 to 33%. Therefore, we conclude that the molecular weight of the polymer catalyst and the acid density, within the tested ranges, are no key parameters for the acid-catalysed conversion of cellulose to LA.

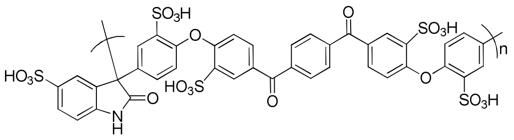


Fig. 1 Schematic representation of the sulfonated linear poly(arylene oxindole)s.

For comparison, a new linear polymer was synthesized via superelectrophilic arylation of A_2 monomer isatin with B_2 monomer 1,4-phenylenebis((4-phenoxyphenyl)methanone) in super acidic media, followed by further sulfonation treatment to give rise to sulfonated linear poly(arylene oxindole)s, as shown in Fig. 1. The details on both synthesis and characterization of this sulfonated linear polymer can be found in the ESI. Under the same reaction conditions, this sulfonated linear polymer was also tested in the catalytic degradation of cellulose, giving a comparable yield of LA (32%) to its corresponding non-substituted sulfonated hyperbranched polymers. However, considering the synthetic difficulty, like requiring the harsh trifluoromethanesulfonic acid instead of methanesulfonic acid as the solvent for polymerization, and physical properties of linear polymer, such as high viscosity and low solubility, the macromolecular catalyst with hyperbranched polymer structure is still the preferable catalyst of choice.

To understand why halogen substituents on sulfonated hyperbranched polymers could bring notable promotion in the catalytic hydrolysis of cellulose into LA, both sulfonated 5-chloroisatin (SO_3H-5-Cl-Isatin) and sulfonated B_3 monomer (SO_3H-B_3), two structural constituents in the 5-Cl-SHPAOs catalyst, were prepared under identical reaction conditions and investigated as acid catalyst in the selective catalytic cellulose to LA conversion in water with the same molar amount of acidity, *viz*. 0.17 mmol, based on the sulfonic acid groups.

As illustrated in Fig. 2, the distribution of soluble products from the two sulfonated monomers seems evidently different. SO_3H-5-Cl-Isatin provided LA and glucose, the main degradation products, with 24% and 37% yield respectively, whereas a 31% yield of LA was observed from SO_3H-B_3 as the only main product. Besides, small amounts of hydrolysis products such as fructose, levoglucosan, HMF and furfural were detected in both monomer catalytic reaction systems. Moreover, in the SO_3H-5-Cl-Isatin catalytic system, a 70% combined yield of the products was obtained, which is much higher than the 36% yield in the presence of the SO_3H-B_3 system. These results seem to indicate a dominant cellulose hydrolysis role of the SO_3H-5-Cl-Isatin system, while the SO_3H-B_3 part of the polymer system seems relatively faster in converting hexoses into LA within the cascade.

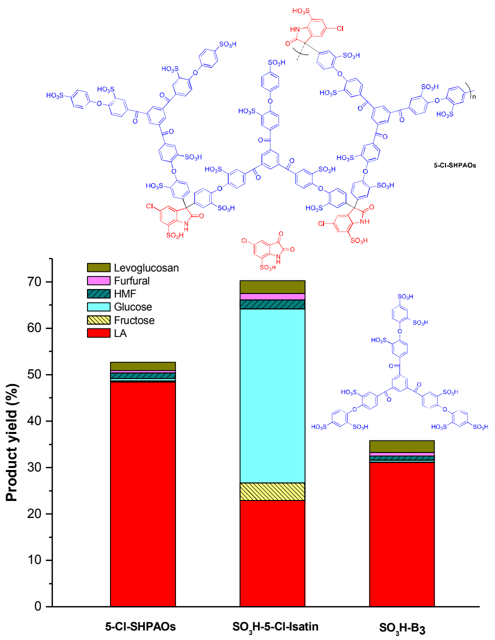


Fig. 2 Comparison of sulfonated monomers with 5-Cl-SHPAOs for the catalytic degradation of cellulose. Reaction conditions: 0.17 mmol H^+ in added catalyst, 40 mg of celllulose, 2 ml of H_2O, 165 °C, 5 h. On top of the bars, the structure of SO_3H-5-Cl-Isatin is shown in red, while the representative structure of SO_3H-B_3 is presented in blue.

