Poly(vinylsulfonic acid)-grafted solid catalysts: new materials for acid-catalysed organic synthetic reactions

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The synthesis, characterisation and application of novel high-density poly(vinylsulfonic acid)-grafted solid acid catalysts are described. A graft, radical polymerization procedure was employed, allowing the immobilisation of the acid form of vinylsulfonic acid monomer onto various carrier materials, such as polystyrene, silica or polysaccharide-based gels. The highest acid-exchange capacity (as determined by acid–base titration methods) achieved with these new materials was 5.2 mmol H^+ g^{-1}. The properties of these PVS-grafted materials as solid state acid catalysts have been examined from several perspectives, including their fundamental properties as materials with extremely high acid dissociation characteristics, their structural features as revealed from IR and solid-state NMR measurements, their thermal stability properties, and their surface morphologies, humidity dependencies and functionality. Compared to many other types of acid catalysts, these high-density poly(vinylsulfonic acid)-grafted materials demonstrated superior catalytic performance in esterification, Friedel–Crafts acylation, and condensation reactions. Moreover, these novel materials show high stability, significant anticorrosion capability and can be easily recycled.

Introduction

The use of recyclable catalysis for chemical reactions is a key green chemistry goal.[1] Acid catalysed reactions is one area where the use of recyclable catalysts would have great scope. For example, acid-catalyzed synthetic reactions such as esterification, Friedel–Crafts acylation and other condensation reactions have found numerous important applications, producing many value-added organic intermediates and other products.[2] Preparation of organic esters and aromatic ketones using acid-catalyzed esterification and ketonization reactions is of particular importance in the industrial manufacture of compounds used as food preservatives, pharmaceuticals, cosmetics, perfumes, plasticisers, solvents and other chemical auxiliaries. For example, bisfurylalkanes obtained by condensation reactions are relevant intermediates in several fields of macromolecular chemistry, with their derivatives used in many applications, *e.g.* as foundry cores and moulds, corrosion-resistant materials, and as precursors for graphitic composites and adhesives.

In conventional practice, strong mineral acids catalysts, such as sulfuric acid or hydrogen fluoride, are deployed as single use reagents in homogeneous systems due to their miscibility in the reaction medium. Lewis-acid catalysts like anhydrous aluminium trichloride, trifluoroborane or organotin chloride, have been similarly used for such reactions.[2,3] Although high yield and selectivity can be obtained with such catalysts, the use of corrosive mineral acids however necessitates a neutralization step after the reaction is completed to separate the product from the hazardous acids, generating considerable waste. Similarly, metal-containing Lewis-acid catalysts also require careful removal after the reaction by adsorption onto, *e.g.* Fuller's earth, which also produces a large amount of waste. For example, a minimum of four moles of hydrochloric acid and one mole of hydrated aluminium salt waste are generated for every mole of product for the majority of industrial Friedel–Crafts processes involving the reaction of phenyl ethers with acyl chlorides.[4] Therefore, to achieve minimal waste production, easier product recovery and greater atom efficiencies, it is imperative that "greener" catalytic processes are developed.

Within an industrial setting, the use of heterogeneous catalysis is often favoured for many synthetic reactions. The deployment of heterogeneous methods with an active acid species can result in improvement in the overall economical efficiency of the process and is usually preferable from an environmental point of view.[5] Many heterogeneous catalysts have been previously developed and reported for use in acid-catalyzed organic reactions, including heteropolyacids, zeolites, and titania.[6] In the absence of co-additives, these types of heterogeneous catalysts suffer from the disadvantages of relatively low catalytic activity under equimolar conditions, acidities that are difficult to adjust, and a lack of stability.

The use of sulfonic acid immobilized inorganic materials has also attracted attention.[7] Such acid immobilized inorganic materials characteristically combine extremely high surface areas and larger pore diameters than conventional inorganic acids such as zeolites and can be used at lower temperatures. However, these materials also suffer from the same limitations as many

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other currently used heterogeneous acid catalysts, requiring special conditions, such as stoichiometric imbalance reactions to achieve high catalytic activities. For example, when such heterogeneous acid catalysts are used in esterification reactions, carboxylic acids are often reacted with large molar excesses of the alcohol to bias the chemical equilibrium. Nevertheless, when compared to the mineral or Lewis acid type of acid catalysts, such solid acid catalysts have a number of distinct advantages, including their potential for improved ease of handling and re-use in batch or continuous (flow) liquid phase reactions, coupled with the possibility for lower toxicity and corrosiveness.

Recently, in a preliminary report we described the use of a poly(vinylsulfonic acid) (PVS)-grafted polystyrene acid catalyst as an organic solid state acid catalyst.[8] The preparation of this catalyst involved the macromolecular introduction *via* a graft polymerization procedure of multiple sulfonic acid groups as part of the polymer coating onto the carrier surface. The catalytic properties of this new solid acid catalyst were thus not dependent on the surface area of the carrier material *per se* but rather involved a readily accessible surface cladding with many sulfonic acid groups juxtapositioned within a polymeric network. We have now extended this earlier study and describe below the applications and synthesis of the highest acid density sulfonic acid polymer yet prepared as a grafted material polymer generated by radical polymerization of the acid form of vinylsulfonic acid (VSA)[9] resulting in an immobilised poly(vinylsulfonic acid) (PVS, ion-exchange capacity: IEC = 5.2 meq g^{-1}), as the solid state analogue of sulfuric acid. In this manner, a high density solid acid catalyst was generated *via* polymer synthesis with the favourable attributes of reusability. Moreover, with the immobilised grafted PVS, it can be noted that the sulfonic acid groups exist in a grafted 'tentacular' environment whereby the diffusional paths and access of the reagents to the catalytic sites do not have the same constraints as found with porous silica materials bearing immobilised sulfonic acids as polymeric monolayers. With such monolayer silica-based materials, higher catalytic efficiencies can often be achieved when the acid density is lower rather than higher. In contrast, with high density immobilised grafted PVS, the catalytic site accessibility and dispersivity will be different when porous silica is employed rather than other types of materials because of the higher order architecture of silica, and these features will differentiate the catalytic activities. The immobilized PVS's were thus expected to have broad application uses, such as a strong cation exchange for use in water retention, as an anti-static agent, as a capture material for amines and other basic compounds, and as heterogeneous acid catalysts allowing high substrate turn-over numbers due to their high acidity and selectivity, coupled with their capability to be reused.

