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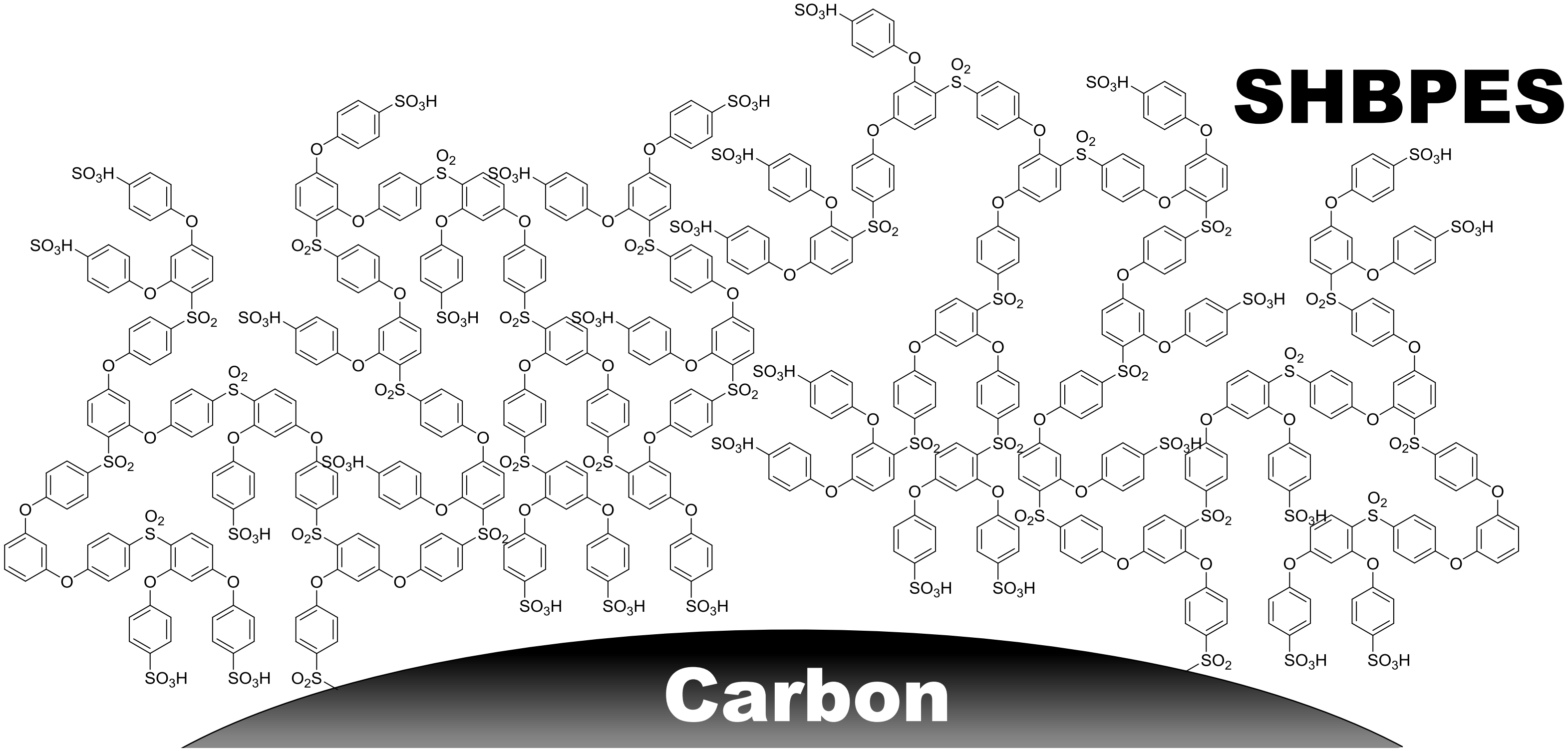
A Novel Solid Acid Catalyst



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Sulfonic Acid Functionalized Hyperbranched Poly(ether sulfone) as a Solid Acid Catalyst