Expectedly, the result of the product distribution from the hyperbranched 5-Cl-SHPAOs system was a perfect combination of results from both sulfonated monomers. In this polymer catalyst system, an obvious increase in LA yield was observed when compared to the SO_3H-B_3 system. At the same time, a significant drop in glucose yield was also found when compared to the SO_3H-5-Cl-Isatin system. Therefore, the results demonstrate that the sulfonated 5-chloroisatin is the crucial part of the 5-Cl-SHPAOs catalyst, playing an important

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Table 1 Acid-catalyzed conversion of cellulose into levulinic acid in water using various sulfonated hyperbranched poly(arylene oxindole)s[a]

Entry	Catalyst	Average $\overline{M}_n$	Acid density (mmol H^+/g)	Product yield (%)						Carbon balance (%)
				LA	Glucose	Fructose	HMF	Furfural	Levo glucosan	
1	5-Br-SHPAOs	10.1×10^3	4.3	40	0.9	0.6	1.0	0.4	1.4	44
2	5-Cl-SHPAOs	11.2×10^3	4.1	48	0.5	0.3	1.2	0.5	1.8	53
3	5-F-SHPAOs	12.1×10^3	4.4	47	0.8	0.4	0.9	0.6	0.7	51
4	5-MeO- SHPAOs	6.4×10^3	3.6	38	0.7	0.6	0.9	0.5	1.6	43
5	5,7-Cl_2-SHPAOs	20.6×10^3	3.4	41	0.3	0.2	0.7	0.3	2.1	45
6	Methylated 5-Cl-SHPAOs	12.0×10^3	3.8	41	0.8	0.4	0.7	0.5	0.9	45
7	H_2SO_4	–	–	29	0.6	0.6	1.2	0.6	1.4	33
8	HCl	–	–	32	0.6	0.4	0.8	0.5	1.1	36

[a] Reaction conditions: 0.17 mmol H^+ in added catalyst, 40 mg of celllulose, 2 ml of H_2O, 165 °C, 5 h.

Table 2 Catalytic hydrolysis of other biomass-derived carbohydrates using sulfonated 5-Cl-SHPAOs[a]

Entry	Substrate	Time (h)	Product Yield (%)						Carbon balance (%)
			LA	Glucose	Fructose	5-HMF	Furfural	Levoglucosan	
1	5-HMF	1	79	0.1	0.2	–	–	0.5	80
2	D-Fructose	1	66	1.1	–	–	0.8	2.2	70
3	D-Glucose	5	51	0.2	0.2	2.1	0.6	0.8	55
4	Xylose	1	–	–	–	–	33.2	–	33
5	Sucrose	5	55	0.6	0.8	0.7	0.4	1.6	59
6	Cellobiose	5	43	19.3	1.3	0.9	0.7	0.6	66
7	Inulin	5	63	0.9	0.4	–	0.3	0.7	65
8	Starch	5	30	24.5	2.8	0.9	0.6	1.3	61
9	Starch	7	50	0.3	0.3	0.5	0.6	1.1	53

[a] Reaction conditions: 5-Cl-SHPAOs catalyst (0.17 mmol H^+), 40 mg of each substrate, 2 ml of H_2O, 165 °C. Full conversion (>99%) was achieved in all cases.