In this paper, we firstly document the extremely high acidity of VSA in its acid form in both aqueous and water-free state. Secondly, we describe in detail the synthetic approach employed for the immobilization of VSA onto various carriers such as polystyrene, silica and polysaccharide materials under various experimental conditions to achieve high protonic ion exchange capacities. Based on this approach, we have obtained PVS densely-grafted onto different carrier surfaces using a very high acid purity (>98.1 wt%) and metal-free (<20 ppb) state acid form of the VSA, thus overcoming previous constraints due to difficulties in the purification of the acid form of the VSA monomer by cation exchange from the sodium salt of VSA. Moreover, these studies document the general versatility of the immobilised PVS as a solid acid catalyst and demonstrate the catalytic activity of the fully characterized PVS-grafted polystyrene (PSt) and related materials in typical acid-catalyzed reactions such as esterification, acylation and condensation reactions.

Experimental

Chemicals

Vinylsulfonic acid (VSA) was supplied from Asahi Kasei Finechem Co., Ltd. and purified as described previously.[8] The purified VSA did not contain any polymerization inhibitor. The monomer conversion was 98.1% (0.7% water), and its metal content was 3 ppb Fe, < 20 ppb Ca, < 10 ppb Na, < 1 ppb Cr, < 2 ppb Cu. The VSA purity was also monitored by ^{1}H NMR and ^{13}C NMR measurements. ^{1}H NMR (500 MHz, D_2O; ppm) $\delta = 6.22$ (1H, dd, $J = 16.6, 10.2$ Hz, $CH_2{=}CH$), 5.58 (1H, d, $J =$ 16.6 Hz, $CHH{=}CH$), 5.33 (1H, d, $J = 10.2$ Hz, $CHH{=}CH$); ^{13}C NMR (125 MHz, D_2O; ppm) $\delta = 138.6, 123.4$. The radical initiator, 4,4′-azo-bis(4-cyanovaleric acid) (ACV, Fluka) was used after drying at 25 °C *in vacuo*. *N*-Ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), aminomethylated polystyrene beads (4.0 mmol g^{-1} NH_2 loading; NH_2-PSt beads) and 3-aminopropyl-functionalized silica (1.0 mmol g^{-1} NH_2 loading; NH_2–Si) were purchased from Aldrich. Sepharose® 6 FF was purchased from GE Healthcare. Other chemicals were of analytical reagent grade.

Synthesis procedure for ACV-attached PSt

The ACV-attached PSt was synthesized as follows. ACV (32 mmol) and EEDQ (64 mmol) were dissolved in DMF (400 mL) in a three-necked flask. The solution was bubbled with Ar gas for 30 min. NH_2-PSt beads (4 g) were then immersed in the solution, and the mixture degassed again for 30 min before commencement of the reaction, which was carried out at 25 °C for 8 h under an Ar atmosphere. The ACV-attached PSt beads were washed consecutively with DMF and ethanol and dried *in vacuo* at 30 °C for 1 day. The ACV-attached PSt beads (9 g) were obtained as a faint yellow powder. Elemental analysis; C: 70.6%. H: 7.2%, N: 12.3%.

Synthesis procedure for the PVS-grafted PSt solid acid catalyst

The poly(vinylsulfonic acid) (PVS)-grafted PSt was synthesized as follows. VSA (40 mmol) and the ACV-attached PSt beads (0.5 g) were added in a round-bottom flask. The reaction was carried out at 65 °C for 2 days under an Ar atmosphere. The PVS-grafted PSt beads were filtered and extensively washed three times with water, methanol, and acetone by decantation to remove any non-immobilized PVS and monomers. The product was then dried *in vacuo* at 90 °C for 2 days. The PVS-grafted PSt beads (0.8 g) were obtained as a pale brownish powder. Elemental analysis; C: 40.7%. H: 6.0%, N: 2.0%, S: 17.6%.

Synthesis procedure for PVS-grafted Sepharose®

First, epoxy-activated Sepharose® was synthesized as follows. Suction-dried Sepharose® 6 FF (250 g), thoroughly washed with water (5 mL × 300 mL), was placed in a round bottom flask and mixed with 2 M NaOH (250 mL) and $NaBH_4$ (12.4 mmol) at room temperature for 2 h by means of an overhead mechanical stirrer. Epichlorohydrin (150 mL) was then added and the suspension stirred for a further 21 h. The resulting epoxy-activated gel was collected by vacuum filtration and washed with water (5 × 300 mL), 20% ethanol aqueous solution (5 × 300 mL), and once more with water (5 × 300 mL). Secondly, the aminated Sepharose® was prepared as follows. An aliquot of the wet cake of the epoxy-activated gel (240 mL) was suspended in 2 M NH_4OH (240 mL) and gently shaken for 21 h at 28 °C. The aminated Sepharose® gel was then washed with 10 volumes of distilled water. The process employed for the graft polymerization with VSA after preparation of the aminated carrier was similar to the procedures used for the preparation of the ACV-attached PSt and the PVS-grafted PSt.

