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ORIGINAL PAPER

N-sulfonic acid poly(4-vinylpyridinium) chloride: an efficient and reusable solid acid catalyst in *N*-Boc protection of amines

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Abstract *N*-sulfonic acid poly(4-vinylpyridinium) chloride is easily prepared by the reaction of poly(4-vinylpyridine) with neat chlorosulfonic acid. This reagent can be used as an efficient catalyst for the *N*-Boc protection of amines at room temperature and neat conditions. This new method consistently has the advantages of excellent yields and short reaction times. Further, the catalyst can be reused and recovered for several times.

Keywords *N*-sulfonic acid poly(4-vinylpyridinium) chloride · Solvent-free conditions · *N*-Boc protection · Poly(4-vinylpyridine) · Heterogeneous catalysis

Introduction

Solid acids have many advantages over liquid acids in organic catalysis. They are less harmful to environment and have no corrosion or disposal of effluent problems. They are reusable and easy to be separated from liquid products. As economically and ecologically benign catalysts, their research and application have attracted much attention in chemistry and industry. There are more than 100 industrial processes using over 103 solid acid catalysts at the end of last century [1]. However, the use of solid acid catalysts suffers from some disadvantages. Supported catalysts are in trouble with 'leaching' that leads to the loss of activity [2]. Although zeolites have higher activity, their application is accompanied with the formation of undesired by-products due to the higher temperature needed for the reaction. On the other hand, ion exchange resins are limited in application because they are thermally unstable above 120 °C in the acid form [3]. Consequently, introduction of new solid acid catalysts that address these drawbacks is desirable.

In several industrially important processes, a large amount of sulfuric acid is required because the water by-products lower their action by diluting the acid. At the end of these processes, a large amount of ''spent acid'' is obtained which, in batch reactions, is usually neutralized and disposed of, while in continuous processes, it has to be recycled by complex techniques. Moreover, sulfuric acid is corrosive and dangerous to transport and handle. The above-mentioned disadvantages for the application of concentrated sulfuric acid led to a substantial effort to develop viable alternatives, using different types of new solid acids replacing sulfuric acid [4].

Protection and deprotection of organic functional groups play an essential role in multistep organic synthesis. The presence of an amino group in various biologically active compounds makes its protection a necessity during their synthesis. The *tert*-butoxycarbonyl (Boc) group is one of the most useful functionalities for the protection of amines and amine derivatives, owing to its stability toward nucleophiles and catalytic hydrogenation and because of its easy removal [5, 6].

In recent years, various methods have been developed for the protection of amines in their *N*-Boc form, either in the presence of basic catalysts such as DMAP [7], aq. NaOH [8] or NaHMDS [9] and Lewis acid catalysts like $Zr(ClO_4)_2{\cdot}6H_2O$ [10], $ZrCl_4$ [11], $LiClO_4$ [12] and Yttria–Zirconia [13]. Brönsted acid ionic liquid [(HMIm)BF_4] [14], sulfamic acid [15], sulfonic acid-functionalized silica [16], β-cyclodextrin [17], thiourea [18], CsF [19], $H_3PW_{12}O_{40}$ [20], montmorillonite K10 and KSF [21] and

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Indion 190 resin [22] are also employed for the *N*-Boc protection. However, despite the potential utility of these catalysts, many of these methodologies are associated with several shortcomings such as extended reaction time, elevated temperatures, tedious work-up, using anhydrous organic solvents, reaction under oxidizing conditions, using strong acids, low yields, harsh reaction conditions, difficulty in the preparation and moisture sensitivity of the catalysts, high cost and high toxicity of the reagents, non-recyclability of the catalyst, and formation of side-products such as isocyanates, poly-acylated products, urea and *N, N*-di-Boc derivatives. Therefore, there is a need to develop an alternative method for the *N*-Boc protection of amines.

Experiment

Materials

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Products were characterized by their physical and spectroscopic data and comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by thin layer chromatography (TLC) on silica-gel polygram SILG-UV254 plates.

Instrumentation

IR spectra were run on a Perkin-Elmer bio-spectrometer. The reaction conversions were measured by GC on a Shimadzu model GC-16A instrument. The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. X-ray diffraction (XRD) measurements were performed at room temperature on a Philips PW1830 generator X-ray powder diffractometer, using Ni filter and Cu-Kα radiation ($\lambda = 1.542$ Å). The scanning was over a range of $2\theta = 10$–$70°$. TGA and SEM analyses were performed on Polymer Laboratories TGA-PL thermal analysis instrument (heating rate of 10 °C/min) and on a Quanta 200 microscope (the samples were coated with gold powder on 682 Gatan Inc.), respectively. All measurements were conducted under nitrogen.

Catalyst preparation

Chlorosulfonic acid (1.5 mL, 22 mmol, as a >97 % standard solution) was added to a suspension of powdered poly(4-vinylpyridine) (5.0 g) [Poly(4-vinylpyridine) cross-linked with 2 % DVB ~60 mesh, MW: 60,000; Fluka Chemical] in 10 mL dry CH_2Cl_2 over a period of 5 min. The mixture was stirred at room temperature for 6 h and then dichloromethane was removed under reduced pressure. The solid powder was dried under vacuum at 65 °C for 48 h to afford NSPVPC (6.53 g) as a pale yellow powder.

General procedure for the synthesis of *N*-*tert*-butylcarbamates

Amine (1 mmol) was added to a magnetically stirred mixture of $(Boc)_2O$ (1 mmol) and NSPVPC (5 mg). After completion of the reaction (monitored by TLC), ethyl acetate (15 mL) was added to the reaction mixture and the catalyst was recovered by filtration and washed with ethyl acetate (2 × 5 mL) and dried. The product was purified by column chromatography, using ethyl acetate–petroleum ether (2:8) as eluent.