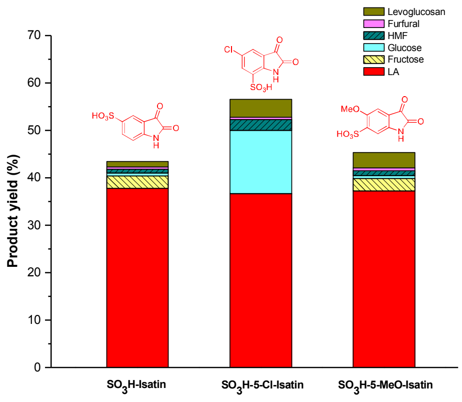

Fig. 3 Comparison of sulfonated isatin monomers in the catalytic performance for the degradation of cellulose. Reaction conditions: 0.23 mmol H^+ in added catalyst, 40 mg of celllulose, 2 ml of H_2O, 165 °C, 5 h. The structure of sulfonated isatin monomer is presented on top of the corresponding bar in red.

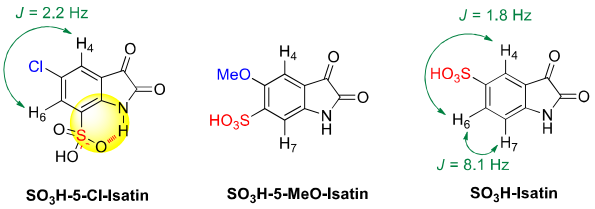

Fig. 4 The structures of different sulfonated isatins.

role in improving the LA yield through efficient hydrolysis of cellulose to glucose, while the sulfonated backbone assists the formation of LA.

To further investigate the effect of the substituent in the isatin constituent, control experiments with three representative sulfonated isatins were conducted. In each reaction, 0.23 mmol of sulfonated isatin monomer was employed for a 5 hours catalytic reaction of cellulose at 165 °C. The results and chemical structures of the isatins are shown in Fig. 3.

SO_3H-5-Cl-Isatin clearly provided the highest overall soluble products around 57% in the reaction solution, with comparable yield of LA (36%) to the other two sulfonated isatins, SO_3H-5-MeO-isatin and SO_3H-isatin. A high glucose yield of 13% was obtained in the presence of SO_3H-5-Cl-isatin, while the amounts of glucose produced from the other two catalytic systems were ignorable. On the contrary, a negligible amount of fructose was detected in the SO_3H-5-Cl-isatin system, while around 3% of fructose still remained in both SO_3H-5-MeO-isatin and SO_3H-isatin catalytic systems. These results suggest that the reaction with SO_3H-5-Cl-isatin is more efficient at the step of forming glucose and consequently it gave more efficient catalytic performance for the conversion of cellulose, compared with the reactions using SO_3H-5-MeO-Isatin or SO_3H-Isatin. As suggested earlier,[112] the binding ability of the chloro-substituent to cellulose through hydrophobic interaction and hydrogen bonding, and the certain positive effect of the chloro substituent on disrupting hydrogen bonds of the cellulose structure, may be considered as possible reasons for the distinct variation in catalytic performance. The exact nature of the interaction however is not yet well understood and will in our view require more dedicated future experiments and modelling work.