Synthesis procedure for PVS-grafted silica

PVS-grafted silica was prepared using NH_2–Si in a manner similar to the ACV-attached PSt and PVS-grafted PSt. The PVS-grafted silica was obtained as a pale brownish powder.

Synthesis procedure for PSS-grafted PSt

Poly(styrenesulfonic acid) (PSS)-grafted PSt was synthesized using NH_2-PSt (4 g) in a manner similar to the ACV-attached PSt and the PVS-grafted PSt. The grafting monomer, 4-styrenesulfonic acid was prepared by cation-exchange of sodium 4-styrenesulfonate. The PSS-grafted PSt was obtained as a pale yellowish powder.

Material characterisation

UV spectra were obtained with a JASCO V-670 UV-vis-NIR spectrometer. The effective range was from 190 nm to 2700 nm. The calculated H_0 values were based on the value at $[H^+] = 1\ mol\ L^{-1}$. The water content of the sulfonic acid derivatives was determined by Karl Fischer coulometry using a Metrohm 831 KF apparatus. Anolyte and catholyte were coulomat AG and AK. The water content of all sulfonic acid derivatives was less than 0.6 wt%. The acid capacities of the solid acid catalysts were determined by acid–base titration with 0.02 M NaOH using a Metrohm 808 Titrando autotitrator & 801 stirrer. The titration experiments were performed in duplicate and the average number for the acid capacities reported. The particle diameters were measured by a Nikon SMZ-2B stereoscopic microscope and a Keyence VHX-900 digital stereoscopic microscope. SEM images were recorded on a Hitachi S4500S field-emission scanning electron microscope. The organic content of the synthesized materials was quantified by elemental analysis performed on a Carlo Erba Elemental Analyser EA CHNS analyzer. Fourier transform infrared (FT-IR) spectra of samples were recorded on JASCO FT/IR-6100 with KBr pellet technique. The effective range was from 400 cm^{-1} to 4000 cm^{-1}. Thermal stabilities were evaluated by thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimeter (DSC). TG-DTA curves of the samples were measured using a Rigaku TG8120. T_g was measured using a TA Q200 differential scanning colorimeter. Water uptake of a hydrated sample was measured by immersing the sample in water at 25 °C for 48 h, the sample was then removed and the recovered samples quickly weighed on a microbalance.

Water uptake was calculated from:

$$\text{Water uptake} = (W_s - W_d)/W_d \times 100\ [\text{wt\%}] \quad (1)$$

where W_s and W_d are the weights of wet and dried samples, respectively.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of the ungrafted free polymer sample were determined by gel permeation chromatography (GPC) at 40 °C using a system equipped with a Tosoh guard column (TSKguardcolumn PW_{XL}, 6.0 mm × 4 cm) and two TSKgel 10 µm columns (G3000PW_{XL} and G4000PW_{XL}) with a differential refractive index detector (Shimadzu, RID-10A). Water containing 20% acetonitrile and 0.2 M $NaNO_2$ was used as an eluent at a flow rate of 1.0 mL min^{-1}. The sample was calibrated with PSS standard samples with M_n value in the range of 1,000,000–910 g mol^{-1}.

^1H solid-state MAS NMR spectra were recorded on a JEOL CMX-400 spectrometer using a double-resonance MAS probe supporting rotors of 2.5 mm o.d. The resonance frequency of ^1H is 399.8 MHz. The dried samples were spun at 24 kHz. The $\pi/2$ pulse lengths were set to 2 µs. A recycle delay of 3 s was used. ^{13}C Solid-state CP/MAS NMR spectra were recorded on a JEOL CMX-400 spectrometer using a double-resonance MAS probe supporting rotors of 5 mm o.d. The resonance frequency of ^{13}C was 100.5 MHz. The dried samples were spun at 10 kHz. A contact time of 5 ms and a recycle delay of 5 s were used. ^{13}C chemical shift was referenced to hexamethylbenzene. XPS data were obtained using a JEOL JPS-9010TR spectrometer with an Mg-Kα line source. All spectra were calibrated with respect to the position of the carbon 1 s peak at 284.6 eV.

Catalytic reactions

The catalytic performance of the new catalysts was tested for esterification, acylation and condensation reactions. Catalytic reactions were carried out in a three-necked round-bottom flask fitted with a reflux condenser to prevent the escape of volatile liquid components. The flask with its content was heated at a constant temperature in a heating oil bath and stirred continuously. The mixture was heated to the desired reaction temperatures, and then the dry catalyst was added with continuous stirring. For the esterification reactions, ten recycling cycles were examined without loss of catalytic activity, whilst the recycling tests for the catalytic condensation reaction of 2-methylfuran with acetone were carried out five times. The used catalyst was filtrated from the reaction mixture and reused in a new reaction cycle without any treatment. In order to monitor the progress of the reaction, reaction products were collected at different time intervals, separated from solid catalyst particles by means of a syringe filter, and analyzed by ^1H NMR in $CDCl_3$ using internal TMS as standard. ^1H NMR spectra were recorded using a JEOL-Lambda 500 and ECX 500 spectrometers. Commercial Amberlyst® 15 catalyst (Aldrich) and Nafion® silica composite catalyst (SAC-13, Aldrich) were also used for the same reaction as the heterogeneous catalyst control of all reactions. Sulfuric acid, vinylsulfonic acid, and benzene sulfonic acid were used as the homogeneous catalyst controls in the esterification reactions.