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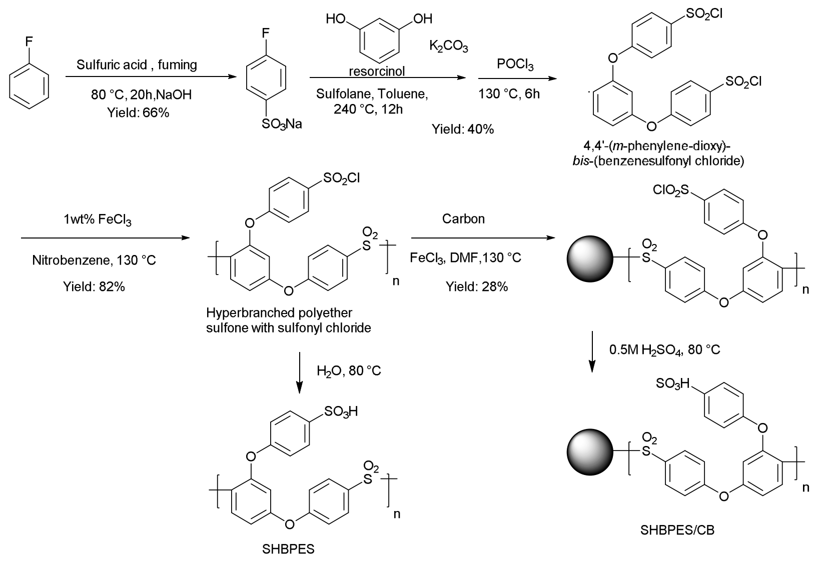
Sulfonic acid functionalized hyperbranched poly(ether sulfone) (SHBPES) was studied as a novel type of solid acid catalyst. Various molecular weights of SHBPESs were tested for the esterification reaction between acetic acid and 1-butanol. The SO_3H terminal groups of the SHBPESs work as catalytically active sites but all tested SHBPESs are totally or partially soluble in the current reaction condition. To overcome the solubility problem, SHBPES was grafted onto a carbon black and this material, SHBPES/CB, shows fairly good catalytic activity and promising recyclability. The turn over frequency of SHBPES decreased by grafting it onto a carbon black, but it is still much better than that of Amberlyst®-15. SHBPES/CB was also tested for the Friedel-Crafts alkylation of anisole and its durability seems to be much better than that of Amberlyst®-15 under an operating condition at 130 ˚C.

Introduction

Acid catalyzed chemical reactions are widely used in the current society to produce various chemicals. In terms of green chemistry, it is quite important to replace liquid acid catalysts such as HF and H_2SO_4 with solid acid catalysts.[1-3] Ion exchanging polymers such as Amberlyst®-15 is one of typical solid acid catalysts; however, they are available only at ambient operating temperature, typically below 120 ˚C, because of low thermal stability of the vinyl based polymers.[4,5] Developing ion exchanging polymers with higher thermal stability will largely expand the applicability of polymer-based solid acid catalyst in various chemical processes.

To develop a stable polymer-based solid acid catalyst, employing aromatic polymers such as poly(arylene ether sulfone) would be a reasonable approach because they are chemically and thermally stable.[6,7] Besides, to develop a highly active catalyst material with such aromatic polymers, our research group is now interested in the hyperbranched structure. Hyperbranched polymers have a large number of end-groups and a dendritic-like structure.[8-10] Unlike dendrimers, hyperbranched polymers can be synthesized in one step process from AB_x-type monomers, where x is two or more. It means that a large number of catalytically active sites can be introduced if the end-groups are converted into catalytically active functional groups. Other properties of hyperbranched polymers might also contribute to the catalytic activity of the end-groups. The end-groups of hyperbranched polymer would be well exposed and accessible for the reactants of catalytic reactions because of a low degree of entanglement. Besides, a large free volume of hyperbranched polymer would enhance mass transport of the reactants and products. For the case of solid acid catalyst, sulfonic acid functionalized hyperbranched polymer could be a good catalyst material.



Scheme 1. Synthetic route of SHBPES and SHBPES/CB.

In this context, we hereby propose sulfonic acid functionalized hyperbranched poly(ether sulfone) (SHBPES)[11,12] as a novel material for solid acid catalysts. This paper discusses the catalytic performance of SHBPESs for 1) the esterification between acetic acid and 1-butanol and 2) the Friedel-Crafts alkylation of anisole with benzyl alchol. In additions, since SHBPES itself will have a solubility problem as a solid catalyst, SHBPES immobilized onto a carbon black (SHBPES/CB) has also been studied.