It is important to realize that the sulfonation of the three isatins occurs at different positions as observed by ^1H NMR of the sulfonated isatins through calculating J-coupling constants (see ESI). It was confirmed that the sulfonic acid group is introduced at the 5, 7, and 6 position in the reactants isatin, 5-chloroisatin and 5-methoxyisatin respectively, as shown in Fig. 4. In the ^1H NMR spectrum of SO_3H-5-Cl-isatin, the value of the coupling constant between two remaining hydrogens in the isatin structure after sulfonation was calculated to be 2.2 Hz, which is in the range of constant values characteristic of meta coupling. This result implies that the sulfonic acid group substitution took place at position 7 of the isatin structure in view of the fact that *meta* hydrogens could only be in position 4 and 6. For SO_3H-isatin, both *ortho*- and *meta*- coupling occurred between hydrogens in the isatin structure with J-coupling constants of 8.1 and 1.8 Hz respectively, indicating that the substitution position was at 5. In the case of SO_3H-5-MeO-isatin, the absence of coupling between two hydrogens is indicative of the *para* position of the remaining hydrogens and the hydrogen at position 6 was substituted with a sulfonic acid group. These substituent differences need to be taken into account in order to understand the variation in the catalytic efficiency for the different sulfonated isatin catalysts in the catalytic conversion of cellulose to LA, in particularly the cellulose hydrolysis step. Thus, besides the binding ability of the chlorine substituent, the superior catalytic performance from SO_3H-5-Cl-isatin more likely results from the close steric distance between the sulfonic acid group and the NH group, which could mimic the separate acid-base pair in the cellulase active site. After protonation of the glycoside oxygen by a sulfonic acid group, the nearby NH group may act as a weak base, interacting with the anomeric carbon of the glucose unit, to facilitate the catalytic hydrolysis process.[113] Moreover, the formation of an intramolecular hydrogen bond between a sulfonic acid group and NH group in the polymer catalyst is important, and could facilitate the proton transfer between these two functional groups to improve the synergistically catalytic efficiency for cellulose hydrolysis. Such peculiar neighbouring effect of an acidic proton to other functionalities like phenolic OH has been suggested also in a systematic study by Fukuoka *et al*. recently; they also announced a particularly beneficial effect on the hydrolysis of cellulose to glucose.[31] They explained such effect due to the synergistic action from both the phenolic and carboxylic acid group for the hydrolysis reaction, in which the phenolic group acts as a cellulose-binding site through ether formation or hydrogen bond formation with hydroxyl groups of a cellulose chain, while the adjacent carboxylic acid function acts as the catalytically active site. In our case, such picture suggests that the oxoindole functionality plays a role as cellulose binding site, and therefore mimics the specific binding protein domains of cellulase enzymes.[114-118] Besides, it is likely acting as a weak base to interact with the anomeric carbon of the glucose unit after protonation of the glycoside oxygen, while the sulfonic acid group is the actual protonating site in the polymer system.

The application of 5-Cl-SHPAOs in acid catalysis was further expanded to other carbohydrates, mostly the intermediates during the cascade of cellulose to LA, with the aim to gain more information on the catalytic process of processing cellulose to LA, and to provide insight into the distinct variations in catalytic efficiency by using different sulfonated hyperbranched polymers for the transformation of cellulose into LA. The results are reported in Table 2.

LA yields of the catalytic conversion of 5-HMF and fructose with catalyst 5-Cl-SHPAOs were 79% and 66%, respectively (Table 2, entries 1 and 2), which showed no significant difference from that with non-substituted SHPAOs, providing 76% and 70%, respectively, as reported in our previous study.[45] However, when it comes to the glucose substrate, distinct differences in catalytic performance between these two acid polymer catalysts were clearly observed. As shown in Table 2 entry 3, 5 h reaction was necessary to achieve full conversion of glucose in the presence of 5-Cl-SHPAOs, whereas only about 1 hour reaction was needed to complete the conversion of glucose in presence of the non-substituted SHPAOs. Compared to the catalytic reaction in the SHPAOs system, the reaction rate for glucose conversion to LA in 5-Cl-SHPAOs system thus seems much slower. Nevertheless, the 5-Cl-SHPAOs catalytic system appears to be a more selective catalyst for LA formation, giving a 51% yield of LA from glucose in this work, compared to only 29% in the presence of SHPAOs catalyst according to our previous study.[45] To the best of our knowledge, this value is the highest reported yield so far of LA from glucose at moderate reaction temperature in diluted acidic aqueous media.