Results and discussion

Acid dissociation ability of the high-purity and metal-free acid form monomer of VSA

The remarkably high acid dissociation ability of the high-purity and metal-free acid form of VSA was elucidated from a combination of spectroscopic and Hammett methods. Thus, the Brønsted acidic scale of various sulfonic acid derivatives was determined using UV-visible spectroscopy with a basic indicator (*p*-nitroaniline; $pK(I)_{aq} = 0.99$).[10] The Brønsted acidity was evaluated from the Hammett acidity functions. The properties of protons depend on both the nature of the solvent and the nature and concentration of the acid. In a given dissociating solvent (s), the Hammett function (H_0) is defined as

$$H_0 = pK(I)_{aq} + \log([I]_s/[IH^+]_s) \quad (2)$$

where $pK(I)_{aq}$ is the pK_a value of the indicator referenced to an aqueous solution, and $[IH^+]_s$ and $[I]_s$ are the molar concentrations of the protonated and unprotonated forms of the indicator in the solvent(s), respectively. Due to the high acidity of the VSA sample, the absorbance at 378 nm of the unprotonated form of the basic indicator decreased (Fig. 1). Hence, the $[I]/[IH^+]$ ratio was determined from the measured absorbance differences after the addition of the acid sample, and the acidity order and the H_0 values of VSA determined.

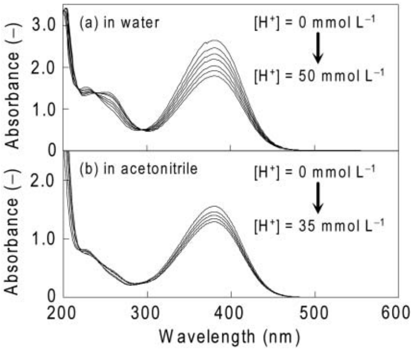
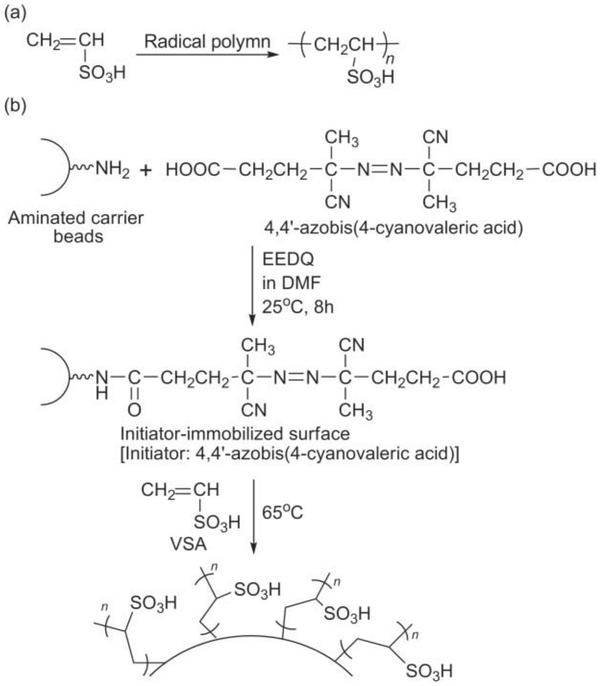


Fig. 1 Absorption spectra of *p*-nitroaniline for various concentrations of VSA (a) in water and (b) in acetonitrile.

From these results, a linear correlation was established between the H_0 values and the proton concentration, with VSA showing a relatively low acid function value ($H_0 = 0.74$) compared to other organic sulfonic acids, such as methanesulfonic acid (MSA; $H_0 = 1.7$) or benzenesulfonic acid (BSA; $H_0 = 2.3$) in water. Moreover, VSA showed surprisingly strong acidity ($H_0 = -1.4$) in non-aqueous solutions. This result indicates that VSA exhibits a very high acid dissociation propensity compared to other sulfonic acid derivatives both in aqueous and non-aqueous solutions. This tendency is derived from the strongly electron withdrawing nature of the vinyl group and concomitant stabilization of the sulfonate anion in VSA. Since in the presence of VSA, individual water molecules behave as a base with a more pronounced solvating behaviour towards ionised protons rather than maintaining the bulk hydrogen bonded network of water as a solvent, the absorbance of the unprotonated form of the indicator increased, and the H_0 value in an aqueous solution was higher than observed for a non-aqueous solution.

Preparation of the PVS-grafted acid catalysts and their characterisation

As part of these investigations, PVS has been grafted onto a variety of carrier surfaces, such as polystyrene, silica and cross-linked agarose, by radical polymerization. Scheme 1 shows an example of the procedure employed with an immobilized initiator and PVS. In this case, the preparation of the grafted PVS catalyst involved two steps: (a) the introduction of the radical initiator onto the carrier surface, and (b) radical polymerization of the acid form of monomeric VSA. Firstly, the aminated carrier surface was allowed to react with 4,4′-azobis(4-cyanovaleric acid) (ACV), a functional free radical initiator.[11] *N*-Ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) was then used as a condensation agent. Previously we have shown that EEDQ, which is available at low cost, allows the coupling of acylamino acids with amino acid esters in high yield in a single one-pot operation.[12] Then, the ACV-attached PSt was mixed with the acid form of VSA and the mixture heated to initiate the polymerization *via* radicals anchored at the carrier surface.



Scheme 1 (a) Polymerization of vinylsulfonic acid; (b) preparation for grafting a carrier surface with poly(vinylsulfonic acid).

