Preparation of a novel poly(vinylsulfonic acid)-grafted solid phase acid catalyst and its use in esterification reactions[†]

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A high-density sulfonic acid polymer, grafted onto a carrier surface, was synthesized from the acid form of vinylsulfonic acid monomer, and its catalytic activity as a new class of heterogeneous acid catalyst demonstrated in esterification reactions.

Poly(vinylsulfonic acid) (PVS) has a high acid density (ion-exchange capacity; IEC = 9.2 meq g⁻¹) and is the solid-state analogue of sulfuric acid. PVS is expected to have various applications, such as strong cationic exchange, for water retention, and as an acid catalyst. Hitherto, the preparation of PVS in very high acid-purity and metal-free state from vinylsulfonic acid (VSA) has presented constraints due to difficulties in the purification of the acid form of the VSA monomer and in the cation exchange of the sodium form of PVS. We have recently succeeded in polymerizing vinylsulfonic acid (VSA) of very high acid-purity (>98.1 wt%) and metal-free (<20 ppb) in water to yield PVS (Scheme 1a).¹ PVS exhibited very high acid properties in both aqueous and waterfree states (acid dissociation constant of VSA: $pK_{HI+A^-} = 0.049$



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† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis, characterization and catalytic properties of the PVS-grafted PSt. See DOI: 10.1039/b823177j in water, -4.9 in acetonitrile), and a very high proton conductivity in dry membrane form (on $10^{-3}-10^{-6}$ S cm⁻¹ in the temperature range from 30 to 150 °C under dry condition).

Esterification is an industrially important reaction, producing organic esters at the level of tonnes per year.² Conventional mineral acid catalysts, such as sulfuric acid, are miscible with the reaction medium, and need to be neutralized after the reaction to separate the product ester from the toxic acid.³ Metal-containing Lewis acid catalysts, like organotin chloride, also require careful removal after the reaction by adsorption onto Fuller's earth, which also produces a large amount of waste.⁴ The use of a heterogeneous solid catalyst system is thus preferable from an environmental and economical point of view.⁵ Distinct advantages of solid acid catalysts can include low toxicity and low corrosiveness; ease of handling, recovery and reuse in liquid phase reactions; and the possibility of their use in a continuous process. Many heterogeneous catalysts have been previously reported in the literature to be active in esterification reactions, including heteropolyacids, zeolites, titania, and sulfonic acid immobilized inorganic materials.^{6,7} However, these types of heterogeneous catalysts suffer from disadvantages of low catalytic activity under equimolar conditions in the absence of additives, such as H2O2, acidities that are difficult to adjust, and typically lack of stability.

In this communication, we describe the synthesis and use of PVS grafted onto a polystyrene (PSt) carrier from the acid form VSA, thus providing a new type of organic solid catalyst. Because of both the high polymerizability of VSA under the developed conditions and the high acid density of PVS, the graft polymerization of PVS resulted in a high density of catalytically active acid sites on the heterogeneous catalyst. We demonstrated the catalytic activity of the PVS-grafted PSt for esterification.

We have grafted PVS onto a PSt carrier by the radical polymerization of VSA. Scheme 1 shows an example of the procedure with immobilized initiator and VSA. This synthesis methodology does not introduce in a one-at-a-time monomolecular fashion sulfonic acid groups through individual covalent anchoring via alkyl chains onto the carrier surface, like a conventional solid acid catalyst,⁷ but rather a macromolecular introduction of multiple sulfonic acid groups as a polymer onto the carrier surface. Firstly, the aminomethyl groups localized at the carrier surface are allowed to react with 4,4'-azobis(4-cyanovaleric acid) (ACV), a functional free radical initiator.8 Next, the ACV-attached PSt was mixed with the acid form VSA and heated to achieve polymerization initiated by the radicals anchored at the carrier surface. VSA was successfully used as the acid form monomer in this direct graft polymerization onto the carrier surface. In addition, we have also studied PVS grafted onto silica and Sepharose®

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Entry		Elemental analysis					
	Sample	С	Н	Ν	S	Immobilized group/mmol g ⁻¹	Water uptake (wt%)
1	NH2-PSt	85.1	9.2	5.7	_	4	17
2	ACV-attached PSt	70.6	7.2	12.3		_	19
3	PVS-grafted PSt	40.7	6.0	2.0	17.6	5.2 ^{<i>a</i>}	174
^a Calcula	ted by titration experimen	ıt.					

Table 1 Characterization of the PVS-grafted PSt

carriers in the same way. However, the carrier was degraded by the high acidity of VSA when Sepharose^{\mathbb{R}} was used.