Experimental

Material synthesis

Scheme 1 shows the synthetic routes of SHBPES and SHBPES/CB. All reagents were used as received. Preparation of the AB_2 monomer, 4,4'-(m-phenylene-dioxy)-bis-(benzenesulfonyl chloride), has been previously reported and the procedure was used with a slight modification.[11,12] The prepared AB_2 monomer (0.30 g, 0.65 mmol) was dissoloved in nitrobenzene (1 mL) with $FeCl_3$ (0.003 g, 0.018 mmol) and heated under N_2 at 130 ˚C for 3-20 h. The mixture was poured into methanol with a small amount of HCl. The precipitate was washed with methanol, and then dried *in vacuo* at 80 ˚C. SHBPES was obtained by hydrolyzing the chloride form polymer in water at 80 ˚C for 20 h. To immobilize the polymer onto a carbon black, the chrolide form polymer (0.2 g) was dissolved in *N,N*-dimethylformamide (DMF) with $FeCl_3$ (0.01 g) and Ketjen Black (EC600JD, 0.1 g) and heated under N_2 at 130 ˚C for 60 h. The resulting powder was stirred in DMF for two nights to remove unimmobilized polymer. SHBPES/CB was obtained by hydrolyzing the polymer/carbon sample in 0.5 M H_2SO_4 at 80 ˚C for 20 h.

To elucidate the effect of the chemical structure of the backbone, the catalytic performances of *p*-toluenesulfonic acid (PTSA) and 4-(phenoxy)benzenesulfonic acid (PBSA) were also studied. PTSA was purchased in a monohydrate form (TCI) and used as obtained. PBSA was prepared by hydrolyzing 4-(phenoxy)benzenesulfonyl chloride, which was synthesized by the literature method.[12]

Measurements

Gel permeation chromatography (GPC) was performed for the chloride form polymer using a Viscotek GPC-1000 system equipped with a TDA 302 triple detector and a TSK-GEL α-M column. DMF with 0.05 M LiBr was used for eluent. The weight average molecular weight (M_w) was calculated based on the light scattering data.

The ion exchange capacity of the prepared samples was determined by neutralization titration. The equivalent point was determined based on the primary differential of the pH-titration curve. For SHBPESs, a polymer powder (20mg) was treated in a 5 M NaCl solution (10 ml) at room temperature and stirred overnight to exchange the protons on the sulfonic acid groups. Then the mixture was titrated with 0.013M NaOH. For SHBPES/CB samples, a sample powder (50mg) was treated in 0.1 M NaOH (3 ml) solution at room temperature and stirred overnight. The mixture was filtrated and the remaining filtrate was titrated with 0.1 M HCl.

CHS elemental analysis was performed using a Perkinelmer 2400-II analyzer.

Transmission electron microscopy (TEM) was performed using a Hitachi H-7650 microscope operated at 100 kV. The sample was stained using a Gd based stainer (EM stainer, Nisshin EM) before the measurement.

Catalytic reaction

The catalytic performance of the materials was tested using a Shibata Chemist Plaza CP100 multi-reactor equipped with 100 mL reactors. The esterification over the prepared catalyst was performed by stirring acetic acid (20 mmol), 1-butanol (20 mmol) and the catalyst (20 mg) at 65 ˚C for 0.5-2.5 h. The Friedel-Crafts alkylation over the prepared catalyst was performed by stirring anisole (18.5 mmol), benzyl alcohol (1.25 mmol) and the catalyst (75 mg) at 130 ˚C for 20 h. The reaction products were quantified with a Shimadzu GCMS-QP2010 Plus equipped with a TC-FFAP column (0.25 mmφ × 30 m). The conversion was calculated based on the peak area ratio of 1-butanol or benzyl alcohol against the internal standard: naphthalene (esterification) or dodecane (Friedel-Crafts alkylation). The product yields were calculated based on the peak area ratios of the reaction products against the internal standard.

Catalyst recycling tests were performed by the following manner. The reaction mixture was filtered after each run of the esterification, and then the residue was used for the next run after drying and weighing.

