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Thiol-promoted catalytic synthesis of diphenolic acid with sulfonated hyperbranched poly(arylene oxindole)s†

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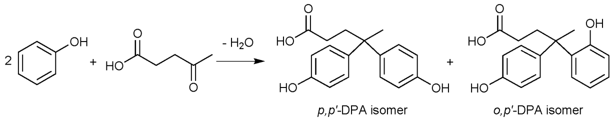
Acid-catalyzed condensation of levulinic acid and phenol into high yields of diphenolic acid (>50%) is possible with a combination of sulfonated hyperbranched polymers and thiol promotors, either added as a physical mixture or bound to the polymer by ion-pairing.

An ongoing objective in the development of biorefineries is the incorporation of carbohydrate-derived platform molecules in existing petrochemical processes.[1] Recent studies suggest that levulinic acid (LA), a hydrolysis/dehydration product of lignocellulosic biomass, can meet this need.[2] One reaction of current interest is the condensation between LA and phenol to form diphenolic acid (Scheme 1), a potential replacement for bisphenol A in the synthesis of polyesters and polycarbonates.[3] To date, the synthesis of diphenolic acid (DPA) has been investigated using acid catalysts such as H_2SO_4,[4] HCl,[5] Cs-substituted Wells–Dawson type heteropolyacids,[6] and mesoporous $H_3PW_{12}O_{40}$–silica composites.[7] However, there is still a considerable incentive for the development of effective alternative acid catalysts.[8]

In this study, we report the use of a new class of acid catalysts, *i.e.*, sulfonated hyperbranched poly(arylene oxindole)s (SHPAOs), of which the unsubstituted precursor is prepared in a one-step $A_2 + B_3$ polycondensation *via* superelectrophilic arylation of isatin.[2a,9] The macromolecular architecture of the resulting hyperbranched polymers gives rise to attractive features for catalytic application such as potentially high functional group densities, improved solubility and low solution viscosity.[10] The present authors have previously reported an efficient method for the functionalization of the polymers by controlled sulfonation in oleum (30% SO_3),[2a] resulting in hyperbranched structures with a relatively high acid density of 4.3 mmol H^+ g^{-1}. Thermogravimetric analysis (TGA) results have indicated a thermal stability of the polymers up to *ca.* 573 K. More details on the synthetic conditions and the characterization of the as-prepared acid catalysts can be found elsewhere.[2a]



Scheme 1 Condensation of levulinic acid and phenol to diphenolic acid.

Table 1 summarizes the catalytic data for the synthesis of DPA using different sulfonic acid-functionalized polymer catalysts and the commercially available $H_3PW_{12}O_{40}$. Entries 1–4 show the conversion of LA, the yield of DPA, the turnover frequency (TOF) at acid sites and the molar ratio of the desired *p*,*p*′-DPA isomer over the *o*,*p*′-DPA isomer after 16 h reaction at 373 K in an inert atmosphere. At a constant amount of acid sites of 0.22 mmol H^+ (equivalent to the amount of protons in 0.05 g of the title catalyst), the activity of SHPAOs exceeds the performance of the ion-exchange resins tested, achieving a yield of 35% DPA and a TOF of 0.77 h^{-1} at 40% conversion. When $H_3PW_{12}O_{40}$ was used, the selectivity for DPA was lower, albeit at a higher conversion of LA (entry 3). Besides the *o*,*p*′-DPA isomer and phenol oligomers, the most abundant by-products identified in this work were C_{10} LA dimers, *e.g.* 3-(2-methyl-5-oxotetra-hydrofuran-2-yl)-4-oxopentanoic acid, formed by acid-catalyzed dehydration and intermolecular esterification of two LA molecules (for the corresponding GC-MS spectrum, see the ESI†).