To have a better understanding of the evolution of the reaction during the catalytic conversion of glucose to LA, a plot of the product distribution against reaction time for the dehydration of glucose in the presence of 5-Cl-SHPAOs at 165 °C was made as shown in Fig. 5. With time, LA and formic acid were progressively formed with gradual consumption of glucose. Full conversion of glucose was accomplished within 5 h, accompanied with up to 51% yield of LA. During the reaction, small amounts of hydrolysis products, such as HMF, furfural and levoglucosan, were observed in the reaction solution. Among these products, HMF was found to constantly stay at very low concentration (< 3%) over the entire reaction period, whereas high intermediate HMF concentrations are usually present in typical experiments when using other acid catalysts, also with the non-substituted SHPAOs. Interestingly, also fructose is hardly detected in the reaction solution, while an independent set of reactions with fructose as substrate for the different catalysts showed similar conversion rates.

These results indicate that the isomerization of glucose to fructose is the rate-determining reaction step in the hydrolysis of glucose to LA, and the step of dehydration of fructose into HMF and the subsequent rearrangement to LA are accomplished very rapidly, when 5-Cl-SHPAOs was used as the acid catalyst. Introduction of the 5-chloro-substituent in the oxindole part of the polymer catalyst, therefore seems to slow down the isomerization rate of glucose into fructose, while slightly increasing the LA formation rate from HMF. Likely the polarity match of the hydrophobic halogen, favours a relatively higher HMF to monosaccharide local concentration. Overall, these dissimilarities in the reaction cascade progress result in lower concentrations of fructose and HMF, the two most reactive intermediates in the reaction media, that otherwise would lead to considerable humin formation. Modelling work is in progress to fundamentally understand whether and how the peculiar sterically demanding H-bonded cyclic structure, as presented in Fig. 4 could possibly impact the rate of sugar isomerization.

Another explanation of the high LA yield, with apparently low HMF and fructose intermediate formation, supports on a recent theoretical study that describes the existence of an alternative pathway to LA directly through glucose without intermediate formation of fructose and HMF.[119] In the latter case, the selective activation of particularly less reactive sugar OH groups should occur, which may happen in the presence of sterically demanding acid sites, like that of the six-membered cyclic molecular arrangement of the 5-Cl-indole acid site.

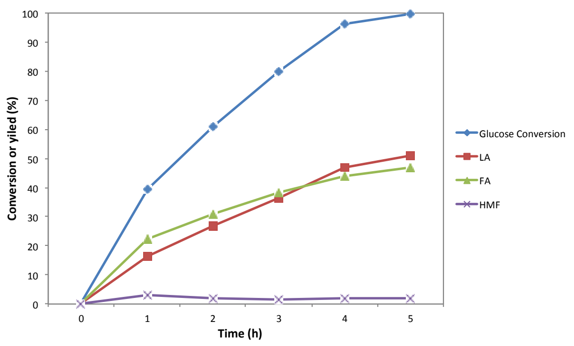

Fig. 5 Product distribution against time in the dehydration of glucose by using 5-Cl-SHPAOs as the acid catalyst at 165 °C

The peculiar role of the chloro-substituted oxindole in the polymer catalyst was also confirmed in the catalytic conversion of sucrose and cellobiose. Sucrose is a disaccharide consisting