The PVS-grafted PSt beads and the ungrafted free PVS polymer were separated by filtration and purified. Since the molecular weight of the polymer grafted on the carrier can be correlated with that of the ungrafted free polymer produced in the reaction solution, the $M_{\rm n}$ of the graft PVS polymer is almost equal or at least proportional to that of the ungrafted free PVS polymer.⁹ The molecular weight of the ungrafted free PVS polymer was $M_n = 1.0 \times 10^4$, $M_w = 2.4 \times 10^4$, $M_w/M_n =$ 2.3. The graft ratio of the PVS-grafted PSt was 128% as calculated from the neutralization titration of the PVS-grafted PSt. The introduction of sulfonic acid polymer onto the carrier surface was confirmed from other several perspectives. The IR spectrum of the PVS-grafted PSt shows a large band, attributed to hydroxyl groups coordinated to sulfonic acid cation, with a maximum at around 3400 cm⁻¹ in the OH stretching region compared to that of the NH2-PSt. The two bands observed at 1200 and 1000 cm⁻¹ correspond to the asymmetric stretching vibration and symmetric stretching vibration bands of the O=S=O, respectively. The ¹H solid-state MAS NMR spectrum of the PVS-grafted PSt shows a sharp peak at δ = 6.1 ppm, which correlates with the presence of a strong hydrogen bond network due to a high density of sulfonic acid protons, in the solid phase state.¹⁰ The ¹³C solid-state CP/MAS NMR spectrum of the PVS-grafted PSt showed a broad peak of the PVS alkyl chain at $\delta = 10-60$ ppm and a short peak of the amide linker between the carrier surface and the graft polymers at $\delta = 178.5$ ppm. Measurement of the acid density by neutralization titration methods provided the number of sulfonic acid groups introduced onto the carrier by the PVS graft polymerization. A sulfonic acid density of 5.2 mmol H^+ g^{-1} for the PVS-grafted PSt could be obtained as a maximum loading (Table 1). Sulfonic acid densities for the PVS-grafted silica were up to 1.8 mmol H^+ g^{-1} . The introduction of the sulfonic acid groups was similarly confirmed from the elemental analysis. This level was much higher than those found for strong Brønsted acid sites in conventional sulfonic acid immobilized solid acid catalysts (in the range 0.5–1.5 mmol H⁺ g⁻¹)⁶ and was approximately 7 times higher than the density of sulfonic acid groups (0.8 mmol H^+ g^{-1}) found for Nafion[®], a highly active perfluorosulfonated ionomer.¹¹

The humidity dependence of water uptake was measured for the PVS-grafted PSt at 25 °C under relative humidity close to 75% (Table 1). The water uptake of the PVS-grafted PSt was 10 times higher than that of aminomethylated PSt (NH_2 -PSt). This result was expected, since water should have little effect on the carrier of the PSt beads, with the water uptake attributed to the water-absorbing properties of the PVS. Furthermore, the PVS-grafted PSt possessed an extremely

$$\bigcup_{OH}^{O} + R - OH \xrightarrow{Catalyst}_{25-95^{\circ}C} \xrightarrow{O}_{OR} + H_2O$$

 $\begin{array}{l} \mathsf{R}=\mathsf{-CH}_3, \,\mathsf{-CH}_2\mathsf{CH}_3, \,\mathsf{-CH}(\mathsf{CH}_3)_2, \,\mathsf{-(CH}_2)_3\mathsf{CH}_3, \,\mathsf{-(CH}_2)_9\mathsf{CH}_3\\ \text{i)} \, \mathsf{PVS}\text{-}\mathsf{grafted} \, \mathsf{PSt}=0.1 \, \mathsf{g}, \, \mathsf{iii}) \, \mathsf{Amberlyst} \, \mathsf{15}=0.1 \, \mathsf{g}, \\ \mathsf{iii}) \, \mathsf{Nafion} \, \mathsf{SAC}\text{-}\mathsf{13}=0.1\mathsf{g}, \, \mathsf{iv}) \, \mathsf{vinylsulfonic} \, \mathsf{acid}=0.45 \, \mathsf{mmol}, \\ \mathsf{v}) \, \mathsf{sulfuric} \, \mathsf{acid}=0.45 \, \mathsf{mmol}, \, \mathsf{vi}) \, \mathsf{methanesulfonic} \, \mathsf{acid}=0.45 \, \mathsf{mmol}, \end{array}$

Scheme 2

high water affinity compared to Amberlyst[®] 15 (114 wt%) and Nafion[®] SAC-13 (95 wt%).