For aminomethylated PSt beads (NH_2-PSt) as a starting material, the conditions for the graft polymerization of VSA are given in Table 1. The number of sulfonic acid groups introduced onto the carrier surface by the PVS graft polymerization was measured by a neutralization titration method. The introduction of the sulfonic acid groups was similarly confirmed by elemental

Table 1 Graft polymerization conditions of vinylsulfonic acid onto a carrier surface[a]

Entry	Carrier	VSA/mmol	Solvent	[Solvent]/mol L^{-1}	[Surfactant[b]]/mmol L^{-1}	Reaction time/h	Immobilized acid groups[c] (mmol H^+ g^{-1})
1	PSt	40	Bulk	—	—	20	3.8
2	PSt	40	Bulk	—	—	48	5.2
3	PSt	20	Water	4	2	48	0.8
4	PSt	20	Water	4	20	48	1.0
5	PSt	20	Water	4	100	20	0.7
6	PSt	20	TEG[d]	4	—	20	2.2
7	PSt	20	DMF	10	—	20	3.0
8	PSt	20	DMF	4	—	20	2.2
9	Si	40	Bulk	—	—	20	1.8
10	Si	20	Water	4	20	20	0.7
11	Si	20	DMF	4	—	20	1.0
12	Sepharose®	20	DMF	4	—	20	Dissolution

[a] ACV-attached PSt = 0.5 g, ACV-attached Si = 0.2 g, ACV-attached Sepharose® = 0.2 g, reaction T = 65 °C. [b] Tween 85. [c] Calculated by titration experiment. [d] TEG: Tetra(ethyleneglycol).

analysis. VSA was successfully used as the acid form monomer in this direct graft polymerization onto the carrier surface. The graft polymerization under the VSA monomer bulk condition shown in Table 1, entries 1–2 gave extremely high sulfonic acid densities (5.2 mmol H^+ g^{-1} as a maximum loading). The graft ratio of the PVS-grafted PSt was 128% as calculated from the neutralization titration of the PVS-grafted PSt. On the other hand, uniformly lower acid densities, approximately 1.0 mmol H^+ g^{-1} (Table 1, entries 3–5), were obtained with reactions in aqueous solution, regardless of the amount of added surfactant. When DMF or tetra(ethyleneglycol) (TEG) was used as solvent, the PVS-grafted PSt was obtained with comparatively high acid introduction levels (2.2–3.0 mmol H^+ g^{-1}). These acid levels of the PVS-grafted PSt were much higher than those found for strong Brønsted acid sites in conventional sulfonic acid immobilized solid acid catalysts (in the range of 0.5–1.5 mmol H^+ g^{-1}).[7] The value of 5.2 mmol H^+ g^{-1} as a maximum loading of the PVS-grafted PSt was also higher than the density of sulfonic acid groups with commercially available solid acid catalysts, such as Amberlyst® 15 (4.7 mmol H^+ g^{-1}) and Nafion® SAC-13 (0.8 mmol H^+ g^{-1}).[13]

In order to determine the molecular weight of the grafted PVS polymer, the molecular weight of the free PVS polymer was first determined. The M_n of the PVS polymer grafted onto the carrier surface was then correlated to that of the ungrafted free polymer produced under similar reaction conditions.[14] Since the molecular weight of the ungrafted free PVS polymer was $M_n = 1.0 \times 10^4$, $M_w = 2.4 \times 10^4$, the value of $M_w/M_n = 2.3$ at a maximum (Table 1, entry 2), whilst for the PSS-grafted PSt, the molecular weight of the ungrafted free PSS polymer was $M_n = 4.3 \times 10^3$, $M_w = 1.3 \times 10^4$, with $M_w/M_n = 3.0$.

Furthermore, the graft polymerization of PVS on silica and Sepharose® carriers was also investigated, utilising the same synthetic approach. In the case of the silica carrier, the introduction levels of VSA were similar to that achieved with the PVS-grafted PSt, *i.e.* the highest acid density (1.8 mmol H^+ g^{-1}) was obtained under the VSA monomer standard conditions. Given the number of the reactive amino groups present in the NH_2-functionalized silica (1.0 mmol g^{-1} NH_2 loading), the acid density of the PVS-grafted Si was comparable to the high levels of the PVS-grafted PSt. This tendency did not change for the PSS-grafted PSt (3.9 mmol H^+ g^{-1}), which was obtained from the radical polymerization of 4-styrenesulfonic acid in a manner similar to the preparation of the PVS-grafted PSt. However, when water/surfactant or DMF solution conditions were used, the introduced levels were not as high as obtained for the PVS immobilized samples prepared with the monomer bulk conditions. When Sepharose® was used as a carrier, the carrier was degraded by the high acidity of the VSA. This outcome did not change even when various other conditions were explored, such as changes in solvent composition or temperature. Accordingly, we selected the PVS-grafted PSt as a particularly promising material for use as the solid acid catalyst.

