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Sustainable Chemistry

Water Tolerant and Reusable Sulfonated Hyperbranched Poly(aryleneoxindole) Acid Catalyst for Solvent-Free Esterification

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Dedicated to George A. Olah

The synthesis of esters directly from alcohols and carboxylic acids plays an important role in organic synthesis because of its utility in diverse fields both in academia and in industry. Innovations to further improve the efficiency and sustainability of the esterification process are highly desirable. To accomplish a green esterification protocol, we used a recoverable sulfonated hyperbranched poly(aryleneoxindole) acid catalyst in the

condensation of various alcohols with acids. The protocol allows high conversion with equimolar amounts of reagents, recovery and reuse up to at least five times with solvent free conditions thus simplifying purification steps and reducing redundancy. Furthermore the reaction medium was deliberately spiked with water to evaluate its influence on the activity of the acid catalyst and excellent tolerance was observed.

Introduction

Esterification continues to play an important role both in organic synthesis and in the chemical industry.^[1] The condensation between an alcohol and an acid is slow and reversible, thus the equilibrium can be shifted to the desired product by adding excess of one of the reagents, removal of water or continuous removal of product. The rate of the reaction on the other hand can be influenced by adding a catalyst such as an acid.^[2] Mineral liquid acids, Bronsted acids (e.g. HCl, H₂SO₄) and Lewis acids (e.g. BF₃·OEt₂, ZnO), are widely used in industry, however their corrosive and hazardous nature, the subsequent need for neutralization generating large quantities of aqueous waste, and the difficulty to separate them from the reaction medium hamper their industrial applicability.

Solid acid catalysts have received much attention as potential replacements for mineral liquid acids.^[3] The advantages of heterogeneous solid acid catalysts include ease of separation from the reaction medium, good recyclability, reduction of corrosion and enhanced product selectivity. Examples of heterogeneous solid acid catalysts used in industry

include Amberlyst 15,^[4] Nafion-H,^[5] zeolites,^[3b] heteropolyacids^[6] and mesoporous materials.^[7] Despite their benefits, heterogeneous acid catalysts suffer from severely decreased or even lost activity in the presence of moisture due to water adsorption on the active sites.^[8] Also lower intrinsic activity may arise due to interaction of acid groups with the support or due to more restricted conformations of intermediate complexes adsorbed onto the solid surface in comparison with homogeneous catalysts.^[9]

Hyperbranched polymers (HBs) are highly branched three-dimensional (3D) macromolecules, which represent an extra polymer architecture next to the linear, branched and cross-linked polymers.^[10] Their unique structure enables some attractive features for catalytic applications, such as ease of synthesis, ease of purification, weak entanglement, tailorable solubility and low viscosity, self-assembly and high number of terminal groups. A convenient approach to hyperbranched poly(aryleneoxindole)s (HBPAOs) was previously developed in the Smet group.^[11] HBPAOs were prepared in a one-step A₂ + B₃ polycondensation via superelectrophilic arylation of isatin, which is a more convenient synthetic strategy than the classical AB_x polycondensation, as the required monomers are usually more easily obtained.^[12] The functionalization of HBPAO by controlled sulfonation afforded a new class of hydrophilic acid catalysts.^[13] The sulfonated hyperbranched poly(aryleneoxindole) SHBPAO was successfully used as acid catalyst in the catalytic conversion of cellulose to levulinic acid (LA) in water at mild temperature. Moreover, it exhibited comparable catalytic performance to sulfuric acid with the valuable benefit of recyclability.^[13a] The SHBPAO also proved to be an efficient catalyst in the thiol promoted acid catalyzed condensation between LA and phenol to form diphenolic acid.^[13b,14] The

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Scheme 1. Synthesis of sulfonated hyperbranched poly(aryleneoxindole) (SHBPAO).

group of Nabae reported a similar sulfonated aromatic hyperbranched polymer as efficient catalyst for esterification.^[15] However the synthesis of the monomer and the AB₂ polycondensation strategy are less convenient and water tolerance was not investigated. In this paper we report the application of SHBPAO as recoverable acid catalyst for the esterification of alcohols and carboxyl acids. Special attention is paid to the influence of water and to conforming the SHBPAO catalyzed esterification protocol towards industrial application. Reactions are performed solvent-free, using equimolar amounts of alcohol and acid, high conversion is pursued to simplify purification and to diminish redundancy thus furnishing an overall as green as possible chemical process.