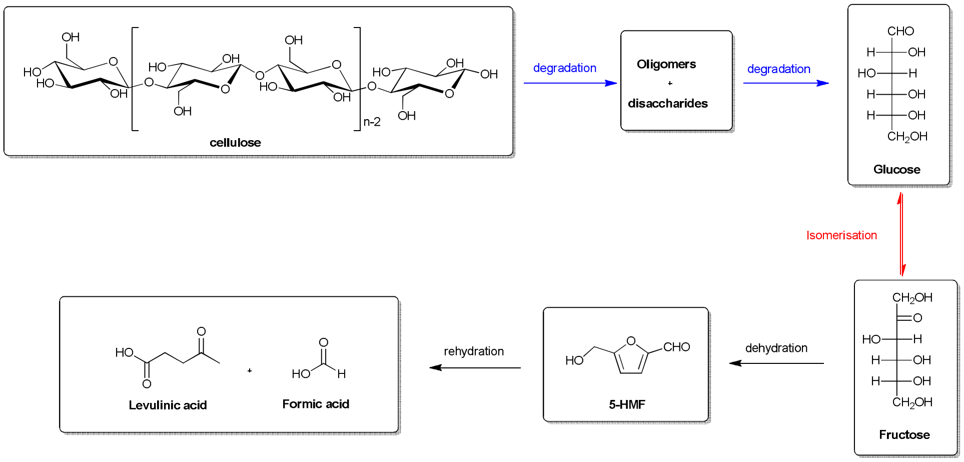

Fig. 6 Reaction pathways for the acid-catalyzed hydrolysis of cellulose to LA.

of glucose and fructose, and cellobiose is a disaccharide consisting of two glucose molecules. The result, presented in Table 2, shows a superior formation of LA of 55% in presence of the chloro-substituent, while only 31% is obtained for the non-substituted polymer. The formation of LA catalyzed by 5-Cl-SHPAOs is also much faster, improving the 40% conversion of sucrose to >99% after 5 h reaction (Table 2, entry 5). Likewise, a clear increase in both LA yield, from 33to 43%, and conversion rate, from 48% to >99% after 5 h, were observed for cellobiose conversion (Table 2, entry 6). Unlike the increase in catalytic efficiency to LA formation, the considerably higher catalytic activity seems surprising considering the slow glucose isomerization rate of 5-Cl-SHPAOs. However, the result is in accordance with the strong hydrolysis capacity of this catalyst when compared with other SHPAOs, as observed in the conversion of cellulose, and likely owing to the peculiar affinity of chlorine to carbohydrate-like substrates in agreement with previous findings of Pan *et al.*[112]

The generally accepted reaction pathways for the acid-catalysed hydrolysis of cellulose into LA acid are shown in Fig. 6. Cellulose is firstly broken down into oligomers and even smaller molecules like disaccharides through cleavage of β-1,4-glycosidic bonds, which is initiated by protonation of the glycosidic oxygens. These hydrolytic products ultimately degrade into glucose. Next, the isomerization of glucose into fructose, proceeding through the enediol form, is widely considered as the key step in the overall cellulose to LA pathway. Through further dehydration of the formed hexoses to 5-HMF and the subsequent rehydration-induced ring cleavage, LA and an equivalent of formic acid are finally formed.

The experimental results provided in this article demonstrate that the chloro-substituents in the sulfonated hyperbranched polymer 5-Cl-SHPAOs catalyst significantly facilitate the decomposition of polysaccharide and oligosaccharide into monomeric sugars, the first two steps shown in Fig. 5, likely due to a favourable binding ability of chlorine next to that of the NH group, to the carbohydrate substrates. Moreover, it was found that the Cl substitution in the oxindole moieties of the polymer catalyst positively contribute to the catalytic efficiency by retarding glucose to fructose isomerization, while facilitating HMF to LA conversion. This contribution likely results from polarity effects and regional steric interaction between the sulfonic acid and NH group of the oxindole through formation of an intramolecular hydrogen bond.

The high catalytic activity and efficiency observed in the conversion of disaccharides to LA using 5-Cl SHPAOs led us to further evaluate the catalytic performance for hydrolysis of other polysaccharides, such as starch, a ubiquitous polysaccharide composed of repeating units of glucose mainly via α-1,4-glycosidic bond linkage. As expected, the starch was completely consumed in the catalytic reaction after 5 h, affording a 30% yield of LA and 25% yield of glucose (Table 2, entry 8). When the reaction time was prolonged for 2 h, the yield of LA increased to 50% with complete consumption of glucose. In addition, inulin, a non-digestible fructose polysaccharide, was also tested as the substrate, giving 62.5% yield of LA after 5 h, which is close to the result of fructose conversion.