Thermal properties of the PVS-grafted PSt acid catalyst

Along with acid–base titration experiments and elemental analysis, the introduction of sulfonic acid polymer onto the carrier surface was confirmed by IR-spectra and ^1H solid state MAS NMR spectra based on procedures reported previously.[8] Thermal gravimetric analysis (TG/DTA) was conducted over a temperature range from 25 to 450 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere for the materials after modification with PVS and compared to the parent support material sample, NH_2-PSt. The TG/DTA curves presented in Fig. 2 revealed that the weight residue between the PVS-grafted PSt and the NH_2-PSt were quite different because of the presence of the

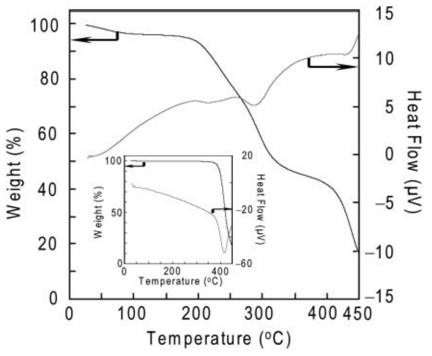


Fig. 2 TG-DTA curves of the PVS-grafted PSt from 25 to 450 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere; inset: TG-DTA curves of the NH_2-PSt.

high-density grafting organic sulfonic acid polymer. A weight loss below 110 °C was observed for the PVS-grafted PSt, which is due to the removal of the physisorbed water from the surface of the grafted polymer.

This physisorbed water is due to the high water absorbing property of sulfonic acid moieties in spite of the strictly reduced-pressure drying. The decomposition of the PVS-grafted PSt was characterised by two general steps, one in the region of 200–300 °C and the other over 400 °C. The former transitional weight loss involves the oxidation and degradation of sulfonic acid groups which probably begin near to 200 °C. The decomposition of cross-linked polystyrene begins near to 400 °C, a tendency that was consistent with that of the NH_2-PSt. Thermal gravimetric analysis results revealed that the PVS-grafted PSt is thermally-stable up to 200 °C in a nitrogen flow atmosphere.

The T_g (glass-transition temperature) of the PVS-grafted PSt was observed at −24 °C measured by DSC over a temperature range from −80 °C to 200 °C at a heating rate of 10 °C min^{-1} and at a cooling rate of 30 °C min^{-1} under an Ar atmosphere, and was almost the same as found for the PVS homopolymer (−27 °C). The slight difference in T_g values between the PVS-grafted PSt and PVS homopolymer can be attributed to immobilization onto the carrier surface.

Surface morphology and humidity behavior of the PVS-grafted PSt acid catalyst

The particle diameter distribution of the PVS-grafted PS t was 80–100 µm, similar to the starting material as measured by a stereoscopic microscope, though the particle shape of the NH_2-PSt was unequal in size and distinctly heterogeneous.

The surface morphology of the PVS-grafted PSt was monitored by field-emission scanning electron microscopy (FE-SEM). Typical SEM images are shown in Fig. 3. It is apparent from these SEM images that the surface morphology of the PVS-grafted PSt is quite different from the NH_2-PSt. The PVS-grafted PSt had a more planar surface than the NH_2-PSt due to the high-density graft polymerization of PVS onto the carrier surface.

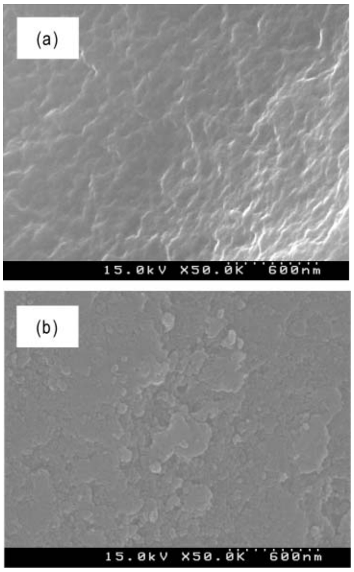
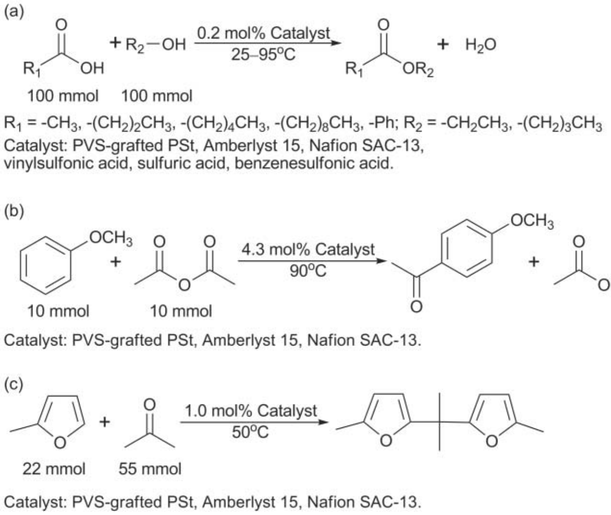


Fig. 3 Field-emission scanning electron micrographs of the surface observation of (a) PVS-grafted PSt and (b) NH_2-PSt.

The humidity dependence of water uptake was measured for the PVS-grafted PSt at 25 °C under relative humidity close to 75%. The water uptake of the PVS-grafted PSt (174 wt%) was 10 times higher than that of the NH_2-PSt (17 wt%). This result was expected, since water should have little effect on the NH_2-PSt beads. Furthermore, the PVS-grafted PSt possessed an extremely high water affinity compared to Amberlyst® 15 (114 wt%) or Nafion® SAC-13 (95 wt%). From a standpoint of a swelling property, the PVS-grafted PSt was expanded by 1.2 times from its initial particle diameter as assessed by optical microscopy.

Catalytic activity of the PVS-grafted PSt

The catalytic performance of the PVS-grafted PSt was evaluated in several acid catalyzed reactions, such as esterification, acylation and condensation reactions. The efficiency of the PVS-grafted PSt was then compared to other known acid catalysts (homogeneous catalyst: sulfuric acid, vinylsulfonic acid, and benzenesulfonic acid; and heterogeneous catalysts: Amberlyst® 15 and Nafion® SAC-13). The experimental conditions were chosen to enable comparative assessment of the best performance of these homogeneous/heterogeneous catalytic materials in these reactions. The schematic for these catalytic reactions is presented in Scheme 2.