Results and Discussion

Synthesis

SHBPAO was prepared via a previously reported A₂ + B₃ polymerization approach.^[13c] As shown in Scheme 1, an aromatic hydrocarbon based B₃ monomer was first prepared via Friedel-Crafts acylation from commercially available 1,3,5-benzenetricarbonyl chloride and diphenyl ether. Next, the obtained B₃ monomer was condensed in superacidic media with the A₂ monomer isatin via superelectrophilic arylation. We decided to employ isatin instead of an isatin derivative (e.g. 5-chloroisatin), despite having shown before that substituents on the oxindole can improve catalytic efficiency,^[13c] since isatin is cheaper. Sulfonation via aromatic substitution of the HBPAO was achieved in oleum, which resulted in the previously reported acid catalyst: the sulfonated hyperbranched poly(aryleneoxindole) (SHBPAO).^[13a,b,16] Commercially readily available reagents are used both in the synthesis of the B₃ monomer and the synthesis of the polymers HBPAO and SHBPAO. Furthermore, the purifications of both the B₃ monomer and the HBPAO were performed by precipitation while the SHBPAO was purified by dialysis. Both precipitation and dialysis are efficient purification techniques regularly used in industry. Via the method described above, a batch of SHBPAO was prepared.

Characterization and all experiments presented in this paper were performed with the same batch of SHBPAO.

Characterization

When comparing the ¹H-NMR spectrum of the HBPAO with that of the A₂ and B₃ monomer, several isolated peaks belonging to the individual monomers can be identified in the spectrum of the HBPAO (Figure S1). When comparing the ¹H-NMR spectra of HBPAO and SHBPAO, a strong difference in the pattern of the aromatic signals is observed due to the presence of the sulfonic acid groups altering the electronic environment of the aromatic protons (Figure S2). Detailed assignment is however difficult due to overlap and complexity of the signals.

Sulfonation of HBPAO to SHBPAO was additionally confirmed by FT-IR. After sulfonation, two intense signals are visible at 1078 and 1016 cm⁻¹, which are attributed to asymmetric and symmetric stretching signals of the O=S=O bonds (Figure S3). Furthermore a broad band at 3347 cm⁻¹ is observed (Figure S4) due to adsorbed water (high water physisorption of the SHBPAO acid catalyst).

The acid density of the SHBPAO (dry sample) was measured after freeze-drying by back titration with a 2 M NaCl and 0.02 M NaOH solution using a Metrohm 848 Titrino Plus. The titration experiment was performed in duplicate resulting in an average acid density of 5.3 mmol H⁺ per g which is in line with the acid densities reported before for this material (3.7–5.4 mmol per g H⁺).^[13a,b,16–17] The variation in acid density can be explained by several factors such as conducting the polymerization and sulfonation under different concentration of SO₃ in oleum and measurement on a wet^[13a] or dry sample.^[17a] The high acid density, higher than the 4.7 mmol H⁺ per g for Amberlyst 15, reduces the total amount of SHBPAO catalyst necessary and thus is more appealing to apply in industry.

The thermal stability was analyzed by thermogravimetric analysis (TGA) shown in Figure 1. Prior to measurement, the SHBPAO was freeze-dried and stored in a desiccator due to the high water physisorption of the SHBPAO (Amberlyst 15 was purchased and stored in a desiccator but not freeze dried). TGA traces of SHBPAO indicate no significant degradation or

Figure 1. TGA trace of SHBPAO (solid line) and Amberlyst 15 (dashed line).

desorption of water in the range of 50–400 °C. A first weight loss of 11% is observed in the range of 400–505 °C and attributed to the decomposition of the sulfonic acid groups. Above 505 °C, the SHBPAO weight rapidly decreases since the polymer itself decomposes. TGA analysis of the purchased Amberlyst 15^[18] was performed for comparison. A first weight loss is observed at 30–150 °C and caused by desorption of water. The weight loss at 220–340 °C and 340–550 °C is due to decomposition of the sulfonic acid groups and the polymer network, respectively. TGA analysis demonstrates the thermal robustness of SHBPAO since decomposition occurs at much higher temperatures compared to Amberlyst 15 (400 vs. 220 °C and 505 vs. 340 °C), which is favorable for catalyst recycling. It also illustrates that adsorption of water can be avoided by keeping the SHBPAO in a water free environment (e.g. in a desiccator).

Esterification

The SHBPAO acid catalyst was evaluated in the esterification of *n*-butanol and acetic acid (Scheme 2).

Scheme 2. Esterification of *n*-butanol.

