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Electronic Supplementary Information for

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

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1 Materials and method

Levulinic acid (98+%), phenol (99.5+%), N-methyl-N-(trimethylsilyl)trifluoroacetamide (97%), pyridine (99+%), 2,4-dimethylphenol (99%), acetonitrile (99.9%), 1-butanethiol (99+%), 1-propanethiol (98%), 2-propanethiol (98%), hydroxylamine hydrochloride (99+%) and 2-methyl-2-propanethiol (99%) were purchased from Acros Organics. 4,4-bis(4-hydroxyphenyl)valeric acid (95%), dimethyl sulfoxide (99,9%), anhydrous pentane (\geq 99%), triethylphosphine oxide (97%), phosphotungstic acid hydrate (H₃PW₁₂O₄₀), Nafion[®] NR50 and Amberlyst[®] 15 hydrogen form (dry, moisture \leq 1.5%) were purchased from Sigma-Aldrich.

Catalytic reactions were carried out in a sealed glass vessel under N₂ atmosphere. In a typical run, 3.4 mmol levulinic acid, 10.2 mmol phenol and 50 mg of the sulfonated hyperbranched polymer were mixed with a magnetic stirring bar and heated to the desired temperature. Prior to product analysis, approximately 0.1 g of the reaction mixture was weighed in a glass vial and mixed with 400 µL of acetonitrile, 100 µL of 2,4-dimethylphenol as external standard and a 1 mL diluted solution of hydroxylamine hydrochloride in pyridine (50 g L⁻¹). After 30 min of heating at 363 K, the samples were derivatized with 1 mL of N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA). To guarantee a complete reaction with MSTFA, the samples were heated for 10-15 min at 363 K. Identification and quantification of the silvlated products were performed using an HP 5890 GC, equipped with a CP-SIL 5CB WCOT fused silica column (30 m x 0.32 mm, DF = 1.0 µm), HP 6890 series injector, HP 7673 controller and FID detector in split/splitless injection mode. One µl of the sample was injected at a split ratio of 1:100 at 553 K. The oven temperature was held at 310 K for 1 min, increased to 348 K at 5 K min⁻¹, followed by a second heating ramp of 12 K min⁻¹ to 563 K and kept there for 25 min.

The formation of phenol oligomers and by-products from levulinic acid condensation was studied by GC-MS using an Agilent 5973 Network Mass Selective Detector coupled to an Agilent 6890N GC with HP5MS capillary column (30 m x 0.25 mm). For example, the representative mass spectrum of by-product 3-(2-methyl-5-oxotetra-hydrofuran-2-yl)-4-oxopentanoic acid is shown in Figure S1.

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Fig. S1 Mass spectrum of 3-(2-methyl-5-oxotetra-hydrofuran-2-yl)-4-oxopentanoic acid detected by an ion trap mass spectrometer.

2 Polymer synthesis and functionalization

The preparation of hyperbranched polymers was achieved by polycondensation of the A_2 monomer isatin and the B_3 monomer 1,3,5-tri-(4-phenoxybenzoyl)-benzene. Synthesis of the latter monomer closely follows the reported procedure,^{1, 2} although the overall product yield could be further optimized up to 79%. To a round-bottom flask both the A_2 (0.11 g) and B_3 monomer (0.50 g) were added and mixed with an appropriate amount of methanesulfonic acid to obtain a concentration of 0.05 M. The polymerization was carried out at 308 K for 2 days under Ar atmosphere. After isolation by precipitation into water, the resulting white powder was filtered, extensively washed with water, again dissolved in CH₂Cl₂ and reprecipitated in large excess of methanol to remove any monomer or oligomer residues.

The polymer (0.52 g) was then treated by sulfonation in oleum at 308 K for 2 days. After dialysis against water for 7–8 days (Spectra/Por CE dialysis membrane; molecular weight cutoff: 3500 Da) and removal of the solvent under reduced pressure, the sulfonated hyperbranched poly(arylene oxindole)s were obtained as brittle flakes (typical recovery 0.53 g), showing excellent solubility in water or methanol but poor solubility in common organic solvents such as THF or CH_2Cl_2 .