The acid strength of sulfonic acid-functionalized catalysts can be characterized by solid-state ^{31}P MAS NMR measurements of the change in chemical shift (δ) of chemisorbed triethylphosphine oxide (TEPO).[11] Increasing δ values are found to be correlated with an increasing acid strength. The ^{31}P NMR spectrum of TEPO chemisorbed on SHPAOs shows a resonance peak at 72.5 ppm with a shoulder at 85.1 ppm (Fig. S3 of the ESI†), indicating the presence of two types of strong Brønsted acid sites. $H_3PW_{12}O_{40}$ shows four signals attributable to the chemisorption of TEPO at 59.2, 68.5, 73.6 and 76.6 ppm, respectively. Similar studies have been reported for the sulfonic acid-functionalized polymer resins, *i.e.*, Amberlyst 15,[12] and Nafion,[13] providing δ values of 86.0 and 88.0, respectively. As both of these polymer catalysts show higher δ values than the SHPAOs, the data in Table 1 suggest that the strength of the acid

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† Electronic supplementary information (ESI) available: Additional experimental and analytical information, GC-MS spectra, solid-state ^{31}P MAS-NMR spectra of the acid catalysts impregnated with TEPO and ^{1}H NMR spectra of the SHPAOs, before and after ionic modification with 2-mercaptoethylamine. See DOI: 10.1039/c2cc30239j

Table 1 Catalytic data for diphenolic acid synthesis[a]

Entry	Catalyst	Additive	Acid density[b]/mmol H^+ g^{-1}	LA conv. (%)	Yield DPA (%)	TOF[c]/h^{-1}	*p,p′* : *o,p′*[d]
1	Amberlyst 15DRY	—	5.00	33.8	17.2	0.49	4.0
2	Nafion NR50	—	0.93	36.3	28.4	0.60	5.8
3	$H_3PW_{12}O_{40}$	—	2.36	55.4	34.2	0.86	8.7
4	SHPAOs	—	4.26	40.0	34.9	0.77	7.6
5	SHPAOs	Benzylthiol	4.26	64.9	44.4	1.15	15.6
6	SHPAOs	Ethanethiol	4.26	69.5	52.9	1.28	19.5
7	SHPAOs	1-Propanethiol	4.26	64.8	51.7	1.05	17.6
8	SHPAOs	1-Butanethiol	4.26	59.5	40.3	0.98	14.0
9	SHPAOs	2-Propanethiol	4.26	53.8	40.8	0.83	12.0
10	SHPAOs	2-Methyl-2-propanethiol	4.26	38.9	28.7	0.70	10.5
11	SHPAOs-MEA[e]	—	4.57	59.2	42.4	0.89	9.8
12	SHPAOs-TEP[f]	—	5.61	56.9	37.1	0.82	15.5

[a] Reaction conditions: 3.4 mmol levulinic acid, 10.2 mmol phenol, 0.22 mmol H^+ in added catalysts, 1 : 1 molar ratio of thiols to sulfonic acid sites (entries 5–12), inert atmosphere, 373 K, 16 h. [b] Determined by acid–base titrations (see the ESI). [c] Calculated as the total number of LA condensation reactions per acid site per hour. [d] Ratio of the *p,p′*-DPA to the *o,p′*-DPA isomer. [e] SHPAOs modified with 2-mercaptoethylamine. [f] SHPAOs modified with 4-(2-thioethyl)-pyridine.

sites is not the only factor determining the catalytic performance for DPA synthesis. In accordance with previous findings,[14] our work seems to provide an example for how catalytic activity can be improved by optimising the accessibility and density of sulfonic acid sites on the dendritic branches of the SHPAOs.

In a first attempt to further improve the yields of DPA, the effect of addition of thiols as a cocatalyst in the reaction medium was investigated (entries 5 to 10). For a 1 : 1 molar ratio of thiols and sulfonic acid groups, significant increases in the TOF, the total selectivity for DPA and in parallel to the desired *p,p′*-isomer are observed. For example, the reaction catalyzed by the physical mixture of SHPAOs and ethanethiol results in 70% conversion of LA with 53% yield of DPA and a *p,p′* : *o,p′* ratio of 19.5 (entry 6). It should be stressed that no condensation products were detected in control reactions with the thiol compounds alone. Whereas the cooperative action of acid–thiol groups is well-established for synthesis of bisphenol A,[15] our results point to a similar catalytic behavior of the SHPAOs for the condensation of LA and phenol. Mechanistically, the cooperative effect originates from the sequential activation of LA, first by protonation of the ketone group, followed by a nucleophilic thiol attack. Zeidan *et al.* have proposed that the formed electrophilic sulfonium intermediate not only accelerates the condensation rate, but also shifts the regioselectivity towards the desired *p,p′*-isomer by introducing steric hindrance due to the side chain of the thiol.[15a–c] The necessity of an accessible thiol function is obvious from the decreased catalytic performance for a series of alkyl thiols with increasing tail length (entries 6–8) or with other kinds of steric protection (entries 9 and 10).