Typically, an esterification is performed at high temperatures (i.e. 60–110 °C), in the presence of an excess of alcohol or acid, by removal of water or with an acid catalyst to overcome the slow kinetics of the reaction. In this paper alcohol and acid were used in equimolar amounts in a closed system, solvent free conditions were applied, no water was removed (e.g. by molecular sieves, Dean-Stark apparatus) and

Figure 2. Conversion of *n*-butanol to *n*-butyl acetate at different intervals determined by *n*-dodecane as internal standard. Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), SHBPAO (2.0–0.1 mol%) at 90 °C.

temperature was kept constant to investigate the influence of the SHBPAO acid catalyst.

90 °C was selected as reaction temperature to optimize the SHBPAO acid catalyst loading. The conversion of *n*-butanol to *n*-butyl acetate was monitored via gas chromatography (GC) with *n*-dodecane as an internal standard (details in the supporting information). The results of the loading optimization are shown in Figure 2. 2.0 mol% of SHBPAO (based on the acid density) acid catalyst, compared to *n*-butanol (and acetic acid), gave excellent results with regards to reaction rate (60% conversion after 20 min) and conversion (98% conversion after 360 min). Only a minor decrease in reaction rate was observed when the SHBPAO acid catalyst loading was decreased (1.0 and 0.5 mol%) but more importantly, the conversion after 360 min remained similar (1.0 and 0.5 mol%, 96 and 95%). A more pronounced negative influence on reaction rate and conversion was observed when lowering the SHBPAO acid catalyst to 0.1 mol%. It should however be noted that even with this low amount of catalyst, still 83% *n*-butyl acetate was obtained after 360 min. At this point, 0.5 mol% of SHBPAO acid catalyst was selected as the optimal loading since a high conversion and high turnover frequency is highly desired for industrial applications.

An interesting trend was observed during the reaction (Figure 3). Firstly, from 0 until 40 min, the reaction mixture was homogeneous and SHBPAO was completely dissolved (Figure 3A). Between 40 and 180 min, SHBPAO started to precipitate and a suspension was observed (Figure 3B). After 360 min the reaction was stopped and SHBPAO was observed as a precipitate (Figure 3C). The solubility of SHBPAO in pure acetic acid, *n*-butanol, and *n*-butyl acetate was tested: it was only soluble in acetic acid. When the esterification is performed, SHBPAO is initially soluble due to the presence of acetic acid while at the end of the reaction almost no acetic acid is present (since equimolar amounts of acid and alcohol were used) and hence the SHBPAO catalyst starts to precipitate, thus combin-

Figure 3. Reaction mixture over time. Reaction after 10 min (A), after 60 min (B), after 360 min (C). Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), SHBPAO (0.5 mol%) at 90 °C.

ing the advantages of a homogeneous and heterogeneous catalyst. It should be noted that this catalyst behavior depends on the reagents and reaction conditions. A similar reaction was performed with palmitic acid, in this specific case the catalyst was heterogeneous from the start (Figure S8). Overall conversion of 88% was achieved after 96 hours with a catalyst load of 2 mol% thus proving that the catalyst can be used with

Figure 4. Conversion of *n*-butanol to *n*-butyl acetate at different intervals determined by *n*-dodecane as internal standard. Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), SHBPAO (0.5 mol%) at different temperatures.

different organic acids (Table S1). The increased reaction time and catalyst loading can be related to the lower reactivity of palmitic acid.^[19] In the case of acetic acid and *n*-butanol, the influence of temperature, at the optimal catalyst loading, was examined. Identical conditions and analytic method as before were applied but the temperature was varied (23 °C (RT), 30 °C, 60 °C, 90 °C). The results are shown in Figure 4. Clearly, there is a large influence on the reaction rate when decreasing the temperature. For example, when looking at the conversion after 60 min, a drop of 26% is observed when the temperature is decreased from 90 to 60 °C. When the temperature is further decreased to 30 °C, a drop of 53% in conversion is detected compared to the reaction at 90 °C. The reaction at room temperature was monitored over a longer period (table S2) and after 48 h, 73% conversion was reached proving that higher conversion at lower temperatures can be achieved by extending the reaction time.