Scheme 2 Various acid-catalyzed reactions: (a) esterification of carboxylic acids with alcohols, (b) acylation of anisole with acetic anhydride, and (c) condensation of 2-methylfuran with acetone.

Esterification is an industrially important reaction, producing organic esters at the level of multi-tonnes per year.[2] Previously, we have described in a preliminary report the catalytic activities of a PVS-grafted PSt for esterification reactions using acetic acid with alcohols using equimolar amounts of reactants.[8] Here, we extend this reaction to various other carboxylic acids. The reaction rate constants for these esterification reactions are shown in Table 2. All these reactions showed much higher conversion levels in the presence of the catalyst than in the absence of catalyst, and the same held for the reaction rate constants.

Table 2 Reaction rate constant of the esterification of carboxylic acids with ethanol catalyzed by various catalysts[a]

	Rate constant k_1 ($\times 10^{-4}$ L mol^{-1} s^{-1})				
Catalyst[b]	Acetic acid	Butyric acid	Caproic acid	Lauric acid	Benzoic acid
PVS-grafted PSt	11	2.9	2.7	0.87	0.21
Amberlyst® 15	5.6	1.5	1.2	0.55	0.022
Nafion® SAC-13	2.0	0.50	0.42	0.21	0.018
VSA	18	12	—	—	—
BSA	13	9.1	—	—	—
Sulfuric acid	18	12	—	—	—
No catalyst	0.44	0.11	0.10	0.076	0.0011

[a] Reaction conditions: carboxylic acid = 0.1 mol, ethanol = 0.1 mol, homogeneous acid catalysts = 0.45 mmol, heterogeneous acid catalysts = 0.1 g, T = 65 °C. [b] VSA: vinylsulfonic acid, BSA: benzenesulfonic acid.

The reaction rate constants generally tended to decrease with increasing alkyl chain length of the carboxylic acid species as the reactant. Moreover, the acid-catalyzed esterification reactions were affected more by the nature of the carboxylic acids than that of alcohols.

Even though the reaction rate constants of the PVS-grafted PSt were lower than that found for the homogeneous catalysts, they were 2–5 times higher compared to the other solid catalysts. Significantly, the rate constants of the PVS-grafted PSt were also higher than that of Amberlyst® 15, which has almost equal acid densities, in these esterification reactions. Moreover, comparison of the PVS-grafted PSt with the Nafion SAC-13 also confirmed that on an equivalent acid basis the PVS-grafted PSt was more catalytically active, *i.e.* with an equivalent acid amount of 0.45 mmol at a temperature of 65 °C the reaction conversion at 2 h with the PVS-grafted PSt was nearly twice that of the Nafion SAC-13. The PVS-grafted PSt structure, due to the nature of the grafted polymer chains containing numerous sulfonic acid groups, is presumed to undergo a significant expansion in the solvent during the esterification reactions. From NMR studies, it was obvious that the reaction sample contained only the reactant and the ester product. Thus, there was no by-product formation or leakage of the PVS from the carrier surface. The PVS-grafted PSt showed high catalytic activity in the case of 1-butanol. The reaction rate of the esterification of ethanol or 1-butanol with acetic acid acid-catalyzed by PVS-grafted PSS (1.1×10^{-3} L mol^{-1} s^{-1} and 7.1×10^{-4} L mol^{-1} s^{-1}, respectively) was much higher than those acid-catalyzed by PSS-grafted PSt (4.4×10^{-4} L mol^{-1} s^{-1} and 2.2×10^{-4} L mol^{-1} s^{-1}, respectively). This result indicates that the grafted polymer, PVS-PSt, has a extremely high capability as an acid catalyst compared to other sulfonic acid polymers such as PSS. This property of the new immobilised PVS-PSt material thus reflects an important advantage of this type of grafted polymeric solid catalyst with its high acidity, which translates to comparatively higher catalytic efficiency and conversion results. Moreover, the results confirm that the PVS-grafted PSt can be reused repeatedly without any significant loss of activity.

Similarly, the use of the PVS-grafted PSt led to efficient Friedel–Crafts acylation of anisole with acetic anhydride. Acetic anhydride was chosen as an acylating agent instead of acetyl chloride, in order to simulate avoidance of formation of the corrosive HCl by-product, which could arise in an actual large scale process. Anisole was reacted with acetic anhydride with the PVS-grafted PSt (molar ratio = 1 : 1 : 0.09) at 90 °C for 1 h in the absence of solvent. The same reaction was repeated with other conventional solid acid catalysts in the same molar proportions (Table 3). In terms of conversion, the catalytic activity of the PVS-grafted PSt was higher than that of Nafion® SAC-13, but lower than that of Amberlyst® 15. The outcome was partially due to the strong adsorption of the *p*-methoxyacetophenone, one of the main products obtained in this reaction, on the acid sites of the PVS-grafted PSt catalyst, and thereby preventing its further catalytic activity. However, the PVS-grafted PSt showed a very high *p*-selectivity, and compared favorably with the other conventional solid acid catalysts.

Table 3 Product conversion and selectivity of the acylation of anisole with acetic anhydride catalyzed by various solid catalysts[a]

Catalyst	Acid capacity (mmol H$^+$ g^{-1})	Conversion (%)	Selectivity (%)
PVS-grafted PSt	4.5[c]	50	98
Amberlyst® 15	4.7	54	97
Nafion® SAC-13	0.8	25	96
VSA	9.2	62	97
No catalyst	—	0	0

[a] Reaction conditions: anisole = 10 mmol, acetic anhydride = 10 mmol, catalyst = 0.2 g, T = 90 °C, reaction time = 1 h. [b] Selectivity toward *p*-methoxyacetophenone. The other product was the *o*-isomer. [c] The sample had the same acid capacity used for the esterification reactions.