The catalytic performance of the PVS-grafted PSt was determined for the esterification of acetic acid with various alcohols (molar ratio 1:1, Scheme 2) and the efficiency of the PVS-grafted PSt was compared to other known homogeneous catalysts (sulfuric acid, vinylsulfonic acid, methanesulfonic acid, and benzenesulfonic acid) and heterogeneous catalysts (Amberlyst[®] 15 and Nafion[®] SAC-13). In these experiments, 0.1 g of the PVS-grafted PSt sample corresponds to acid densities of 0.45 mmol. All the catalysts showed much higher conversion levels than in the absence of catalyst (Fig. 1). This tendency was similar for the reaction rate constant (Table 2). Ester conversion and reaction rate constant generally depended on the nature of the reactant alcohols. From the viewpoint of heterogeneous catalysis, the PVS-grafted PSt gives a reaction rate constant more than 2-10 times higher than other solid catalyst Amberlyst[®] 15 and Nafion[®] SAC-13. It is clear that the PVS-grafted PSt has an extremely high catalytic activity as a heterogeneous catalyst. This high catalytic activity of the PVS-grafted PSt was due to the high sulfonic acid density on the carrier surface, the high affinity for water, and the strong acidity derived from VSA. In comparison, the polystyrenesulfonic acid-grafted PSt (3.9 mmol H^+ g^{-1}) which was obtained from 4-styrenesulfonic acid in a manner similar to the PVS-grafted PSt, or Amberlyst[®] 15 (4.7 mmol H⁺ g⁻¹), did not show the same level of high catalytic abilities as found



Fig. 1 Esterification of acetic acid with ethanol at 65 °C with equimolar amounts of the reactants (\bullet : 0.1 g of the PVS-grafted PSt, \bigcirc : 0.1 g of Amberlyst[®] 15, \blacksquare : 0.1 g of Nafion[®] SAC-13, \square : 0.45 mmol of sulfuric acid, \blacklozenge 0.45 mmol of vinylsulfonic acid, \diamond ; no catalyst).

 Table 2
 Reaction rate constant of the esterification of acetic acid with alcohols catalysed by various catalysts^a

	Rate constant $(k_1 / \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1})$								
Catalyst ^b	Methanol	Ethanol	2-Propanol	1-Butanol	1-Decanol				
PVS-grafted PSt	60	11	2.2	7.1	4.0				
Amberlyst [®] 15	14	5.6	0.56	2.6	2.0				
Nafion [®] SAC-13	4.6	2.0	0.18	1.6	1.3				
PVS		_		9.4	_				
VSA		18		16	_				
MSA		16		13	_				
BSA		13		12	_				
Sulfuric acid		18		17	_				
No catalyst	0.64	0.44	0.068	0.33	0.30				

^{*a*} Reaction conditions: acetic acid = 0.1 mol, alcohols = 0.1 mol, homogeneous acid catalysts = 0.45 mmol, heterogeneous acid catalysts = 0.1 g, temperature = 65 °C. ^{*b*} PVS: poly(vinylsulfonic acid), VSA: vinylsulfonic acid, MSA: methanesulfonic acid, BSA: benzenesulfonic acid.

for the PVS-grafted PSt. No by-product formation, *i.e.* ether formation, or desorption of PVS from the carrier surface was seen, since the NMR spectrum of the reaction sample did not reveal any components other than the reactants and the ester product.

Reusability of a heterogeneous catalyst is key for industrial production. To examine the reusability of the catalyst, the PVS-grafted PSt was filtered from the reaction mixture and reused in a new reaction cycle without any treatment. The progress of the reaction was monitored by taking small aliquots of samples at different time intervals. Fig. 2 shows that every recycled sample demonstrated almost identical conversion to the ester as the fresh catalyst sample, *i.e.* about 55% of ethyl acetate, indicating that there is no significant effect on the activity when the PVS-grafted PSt was reused. It apparently stays chemically stable and active in the presence of water and acetic acid. Furthermore, the corrosion of stainless steel was hardly observed by XPS in the anticorrosion test of the PVS-grafted PSt compared with the case of sulfuric acid. In addition, the catalytic performance of the PVS-grafted PSt was also determined for Friedel-Crafts acylation reaction and condensation reaction, and it showed high catalytic activity. In particular, the synthesis of 2,2-bis(5-methylfuryl)propane using the PVS-grafted PSt highlighted the advantages of this new solid phase catalyst in terms of conversion compared to other catalysts.

In conclusion, the PVS-grafted PSt is one of the ultimate solid acid materials that has both high acid densities and intrinsic strong acid strength derived from VSA in a synergistic manner. The PVS-grafted PSt showed very high catalytic activity as a heterogeneous acid catalyst for esterification. The catalyst can be reused repeatedly without any observed



Fig. 2 Recycling of the PVS-grafted PSt in the synthesis of ethyl acetate (catalyst = 0.1 g, temperature = $65 \,^{\circ}$ C, reaction time = 3 h).

loss of activity, and pollution risks like reactor corrosion are kept to a minimum.

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