To compare the potential of SHBPAO as acid catalyst with conventional catalysts we evaluated the catalytic kinetics of SHBPAO, sulfuric acid (H₂SO₄), *p*-toluene sulfonic acid (PTSA) and Amberlyst 15. Apart from the conventional catalyst we also ran a blank experiment to prove the catalytic effect of SHBPAO. The results are shown in Figure 5. A clear difference is observed when adding an acid catalyst (SHBPAO or a conventional catalyst) compared to the blank proving the necessity of an acid catalyst to overcome the unfavorable kinetics of the reaction. Initially (0–120 min) the SHBPAO catalyzed conversion

Figure 5. Conversion of *n*-butanol to *n*-butyl acetate at different intervals determined by *n*-dodecane as internal standard. Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), acid catalyst (0.5 mol% except for blank where no acid catalyst was added) at 90 °C.

of *n*-butanol (and acetic acid) is slower compared to the traditional acid catalysts sulfuric acid and PTSA, presumably due to the reduced acid strength and diminished accessibility of the sulfonic acid groups owing to their hyperbranched support.^[20] However when continuing the reaction (120–360 min), conversion of the SHBPAO catches up and ends up with a higher conversion than both sulfuric acid (5% less) and PTSA (9% less). When comparing SHBPAO with Amberlyst 15, a conventional heterogeneous catalyst, we observe a faster conversion of the starting materials as well as a higher conversion at the end of the reaction. The higher reaction rate in the early phase can be explained by the initial homogeneous nature of the hydrophilic SHBPAO which reacts faster than heterogeneous hydrophobic Amberlyst 15.^[9a] Higher conversions are also obtained with SHBPAO compared to Amberlyst 15 (14% difference). Moreover, due to the high loading of the SHBPAO (5.3 mmol H⁺ per g) less material had to be added at the beginning in comparison with Amberlyst 15 (4.7 mmol H⁺ per g).

To further evaluate our SHBPAO acid catalyst, we examined two different alcohols in our optimized protocol (benzyl alcohol and cyclohexanol) and the results are shown in Table 1. Benzyl

Table 1. Esterification scope.			
Product	<i>n</i> -butyl acetate	Benzyl acetate	Cyclohexyl acetate
Conversion ^[a]	95% ^[b]	76% ^[c]	71% ^[c]
[a] Reaction conditions: Alcohol and CH ₃ COOH (10.9 mmol), SHBPAO (0.5 mol%), 90 °C. [b] Determined by GC with <i>n</i> -dodecane as internal standard. [c] Determined by qNMR, ¹ H NMR (CDCl ₃).			

acetate and other aromatic esters have a broad range of applications in pharmaceuticals, agrochemicals, perfumery and

cosmetics.^[1] Benzyl alcohol, acetic acid and multiple other compounds (e.g. alcohols, acids, furans, aldehydes, and sugars) are also found in bio oils, upgrading/pre-treatment via a catalytic process such as esterification is a promising way to improve their physicochemical properties.^[21] Secondary alcohols react more slowly and give lower conversions compared to primary alcohols, for this reason cyclohexanol was chosen as a more challenging substrate. High conversion was achieved for both benzyl alcohol and cyclohexanol although lower than *n*-butanol. However, the conversion can be increased by adding an excess of a reagent (alcohol or acid), by adding more SHBPAO acid catalyst or by extending the reaction time.

Water tolerance

An important factor for the applicability in commercial esterification processes of heterogeneous and homogeneous acid catalysts is the catalyst tolerance to water.^[22] When water is added, both homogeneous and heterogeneous acid catalysts tend to become inactive due to physical adsorption of water on the active sites thus reducing acid strength and preventing further conversion of the substrates.^[8,23] Development of water tolerant acid catalyst remains a challenge. The group of Wilson thoroughly investigated the water tolerance of propylsulfonic acid functionalized mesoporous silica (PrSO₃H/SBA-15). In a first report, the acid catalyzed esterification of benzyl alcohol was deliberately spiked with 40 mol% of water with respect to benzyl alcohol.^[24] No impact on the initial reaction rate was observed, however overall conversion decreased from 100 to 60% after 5 h of reaction which was attributed to a displacement of the reaction equilibrium to the reverse hydrolysis reaction. It is also important to note that a ratio of 2:1 (acid:alcohol), toluene and a temperature of 100 °C were used shifting the reaction equilibrium to the desired ester. However most conventional acid catalysts (i.e. Amberlyst 15,^[23a] heteropolyacids^[25]) gave worse performance and activity is already suppressed or stopped by the addition of as little as 1 mol% of water. Hydrophobic octyl chains were introduced on PrSO₃H/SBA-15 to improve the water tolerance and evaluated in the stoichiometric acetic acid and methanol esterification. Under these conditions 40% of ester was formed after 24 h.^[26] The group of Fraile^[27] investigated the water tolerance of sulfonated hydrothermal carbon^[28] (SHTC) in the esterification of methanol and palmitic acid (methanol:palmitic acid molar ratio of 10:1, solvent free), increasing the amounts of water added up to water:palmitic acid molar ratio of 1:1. A decrease in reaction rate was observed but overall conversion remained high (70% after 10 h).^[29] Despite improving overall conversion substantially compared to conventional acid catalysts, we believe that improvement is still possible. We were also interested in the properties of a hydrophilic catalyst as compared to a hydrophobic one, which is usually expected to be more water tolerant.