Results and discussion

Preparation of SHBPES

SHBPESs with various molecular weights were prepared by polymerizing the AB_2 monomer**,** 4,4'-(*m*-phenylene-dioxy)-*bis*-(benzenesulfonyl chloride) for 3-20 h.[11] Table 1 shows M_w and IEC of the SHBPESs prepared with different reaction periods. The results suggest that the molecular weight of SHBPES was successfully controlled in the range of 3.6×10^4 to 2.06×10^5 g mol^{-1}. SHBPES1 shows the highest IEC, 2.2 mmol g^{-1}, whilst the theoretical value is 2.8 mmol g^{-1}; and the IEC slightly decreases as the molecular weight increases. This is probably due to a cross-linking reaction between the SO_3Cl terminals and aromatic rings during the polymerization.

Catalytic performance of SHBPES

The SHBPESs were tested as a catalyst for the esterification reaction between acetic acid and 1-butanol. Figure 1 shows the results of the esterification reaction with the SHBPESs. The results with Amberlyst®-15 and H_2SO_4 are also shown for comparison. H_2SO_4 showed the highest catalytic activity since this is a homogenous catalyst. Amberlyst®-15, SHBPES4 and

SHBPES5 showed similar catalytic performances, whilst SHBPES1, SHBPES2 and SHBPES3 showed better catalytic performances than Amberlyst®-15.

Table 1 Molecular weight and ion exchanging capacity of SHBPES prepared with different polymerization period

Polymer	Reaction period / h	M_w[a]	IEC[b] / mmol g^{-1}
SHBPES1	3	36,000	2.2
SHBPES2	6	66,000	2.2
SHBPES3	8	91,000	2.1
SHBPES4	14	134,000	1.2
SHBPES5	20	206,000	1.1

[a] Chloride form polymer was analyzed by GPC with a light scattering detector. [b] Determined by titration.

Figure 2 shows the results of recycling tests. After the first runs, Most of SHBPES1, SHBPES2 and SHBPES3 could not be collected because the majority of polymer dissolved in the liquid phase. This is the reason why these SHBPESs showed better catalytic performances than Amberlyst®-15. These SHBPESs work as homogenous catalysts in the current reaction condition. The SHBPESs with higher molecular weights, SHBPES4 and SHBPES5, showed better collectability, but the recycled weight gradually decreased as the run number increased, whereas the recycle weight of Amberlyst®-15 was almost 100%. These experimental results suggest that the sulfonic acid terminals on SHBPESs can work as a solid catalyst but the SHBPESs themselves are not suitable for a solid acid catalyst because of the solubility problem.

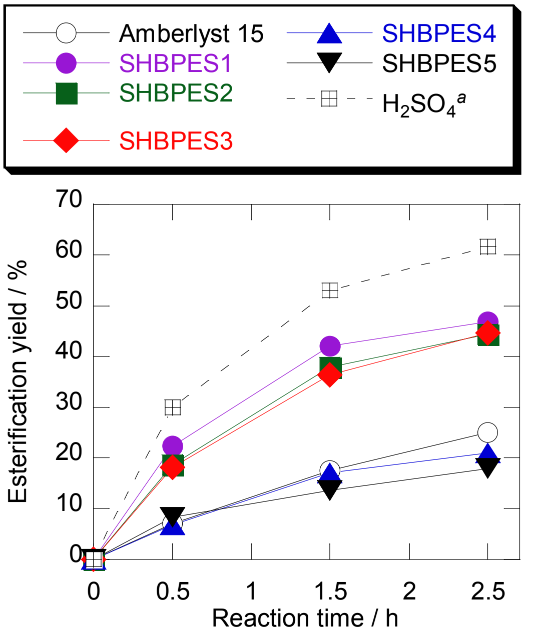


Figure 1. Time course of the esterification yield with various catalysts. Conditions: *T* 65 ˚C, acetic acid 0.02 mol, 1-butanol 0.02 mol, catalyst 20 mg. [a] H_2SO_4 equivalent to Amberlyst®-15 was used.

Immobilization of SHBPES onto Carbon Black

Since the SHBPESs themselves have a solubility problem to consider them as solid acid catalysts, we hereby discuss the immobilization of SHBPES onto a carbon black. Numerous reports have been published about grafting polymers from carbon surfaces.[13-21] Many of them employ hydrolyzable bonds such as ester and amide to graft polymers. To develop a reliable solid acid catalyst, however, such hydrolyzable bonds are not suitable because the materials will be used in strongly acidic conditions. In contrast, the present material, SHBPES, can be directly grafted onto carbon surfaces via the Friedel-Crafts reaction since the polymer can afford numerous sulfonyl chloride terminals.[22] This will result in an aromatic polymer based solid acid catalyst without any hydrolyzable bond and quite high durability can be expected in acidic conditions.