The enhanced catalytic reactivity and regioselectivity achieved with added thiols led us to study the postsynthetic modification of SHPAOs by incorporation of aminothiols. Particular efforts were made for the neutralization of part of the sulfonic acid groups *via* ionic bonding with promotors such as 2-mercaptoethylamine[16] and 4-(2-thioethyl)-pyridine.[17] The incorporation of the thiol promotors as sulfonic acid salts can be monitored by ^1H NMR spectroscopy (see the ESI†). For example, Fig. 1 shows the ^1H NMR spectra of 4-(2-thioethyl)-pyridine and the SHPAOs, before and after modification with 4-(2-thioethyl)-pyridine. In the ^1H NMR spectrum of the modified polymer, the signals of the protons associated with 4-(2-thioethyl)-pyridine shift towards a lower frequency due to changes of the local magnetic field induced by the aromatics of the SHPAOs. However, the protons of the pyridine ring show relatively smaller downfield shifts (<0.2 ppm), which is consistent with a superimposed upfield shift effect of ionic bonding between the amino group of the thiol promotor and the sulfonic acid sites of the SHPAOs.[18]

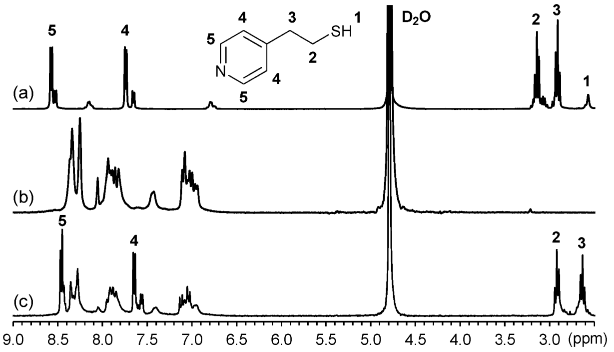

Fig. 1 Comparison of the ^1H NMR spectra of 4-(2-thioethyl)pyridine (a), as-synthesized SPHAOs (b) and SHPAOS after modification with 4-(2-thioethyl)pyridine (c).

Typical results from catalytic reactions with the bifunctional aminothiol-bearing SHPAOs are listed in Table 1. From the data in entries 11 and 12, it is clear that both thiol promotors are responsible for significant increases in regioselectivity for *p,p′*-DPA as well as enhances in the catalytic activity of the SHPAOs. After a prolonged reaction time of 24 h, the yields of DPA could be further increased up to 48% and 45% for the SHPAOs modified with 2-mercaptoethylamine and 4-(2-thioethyl)-pyridine, respectively. In both cases the *p,p′* : *o,p′* ratio remained almost the same at higher conversion values. The relatively lower yields of DPA observed for the modified polymers (entries 11 and 12) compared to those for the reaction with ethanethiol and 1-propanethiol (entries 6 and 7) are tentatively explained by a decreased acid strength of the SHPAOs after modification with the thiol promotors, as was also evidenced by a decreased chemical shift of chemisorbed TEPO in the corresponding ^{31}P MAS NMR spectra (Fig. S4 of the ESI†).

In summary, we have demonstrated how sulfonated hyperbranched poly(arylene oxindole)s in combination with thiol compounds, either added in the reaction mixture as a cocatalyst or bound to the polymer by ion-pairing, act as efficient catalysts for condensation of phenol with levulinic acid to diphenolic acid. Further synthetic studies on fine-tuning the position of thiol and sulfonic acid sites on the hyperbranched poly(arylene oxindole)s are currently ongoing. In parallel, attempts are being made to use the hyperbranched polymers in continuous flow systems,[19] as well as to include lignin-derived phenols as a more sustainable feedstock for the synthesis of renewable bisphenols.[20] Findings from these investigations will be reported in detail elsewhere.

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