3 Modification of the polymer with aminothiol compounds

The thiol modification of the sulfonated hyperbranched poly(arylene oxindole)s was achieved by reacting the polymers with an aminothiol (Figure S2).^{3, 4} To a glass vessel both the polymer (0.1 g) and thiol promotor (0.024 g 2-mercaptoethylamine or 0.030 g 4-(2-thioethyl)-pyridine) were added and mixed with 0.99 g of phenol. The reaction was carried out for 90 minutes at 358 K under N₂ atmosphere.



Fig. S2 Schematic representation of the ionic bonding of 4-(2-thioethyl)-pyridine with the sulfonic acid groups on the sulfonated hyperbranched poly(arylene oxindole)s.

4 Catalyst characterization

Acid-base titrations of the sulfonated hyperbranched poly(arylene oxindole)s and the reference catalysts were performed using a Metrohm 808 Titrando autotitrator & 801 stirrer at room temperature. In a typical experiment, 50 mg of the polymer was added to 10 mL of water containing 2 M NaCl. The resulting mixture was allowed to equilibrate overnight and thereafter titrated potentiometrically by dropwise addition of an aqueous solution containing 0.02 M NaOH.

The acid strength of the catalysts was assessed by monitoring the ³¹P NMR chemical shift of triethylphosphineoxide (TEPO) chemically adsorbed on the acid sites. Based on a procedure reported previously,⁵⁻⁷ 0.1 g of TEPO was dissolved in 4 mL of anhydrous pentane and this solution was mixed with 0.2 g of the dried catalyst. The resulting slurry was allowed to equilibrate under stirring for 25 min before drying at 323 K under vacuum. ³¹P MAS NMR spectra were recorded on a Bruker AMX300 spectrometer (7.0 T), using the single-pulse excitation method. 1046 scans were accumulated with a recycle delay of 60 s. The pulse length was 2.0 us. The samples were packed in 4 mm Zirconia rotors, and the spinning frequency of the rotor was 6 kHz. A solution of 2 mL orthophosphoric acid (85%, Normapur VWR) in 2 mL water was used as chemical shift reference. Figure S3 shows ³¹P NMR spectra of TEPO adsorbed on different acid catalysts: sulfonated hyperbranched poly(arylene oxindole)s (a), sulfonated hyperbranched poly(arylene oxindole)s after modification with 4-(2-thioethyl)-pyridine (b), sulfonated hyperbranched poly(arylene oxindole)s after modification with 2-mercaptoethylamine (c), Amberlyst 15DRY (d) and H₃PW₁₂O₄₀ (e). The ³¹P NMR spectrum of the commercially available $H_3PW_{12}O_{40}$ in absence of TEPO shows a single resonance peak at -15.1 ppm (f).



Fig. S3 ³¹P NMR of chemisorbed TEPO over different acid catalysts: sulfonated hyperbranched poly(arylene oxindole)s (a), sulfonated hyperbranched poly(arylene oxindole)s after modification with 4-(2-thioethyl)-pyridine (b), sulfonated hyperbranched poly(arylene oxindole)s after modification with 2-mercaptoethylamine (c), Amberlyst 15DRY (d) and $H_3PW_{12}O_{40}$ (e). In addition, the ³¹P NMR spectrum of the commercially available $H_3PW_{12}O_{40}$ in absence of TEPO is shown (f).

Structures of the polymers, before and after thiol modification, were confirmed by ¹H NMR spectra (Figure S4), recorded on a Bruker AMX 400 (400 and 300 MHz). Gel permeation chromatography (GPC) was performed with a Shimadzu apparatus (UV and RI detection) with a PLgel D column (Polymer Laboratories) and THF as the eluent at 303 K calibrated with linear polystyrene standards.



Fig. S4 Comparison of the ¹H NMR spectra of 2-mercaptoethylamine (a), as-synthesized sulfonated hyperbranched poly(arylene oxindole)s (b), and sulfonated hyperbranched poly(arylene oxindole)s after modification with 2-mercaptoethylamine (c).

5 References

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