The recycling and reuse of hyperbranched polymer catalyst 5-Cl-SHPAOs were examined in the catalytic production of LA from cellulose. Through ultrafiltration, the polymer acid can be fully recycled, and it exhibited complete retention of catalytic activity and selectivity. To evaluate the leaching of sulfonic acid groups in catalyst during the reaction, an experiment of inductively coupled plasma (ICP) measurement was conducted and the result showed that less than 2.6% of the initial sulfonic acid groups had leached into the filtrate solution throughout the reaction. Leaching after a second and third cycle are 2.1% and 1.7% respectively. The catalytic properties of the recycled polymer catalyst are still retained even after three times of recycling (for spectroscopic details see ESI).

Experimental

Procedure for the synthesis of 1,3,5-tri-(4-phenoxylbenzoyl)benzene (B_3 monomer). To the suspension of phenyl ether (50 g, 300 mmol) and $AlCl_3$ (16 g, 120 mmol) in dichloroethane (140 mL) was dropwise added a 1,2-dichloroethane (60 mL) solution of benzene-1,3,5-tricarbonyl trichloride (8.1 g, 30 mmol) at room temperature. Then the mixture was heated to reflux for 2 h. After the reaction mixture had cooled to room temperature, the reaction was poured into ice cold 10% HCl solution (200 mL). The solution was then neutralized with the addition of 10% NaOH and transferred to an extraction funnel. The aqueous layer was washed with CH_2Cl_2 (3 × 150 mL). The combined organic fractions were then washed with brine (1 × 100 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The product (10.1 g, *ca.* 50% yield) was obtained in pure form by two crystallizations from heptane. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 3H), 7.84 (dd, *J* = 6.9, 2.0 Hz, 6H), 7.42 (t, *J* = 7.6 Hz, 6H), 7.22 (t, *J* = 7.4 Hz, 3H), 7.11 (dd, *J* = 8.7, 1.1 Hz, 6H), 7.04 (dd, *J* = 6.9, 2.0 Hz, 6H).

General procedure for the preparation of hyperbranched polymers. To a round-bottomed flask both the A_2 monomer substituted isatin (2.26 mmol) and the B_3 monomer 1,3,5-tris-(4-phenoxybenzoyl)benzene (1.50 g, 2.26 mmol) were added as solids in an equimolar amount, and the appropriate amount of methanesulfonic acid (23 mL) was added. The resulting solution was stirred at 35 ^{o}C for 2 days under N_2. Afterwards, the solution was dropped slowly into ice water. The precipitate was collected by filtration and washed with abundant water and methanol. The solid was dissolved in dichloromethane and then precipitated into methanol. After filtration and washing with methanol, the desired product was obtained. For 5-Cl-HPAOs, product (1.79 g, *ca.* 94 %). ^{1}H NMR (300 MHz, DMSO): δ = 11.00 (br, 1H), 8.19 (br, 3H), 7.85 (br, 6H), 7.69 (br, 1H), 7.09–7.40 (m, 21H); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 177.7, 161.5, 161.1, 154.7, 154.1, 149.1, 140.3, 137.7, 137.6, 133.3,132.7, 132.4, 130.8, 130.6, 130.0, 129.7, 126.3, 124.9, 120.2, 118.7, 117.4, 117.1, 111.8, 61.5. $\overline{M}_n$= 11.2 × 10^3, $\overline{M}_w$/ $\overline{M}_n$= 1.76.