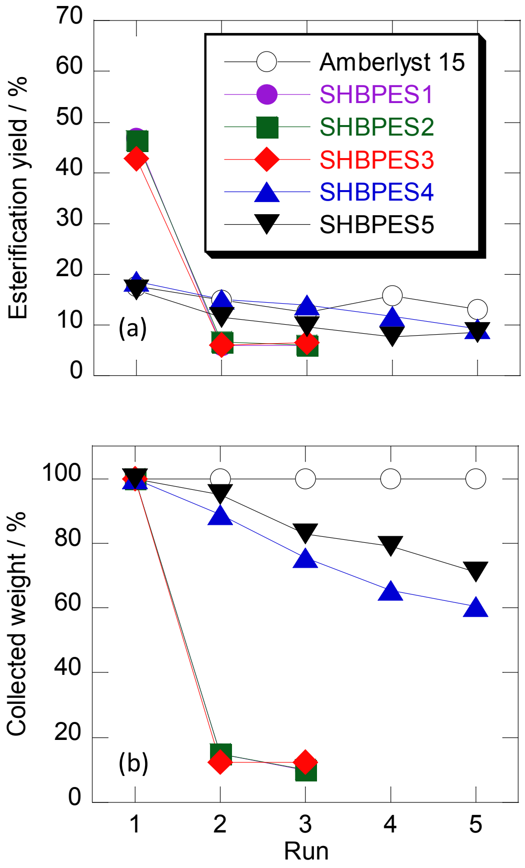


Figure 2. (a) Esterification yields with the fresh catalyst (1st run) and the recycle catalysts (2-5nd run), and (b) the relative amounts of used catalyst which were collected from the previous run. Conditions: idem as Fig 1 but the reaction period was 2.5 h.

Table 2 Results of the immobilization of SHBPESs onto a carbon black

Catalyst	IEC mmol g^{-1}	Elemental analysis wt%			Polymer loading wt%	
		C	H	S	IEC[a]	EA[b]
SHBPES1/CB	0.87	77.3	2.2	5.1	38	35
SHBPES2/CB	0.73	76.7	2.1	5.1	32	35
SHBPES3/CB	0.89	75.9	2.3	5.3	39	36

[a] Evaluated from the change in IEC before and after the immobilization. [b] Calculated from the S content of elemental analysis.

Table 2 summarizes the results of immobilization of SHBPESs onto a carbon black via the Friedel-Crafts reaction as illustrated in Scheme 1. SHBPES1, SHBPES2 and SHBPES3 were selected for the immobilization considering the affinity between the polymer and the reaction phase for catalytic reactions. The IECs became 0.73-0.89 mmol g^{-1}, whereas they were 2.08-2.20 mmmol g^{-1} before the immobilization. These IECs correspond to the polymer loading of 31.7-38.7 %. The polymer loading was also evaluated by CHS elemental analysis and the results are in good agreement with the values from the IECs. Although the polymer loading was not quite different among three samples, SHBPES3/CB showed the highest polymer loading. Thus obtained SHBPES3/CB was analyzed by TEM. Figure 3 shows TEM images of SHBPES3/CB and pristine carbon black. Compared to pristine carbon black, the particle size of SHBPES3/CB seems slightly large. In the enlarged images, SHBPES3/CB seems to have a uniform polymer layer with a thickness of 10-20 nm. These experimental results suggest that SHBPES can be successfully grafted onto carbon black by the Friedel-Crafts reaction.

