



# Taming of superacids: PVP-triflic acid as an effective solid triflic acid equivalent for Friedel–Crafts hydroxyalkylation and acylation



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## ABSTRACT

The application of poly(4-vinylpyridine) supported trifluoromethanesulfonic acid (PVP-TfOH, 1:10) as a convenient solid superacid catalyst system in Friedel–Crafts reactions is described. In the presence of PVP-TfOH, one pot solvent-free synthesis of a wide variety of diarylacetic acid derivatives was achieved by Friedel–Crafts hydroxyalkylation reaction of glyoxylic acid with arenes under mild conditions. Acylation of both activated and deactivated aromatic compounds with acetyl chloride was also achieved using PVP-TfOH complex under solvent-free conditions at room temperature. As the polymer supported triflic acid was found to be a very efficient and an easy-to-handle solid acid, it can be a useful addition to environmentally more adaptable strong acid catalyst systems.

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## 1. Introduction

The Friedel–Crafts reaction is one of the most fundamental and useful reactions for C–C bond formation in organic chemistry [1]. The Friedel–Crafts reaction generally requires Lewis or Brønsted acid catalysts in large quantities, which quite often lead to many difficulties. Many of these catalysts are generally corrosive and difficult to recycle. Thus, there are still enormous demands for clean and eco-friendly Friedel–Crafts processes. Recently, considerable attention has been given towards the development of Friedel–Crafts reactions heterogeneously catalyzed by solid acid catalysts such as zeolites, clays, Nafion-H, heteropolyacids (HPA), etc. [2], in which the acidity is an intrinsic property of the compounds and part of their chemical structure [3]. Nafion<sup>®</sup>-H (1), a perfluoroalkanesulfonic acid resin, has been found to be a viable solid acid catalyst with catalytic activity for many reactions giving high selectivity [4]. As the solid catalyst can be easily recycled, the work-up of such reactions is usually very feasible. Therefore, large scale synthesis of many useful products can be achieved with significantly reduced cost. One major drawback of this catalyst is its inefficient swelling by aprotic organic solvents, which generally leads to low reaction rates. Polymer bound superacids that can be

efficiently swollen by organic solvents are thus desired [5a]. Up to now, several polymer bound Lewis acids and Brønsted acids have been reported [5b]. It is believed that polystyrene bound super Brønsted acid 2 is a strong carbon acid among known solid acids [5]. Different types of polymer tethered Lewis acid catalysts namely “immobilized” or “microencapsulated” Lewis acids such as 3 have been documented [6a]. New polymer supported acid catalysts such as Cross-linked polystyrene-supported aluminum triflate {Ps–Al(OTf)<sub>3</sub>} [6b], aluminum chloride immobilized on cross-linked polyvinyl alcohol microspheres [6c], and poly(vinyl-sulfonic acid)-grafted polystyrene [6c] have also been reported recently (Fig. 1).

Our group observed that PVP {poly(4-vinylpyridine)} is an effective solid support for various gaseous and liquid acidic reagents. The preparation of a polymer supported hydrogen fluoride reagent, poly(4-vinylpyridinium) poly(hydrogen fluoride), was previously reported by Olah et al. Pyridinium poly(hydrogen fluoride) (PPHF, known as the Olah reagent) is an ionic liquid with a high dielectric constant and has been used as a fluorinating agent for alkenes, alkynes and alcohols [7]. Another Lewis acid complex, PVP-SO<sub>2</sub> was used as mild solid acid catalyst for three component Strecker synthesis of α-aminonitriles [8]. PVP-H<sub>2</sub>O<sub>2</sub>, a solid H<sub>2</sub>O<sub>2</sub> equivalent, was exploited for *ipso*-hydroxylation of arylboronic acids to phenols, selective oxidation of sulfides to sulfoxides and conversion of ketones to *gem*-dihydroperoxides [9]. Trifluoromethanesulfonic acid (triflic acid) is a strong non-oxidizing Brønsted superacid, extensively utilized in acid catalyzed synthetic transformations. We have now immobilized triflic acid onto cross

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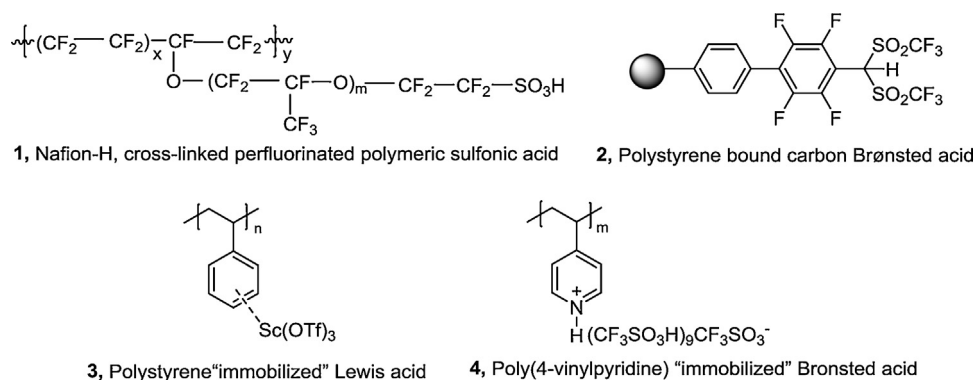


Fig. 1. Polymer-bound superacids.

linked poly(4-vinylpyridine) expecting the formation of a stable PVP-TfOH complex **4**, which represents a convenient solid form of triflic acid (Fig. 1).