Different amounts of water were added to *n*-butanol, which was then subjected to the optimized protocol to evaluate the SHBPAO catalyst performance. The results are shown in Figure 6. Outstanding results were obtained for SHBPAO water

Figure 6. Conversion of *n*-butanol to *n*-butyl acetate determined by *n*-dodecane as internal standard. Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), SHBPAO (0.5 mol%), H₂O (0–510 mol%) at 90 °C.

tolerance. When adding 40 mol% of water (compared to *n*-BuOH and CH₃COOH), the conversion only decreased by 2% compared to the water-free model reaction. Even after adding 100 mol% of water the formation of *n*-butyl acetate only decreased by 15% and still 80% overall conversion was achieved (Figure S11). We also tried to work in a biphasic reaction mixture (Figure S12) by adding 0.5 mL (255 mol%) and 1.0 mL (510 mol%) of water, in this case, conversion decreased to 52 and 41%, respectively, which still is an excellent result. The conversion, in the case of the biphasic reaction mixture (0.5 mL water), could be increased to 71 and 82% by changing the ratio of acid:alcohol from 1:1 to 1:5 and 1:10, respectively (Figure S13).

Recovery and reuse

To further evaluate the stability of SHBPAO, recovery and reuse experiments were performed. Recovery was performed via two strategies. In the first case the reaction mixture was distilled while in the second case the hydrophilicity of the catalyst was exploited by adding water followed by phase separation and lyophilisation (details in the supporting information). In both cases the catalyst was recovered and no decrease in activity was observed over five runs as shown in Figure 7. It should be noted that recovery by distillation depends on the boiling point of the product, however the biphasic separation should be possible for products with a high boiling point. In the case of the esterification of palmitic acid with *n*-butanol, the product, *n*-butyl palmitate, has a high boiling point (*B_p* of 360 °C at 1 atm.). In this case the catalyst was successfully recovered by biphasic separation (Figure S14). The recovered SHBPAO was analyzed by ¹H NMR and no degradation was observed (after five runs for both strategies in the case of acetic acid and after one run in the case of palmitic acid esterification) thus illustrating the stability of the SHBPAO.

Figure 7. Recovery and reuse experiment, recovery by distillation (bleu) and by biphasic separation (red). Reaction conditions: *n*-BuOH and CH₃COOH (10.9 mmol, 1.0 eq.), SHBPAO (0.5 mol%) at 90 °C.

Conclusions

Esterification will continue to play an important role both in organic synthesis and in the chemical industry. Not only esterification but all chemical processes, should be as optimal as possible. For this purpose, a sulfonated hyperbranched poly(aryleneoxindole) acid catalyst is prepared from readily available commercial reagents and successfully applied in the esterification of alcohols and carboxylic acids. SHBPAO has excellent catalytic activity in esterification, better than that of Amberlyst 15 and comparable with that of sulfuric acid and PTSA. Special attention is given to the development of an efficient green esterification process. High conversion (95%) with equimolar amounts of reagents is reached and the catalyst is recycled and reused five times thus simplifying purification steps and reducing redundancy. SHBPAO water tolerance was tested, by deliberately adding water to the esterification process, and excellent results were obtained.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Esterification • Hyperbranched Poly(aryleneoxindole) • Solvent-Free • Supported Catalyst • Water Tolerant

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FULL PAPERS

- ✓ SHBPAO Hydrophilic Acid Catalyst
- ✓ Thermally Stable
- ✓ High Acid Density (5.26 mmol H⁺/g)
- ✓ Solvent-Free Esterification
- ✓ Catalyst Recovered and Reused
- ✓ High Water Tolerance

Esterification plays an important role in organic synthesis because of its utility in diverse fields both in academia and in industry. A green esterification protocol is designed allowing high conversion with

equimolar amounts of reagents, with a reusable sulfonated hyperbranched poly(aryleneoxindole) acid catalyst, under solvent free conditions and water tolerant.

*T. Verheyen, Prof. M. Smet,
Prof. W. M. De Borggraeve**

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Water Tolerant and Reusable Sulfonated Hyperbranched Poly(aryleneoxindole) Acid Catalyst for Solvent-Free Esterification