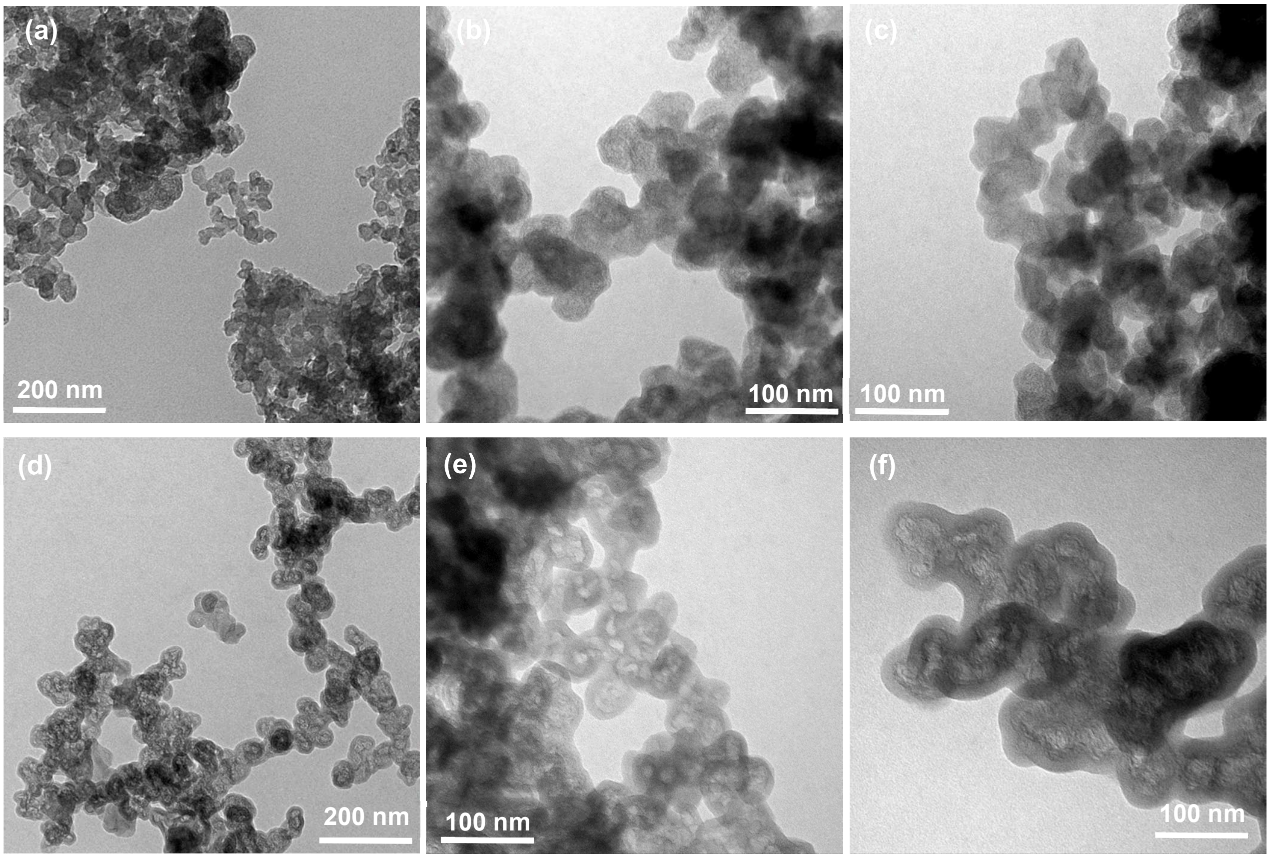


Figure 3. TEM images of (a-c) pristin carbon black and (d-e) SHBPES3/CB.

Table 3 Comparison of the ion exchanging capacity and catalytic performance between SHBPES3/CB and other control samples[a]

Catalyst	IEC mmol g^{-1}	Catalyst amount / mg	Reaction period / h	Conversion / %	Yield / %	TOF[b] min^{-1}
blank	–		2.5	3	4	–
Ketjen black	–	20	2.5	4	4	–
PTSA[c]	5.3	10	0.5	33	26	3.21
PBSA[d]	4.0	10	0.5	26	21	3.56
SHBPES3	2.1	20	0.5	20	18	2.85
SHBPES3/CB	0.89	20	2.5	13	13	0.97
Amberlyst®-15	4.7	20	2.5	20	21	0.30

[a] Reaction conditions: idem as Fig 1 but the reaction period and catalyst amount. [b] Calculated from the IEC and the esterification yield. [c] *p*-Toluene sulfonic acid. [d] 4-(Phenoxy)benzenesulfonic acid.