General procedure for the synthesis of sulfonated hyperbranched polymer. To a round-bottomed flask hyperbranched polymer (1.5 g) and 30% oleum (15 mL) were added and the mixture was stirred at 35 ^{o}C for 2 days under N_2. Afterwards, the solution was slowly added into ice and stirred vigorously. After dialysis against water for 7 days (Spectra / Por CE dialysis membrane; molecular weight cutoff: 3500 Da) and removal of water under reduced pressure, the brownish sulfonated product was obtained. For 5-Cl-SHPAOs, product (1.14 g). ^{1}H NMR (300 MHz, D_2O): δ 8.23–8.33 (m, 6H), 7.39–7.91 (m, 10H), 6.92–7.09 (m, 5H); ^{13}C NMR (75 MHz, D_2O): δ = 190.7, 177.8, 174.4, 152.9, 150.0, 133.7, 132.5, 132.4, 130.4, 130.3, 130.1, 129.7, 129.6, 129.2, 128.5, 127.7, 126.4, 126.0, 125.8, 125.6, 123.7, 123.4, 123.1, 121.0, 117.7, 117.1, 117.0, 115.6, 115.0, 94.8, 56.6.

Catalytic reaction procedure. Catalytic experiments were performed in a stainless steel autoclave, equipped with a thermocouple and a magnetic stirrer. For typical runs, 40 mg of substrate, 0.17 mmol H^+ of acid catalyst and 2 mL of water were loaded into a batch reactor under air and mixed by using a magnetic stir bar. The autoclave was then heated at 165 ^{o}C for a specific time under continuous stirring. After the reaction, the reactor was removed from the heating and rapidly cooled down in an ice bath. The product mixture was sampled, syringe filtered with a 0.45 µm PTFE membrane and submitted to analysis.

Analysis procedure for catalytic experiments. Reaction samples such as levulinic acid, glucose, fructose, HMF, furfural and levoglucosan were analyzed by high-pressure liquid chromatography (HPLC) in an Agilent 1200 Series system equipped with isocratic pump and refractive index (RI) detector on a Varian Metacarb 67H column (300 x 6.5 mm), using an aqueous solution of sulfuric acid (5 mM) at a flow rate of 0.7 mL min^{-1} and a column temperature of 35 ^{o}C. Quantification of each compound was based on calibration curves obtained by analysing standard solutions with known concentration.

More details on the synthesis and characterization of the acid catalysts, and experimental procedures are provided in the ESI.

Conclusions

Levulinic acid (LA) is one of the most unique chemicals that can be derived from carbohydrate biomass. Though the reaction cascade is rather complex, acid catalysis allows its direct formation through subsequent hydrolysis, isomerization, dehydration, rehydration and rearrangement steps. To efficiently convert carbohydrates like cellulose to LA, many different catalytic requirements need to be fulfilled by the acid. In an attempt to overcome such challenge and to bring variation in the properties of the (neighbourhood of the) catalytic acid sites, a series of sulfonated hyperbranched poly(arylene oxindole)s were prepared containing different sulfonic acid sites, an aromatic one at the polyaryl backbone and one located at the heterocyclic oxindole moiety. Both acid sites were able to convert carbohydrates into LA, but the heterocyclic one seems most efficient in the hydrolysis step. Though the acid density and the molecular weight of the polymer has less impact on the catalysis, variation of substituents on the oxindole part reveals large effects. Best results were obtained with 5-Cl-SHPAOs, which afforded record values of up to 50% LA yield from cellulose in water. The presence of the 5-Cl, next to the indole group, facilitates the hydrolysis of glycoside bonds, likely due to the binding effect of the NH group close to the sulfonic acid, resembling the cellulose active site, while the peculiar molecular arrangement of the sulfonic acid, e.g. via the formation of a 6-membered ring hydrogen bond, also leads to a retardation of glucose isomerization and a slight fastening of HMF to LA conversion. Though the molecular understanding requires deeper future modelling efforts, the experiments overall demonstrated that such proximity effects beneficially influence the cascade kinetics towards more LA formation by avoiding (a high concentration of) the two most reactive intermediates, fructose and HMF. The enormous flexibility of polymer chemistry will be further explored in future research with other binding sites and different molecular organisation of the acid sites in order to further improve the yields of LA from cellulose by molecular design.

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