In continuation of our studies on superacid catalyzed Friedel–Crafts reactions, we disclose the application of the new PVP-TfOH (1:10) complex, the "immobilized" superacid as an efficient catalyst for the hydroxyalkylation and acetylation of aromatic compounds at room temperature.

## 2. Results and discussion

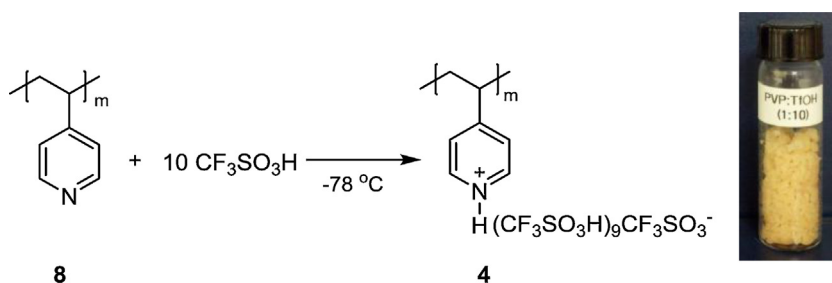
### 2.1. Preparation and properties of poly(4-vinylpyridinium) poly(triflic acid)

Poly(4-vinylpyridinium) poly(triflic acid) in the solid form, was conveniently prepared from poly(4-vinylpyridine) and triflic acid. Commercially available 2% cross linked poly(4-vinylpyridine) was carefully added to triflic acid in small portions at  $-78\text{ }^{\circ}\text{C}$  under nitrogen in the absence of solvents and mixed thoroughly until uniform complexation. A stable creamy white solid powder (slightly wet) was obtained when the loading ratio of the polymer

and triflic acid reached to a 1:10 ratio (Scheme 1). The ratio 1:10 is more preferred for its use as a catalyst because the addition of more triflic acid resulted in a wet solid. The reagent PVP-TfOH (1:10) contains 93% triflic acid by weight and was found to be a very useful and efficient catalyst for the Friedel–Crafts reactions. However, a less acidic form was obtained in a drier solid form if the ratio is less than 1:10.

Poly(4-vinylpyridine) acts as a suitable solid phase reservoir for triflic acid, making the complex more convenient and safer for use. Although the light creamy colored polymer powder slightly fumes when exposed to air, it can be stored in well sealed Nalgene bottles in a refrigerator for months without the detectable loss of the catalytic activity. The surface morphology of the polymer samples was also determined through scanning electron microscope (Fig. 2).

In addition to the SEM characterization, we have also performed TGA analysis of PVP-TfOH (1:10). Initial weight loss of 87% at  $\sim 80\text{--}220\text{ }^{\circ}\text{C}$  in the TGA diagram is probably due to the loss of loosely bound triflic acid molecules which are distant from the pyridinium center in the poly(triflic acid) chain. Additional 12% weight loss occurred at  $\sim 280\text{--}480\text{ }^{\circ}\text{C}$  possibly due to the decomposition from



Scheme 1. Preparation of poly(4-vinylpyridinium) poly(triflic acid).

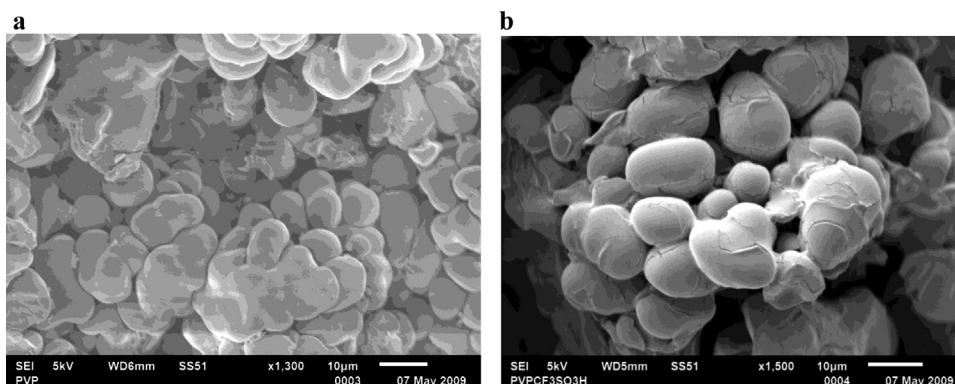


Fig. 2. (a) Surface morphology of 2% cross linked poly(4-vinyl pyridine), (b) Surface morphology of poly(4-vinylpyridinium) poly(triflic acid) (1:10).

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