SHBPES3/CB was studied as a solid acid catalyst for the esterification between acetic acid and 1-butanol. Table 3 compares the IEC and catalytic performance of several catalysts. The IEC of SHBPES3/CB was 0.89 mmol g^{-1} whereas that of SHBPES3 was 2.1 mmol g^{-1}. SHBPES3/CB shows a fairly good catalytic activity: 13 % of esterification yield against 46 % by SHBPES3. The turn over frequency (TOF) of SHBPES3/CB is smaller than that of SHBPES3, but still better than that of Amberlyst®-15. The higher TOF against Amberlyst®-15 is probably due to the flexibility of the SO_3H terminals on HBPES. The catalytic performance of SHBPES3/CB against other state-of-the-art catalysts could be supposed based on the comparison against that of Amberlyst®-15. Liu et al. compared various catalysts for the esterification between acetic acid and 1-butanol at 90 °C, and reported that H-PDVB-1.5-SO_3H (IEC: 1.86 mmol g^{-1}), SBA-15-SO_3H (1.26 mmol g^{-1}), H-beta zeolite (1.21 mmol g^{-1}) and H-USY zeolite (2.06 mmol g^{-1}) showed 9.3, 7.6, 6.7 and 4.1 min^{-1} of TOFs whereas Amberlyst®-15 showed 3.0 min^{-1}.[23] Considering the TOF of SHBPES3/CB in Table 3, which is three times better than that of Amberlyst®-15, it can be presumed that the inherent catalytic activity the acidic terminal groups on HBPES are as good as the active sites of the state-of-the-art catalysts, although the mass catalytic activity is not because of the lower IEC.

One might wonder if the chemical structure of the polymer backbone significantly affects the catalytic activity of the terminal functional groups. To elucidate the effect of the backbone, the homogenous catalysis of model compounds was studied. Table 3 shows the catalytic performances of PTSA and PBSA for the esterification between acetic acid and 1-butanol. PBSA showed a slightly better TOF but the catalytic activities of these two compounds were not very different. Therefore, the better TOF of SHBPES3/CB compared to that of Amberlyst®-15 presumably derives from good flexibility of the terminals on the hyperbranched strucutre rather than their chemical structures.

Recycling of SHBEPS3/CB was tested in the same manner as the experiments for SHBPESs and the results are shown in Figure 4. Although the collecting yield of SHBPES3/CB is not 100%, SHBPES3/CB over 90 % was successfully collected even after 5 runs. In the meantime, the catalytic activity of SHBPES3/CB seems fairly stable. It could be concluded that the stability of SHBPES3/CB are quite promising.

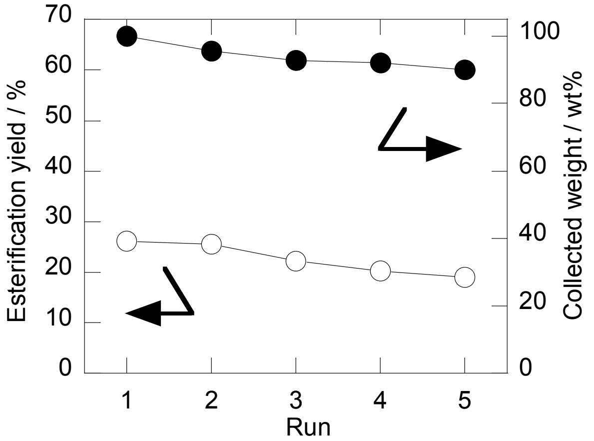
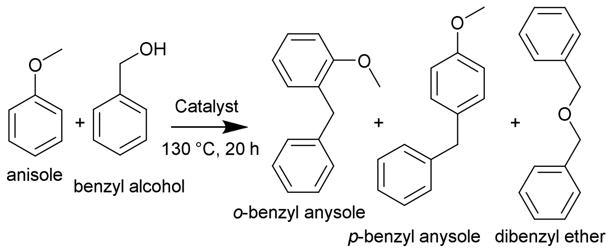


Figure 4 Esterification yields with the fresh catalyst (1st run) and the recycle catalysts (2-5nd run), and the relative amounts of catalyst against the 1st run. Conditions: idem as Fig 1 but the catalyst amount was 60 mg and the reaction period was 2.5 h.