The catalysis by the PVS-grafted PSt in the condensation of 2-methylfuran and acetone to 2,2-bis(5′-methylfuryl)-propane (bisfuran) at 50 °C (molar ratio = 1 : 2.5 : 0.037) were also compared with those of several other solid acid catalysts. Table 4 shows the results for these various solid acid catalytic reactions. The PVS-grafted PSt showed excellent catalytic activity. The catalytic activities of the other solid acid catalysts, such as Amberlyst® 15 and Nafion® SAC-13 under the same catalytic conditions were much lower than that shown by the PVS-grafted PSt. The faster reaction progress in the case of the PVS-grafted PSt compared to the other solid acid catalysts is also shown in Fig. 4.

From the results of various catalytic reactions, the PVS-grafted PSt has been found to be highly active even with water-generating reactions. This behaviour is significantly different to that found with Amberlyst® 15, which is known to be deactivated by water solvation. This property reflects a remarkable advantage of the PVS-grafted PSt due to the characteristic high water retentivity of PVS, which favours the equilibrium moving towards the formation of the targeted product. In order to establish the reusability of the catalyst for this condensation

Table 4 Product conversion and selectivity of the synthesis of 2,2-bis(5-methylfuryl)propane using the PVS-grafted PSt in comparison with commercial solid acid catalysts and literature precedents[a]

Catalyst	Acid capacity (mmol H^+ g^{-1})	Time/h	Conversion (%)	Selectivity[b] (%)
PVS-grafted PSt	4.5[c]	2	82	99
Amberlyst® 15	4.7	2	59	94
Nafion® SAC-13	0.8	2	18	96
HMS-proSO_3H[d]	1.0[e]	24	73	98
MCM41-SO_3H[d]	1.0[e]	24	85	96
VSA	9.2	2	99	98
No catalyst	—	—	0	0

[a] Reaction conditions: 2-methylfuran = 22 mmol, acetone = 55 mmol, catalyst = 0.18 g, T = 50 °C. [b] Selectivity for 2,2-bis(5-methylfuryl)propane, based on 2-methylfuran. [c] The sample had the same acid capacity used for the esterification reactions. [d] Ref. 7(g). [e] Based on the lowest value in the range quoted in reference.

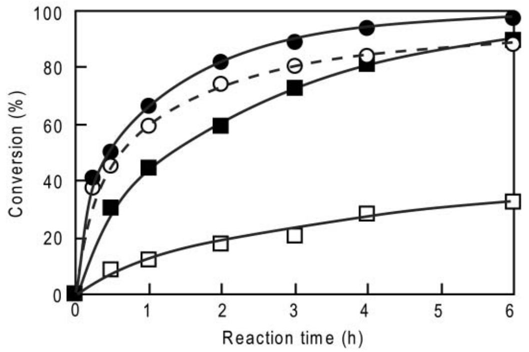


Fig. 4 Time-conversion curves for condensation reaction of 2-methylfuran with acetone at 50 °C (●: the PVS-grafted PSt, ○: the 5th time of recycling PVS-grafted PSt, ■: Amberlyst® 15, □: Nafion® SAC-13).

reaction, the catalyst was recovered by filtration and reused in subsequent cycles. The catalyst was found to retain its activity for at least five cycles of reuse. Although the product yield was slightly decreased from 82 to 74% after the fifth cycle, this difference was due to the small handling losses of the catalyst upon recovery. The selectivity remained almost constant over 90% for all the recycle experiments.

Anticorrosion test for the PVS-grafted PSt

The anticorrosion properties of the PVS-grafted PSt catalyst samples, together with sulfuric acid as a control, were tested on a stainless steel (SUS304) at 100 °C under an air atmosphere. SUS304 is a common austenite type of stainless steel containing Ni (8–10.5%) and Cr (18–20%). After the test, the stainless plate was observed visually and the surface corrosion condition of the stainless plate analyzed by X-ray photoelectron spectroscopy (XPS). While sulfuric acid corroded the stainless steel rapidly and extensively, the stainless steel exposed to the PVS-grafted PSt remained unchanged for long periods of time. From XPS analyses, oxidized sulfur was detected at 169 eV of the S2p binding energy from the stainless plate surface treated with sulfuric acid. The O1s binding energy was found at 532 eV, which can be attributed to the surface oxidization of the stainless steel by sulfuric acid corrosion. Visually, the corrosion of stainless steel was hardly observed by XPS in the case of the PVS-grafted PSt compared with the case of sulfuric acid.

Conclusions

In conclusion, high-density PVS-grafted PSt has been synthesized by graft polymerization of PVS onto the carrier surface and applied as a new class of solid acid catalysis material. With the synthetic conditions described, an acid density of 5.2 mmol H^+ g^{-1} for the PVS-grafted PSt could be obtained as a maximum loading. The PVS-grafted PSt has been found to be very effective as a heterogeneous acid catalyst in various synthetic esterification, acylation, and condensation reactions with very high selectivity. The high catalytic activity of the PVS-grafted PSt was due to the high density and strong acidity of the sulfonic acid groups on the carrier surface. As such, this study introduces a new avenue to carry out such solid phase acid catalysed synthetic reactions in a more benign, green chemical manner, whilst minimizing pollution/contamination risks due to reactor corrosion and allowing the same catalyst to be used repeatedly in a recycling mode of operation.

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