Catalytic Reaction at High Temperature

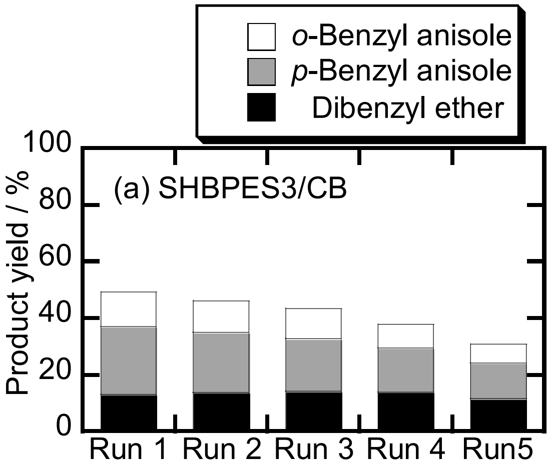
One advantage of the SHBPESs as a polymer-based solid acid catalyst is the thermal stability of the poly(ether sulfone) backbone; therefore, a higher operating temperature can be expected compared to Amberlyst®-15. In this context, the Friedel-Crafts alkylation of anisole with benzyl alcohol was studied using the SHBPES3/CB as illustrated in Scheme 2.



Scheme 2. Friedel-Crafts alkylation of anisole with benzyl alcohol.

Figure 5 summarizes the results of the Friedel-Crafts alkylation of anisole with benzyl alcohol over SHBPES3/CB and Abmerlyst®-15. A blank test under the same reaction condition but without the catalyst showed only trace amounts of reaction products. In contrast, SHBPES3/CB showed a certain catalytic activity for this reaction. Furthermore, the catalyst was successfully collected after the reaction and used for the following four runs, although the performance slightly degraded as the run number increased. Amberlyst®-15 also a catalytic activity under the same condition, but the reaction mixture became turbid immediately at the early stage of the reaction, and it was impossible to collect the catalyst. Probably, Amberlyst®-15 was decomposed in the present reaction condition and worked as a homogenous catalyst. These experimental results clearly suggest that the stability of the SHBPES/CB catalyst is much better than that of Amberlyst®-15 under such a high temperature.

Interestingly, the product selectivities are slightly different between SHBPES3/CB and Amberlyst®-15. SHBPES3/CB produced dibenzyl ether whereas Amberlyst®-15 did not. This different selectivity might derive from the difference in the solubility of the reactants into the polymer matrix. This result suggests that the HBPES derived solid acid catalyst might exhibit a molecular sieving effect if the polymer matrix and the reaction were appropriately designed.



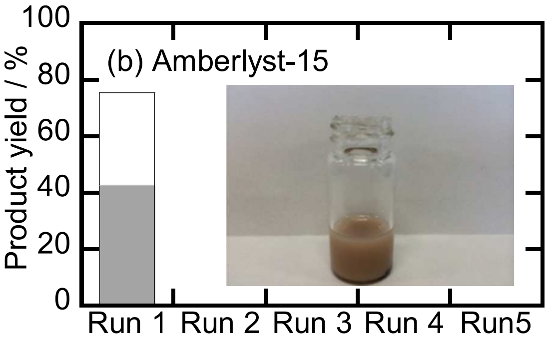


Figure 5. The results of the Friedel-Crafts alkylation over the (a) SHBPES3/CB and (b) Amberlyst®-15. Conditions: anisole 18.5 mmol, benzyl alcohol 1.25 mmol, catalyst 75 mg, 130 ˚C, 20 h. Inset: the reaction mixture after the 1st run with Amberlyst®-15.

Conclusions

Sulfonic acid functionalized hyperbranched poly(ether sulfone) (SHBPES) has been investigated as a novel type of solid acid catalyst. Various molecular weights of SHBPESs were tested for the esterification reaction between acetic acid and 1-butanol. The SO_3H terminal groups of the HBPESs works as catalytically active sites for the esterification but all tested SHBPESs are totally or partially soluble in the current reaction condition. To overcome the solubility problem, SHBPES was grafted onto a carbon black and those materials show fairly good catalytic activity and promising recyclability. It should be noted that SHBPES has been immobilized without any hydrolyzable bonds, which will contribute to high chemical stability in acidic conditions. As a model reaction at a high operating temperature, the Friedel-Crafts alkylation of anisole at 130 ˚C was studied and it has been revealed that SHBPES3/CB exhibits much better stability than Amberlyst®-15. Indeed the mass catalytic activity of the current material is not as good as those of the state-of-the-art catalysts; however, it will be much improved if the concentration of acidic sites could be more increased. Further studies require to be done to increase the concentration acidic sites and expand the applicability of these catalysts to other acid catalyzed chemical reactions.

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Notes and references

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