Spectral data of the selected products

8b: Brown solid, m.p. 52–54 °C; IR (KBr): $\nu = 3{,}320$, 2,990, 2,920, 1,690, 1,600, 1,530, 1,450, 1,420, 1,362, 1,285, 1,240, 1,160, 1,045, 1,032, 960, 870, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55 (s, 9H), 3.82 (s, 3H), 6.61 (dd, $J = 8.0$ and 8.4 Hz, 1H), 6.64 (br s, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 7.14 (s, 1H), 9.19 (dd, $J = 8.0$ and 8.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.4, 55.3, 80.5, 104.1, 108.9, 110.7, 129.7, 139.7, 152.7, 160.3 ppm.

13b: White solid, m.p. 99–101 °C; IR (KBr): $\nu = 3{,}310$, 3,300, 3,110, 3,090, 2,990, 1,773, 1,710, 1,650, 1,540, 1,446, 1,278, 1,250, 1,222, 1,150, 1,112, 1,080, 1,045 cm^{-1}; ^{1}H NMR (DMSO-d6, 300 MHz): δ 1.63 (s, 9H), 7.31–7.52 (m, 4H), 11.7(s, 1H) ppm; ^{13}C NMR (DMSO-d6, 75 MHz): δ 28.3, 87.8, 113.4, 123.5, 125.1, 127.9, 133.8, 147.7, 161.5, 167.5 ppm.

15b: Off-white solid; m.p. 72–73 °C; IR (KBr): $\nu = 3{,}395$, 2,980, 2,920, 1,680, 1,600, 1,508, 1,360, 1,320, 1,295, 1,260, 1,172, 1,000, 858, 761, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.50$ (s, 9H), 2.36 (s, 3H), 4.30 (d, $J = 5.2$, 2H), 4.88 (br s, 1H), 7.16 (d, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 21.1, 28.4, 44.5, 79.4, 127.5, 129.3, 135.9, 137.0, 155.9$ ppm.

16b: Colorless oil; IR (KBr): $\nu = 3{,}390$, 2,988, 2,930, 1,686, 1,610, 1,508, 1,358, 1,317, 1,289, 1,258, 1,170, 998, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.50$ (s, 9H), 1.83 (qin, $J = 7.2$, 7.6 Hz, 2H), 2.67 (dd, $J = 7.6$ and 8.0, 2H), 3.18 (d, $J = 6.0$ Hz, 2H), 7.22 (dd, $J = 5.6$ and 7.6 Hz, 3H), 7.32 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 28.5$, 31.8, 33.2, 40.3, 125.9, 128.40, 128.44, 141.6, 156.1 ppm.

18b: Out-white solid; m.p. 57–59 °C; IR (KBr): $\nu = 3{,}320$, 2,910, 2,860, 1,680, 1,520, 1,450, 1,360, 1,317,

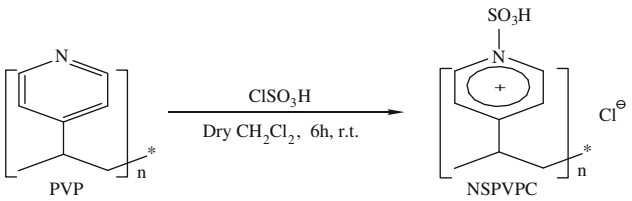
1,248, 1,170, 1,010, 875 cm^{-1}; ^1H NMR (DMSO-d6, 300 MHz): $\delta = 1.32–1.39$ (m, 10H), 1.42–1.57 (m, 8H), 1.70–1.73 (m, 2H), 3.34 (bs, 1H), 6.72 (d, $J = 7.7$ Hz, 1H) ppm; ^{13}C NMR (DMSO-d6, 75 MHz): δ 24.1, 28.2, 28.7, 35.0, 51.6, 77.6, 155.1 ppm.

19b: Colorless oil; IR (neat): $v = 2{,}912$, 2,858, 1,680, 1,518, 1,442, 1,366, 1,275, 1,158, 1,010, 904 cm^{-1}; ^1H NMR (CDCl3, 400 MHz) $\delta = 1.40$ (s, 9H), 1.48–1.57 (m, 4H), 1.87–1.94 (m, 4H), 2.05–2.07 (m, 2H), 3.14–3.15 (m, 2H), 4.60 (br s, 1H), 5.40 (s, 1H) ppm; ^{13}C NMR (CDCl3, 100 MHz) $\delta = 28.4$, 28.5, 31.1, 38.0, 38.2, 38.3, 78.9, 123.2, 146.7, 155.9 ppm.

21b: Colorless oil; IR (neat) $v = 2{,}900$, 2,860, 1,678, 1,520, 1,448, 1,362, 1,317, 1,272 1,160, 1,020, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.06–1.21 (m, 2H), 1.36 (s, 9H), 1.58–1.71 (m, 8H), 3.10 (s, 3H), 3.50 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): δ 24.9, 27.9, 28.6, 31.0, 32.4, 54.4, 77.9, 156.9.

22b: Colorless oil; IR (neat): $v = 2{,}900$, 2,860, 1,678, 1,520, 1,448, 1,362, 1,317, 1,272 1,160, 1,020, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.12$ (t, $J = 7.2$ Hz, 6H), 1.48 (s, 9H), 3.24 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.84$, 28.44, 41.32, 78.90, 155.34 ppm.

24b: Yellow solid, m.p. 55–57 °C; IR (KBr): $v = 3{,}380$, 2,990, 2,940, 2,840, 2,820, 1,680, 1,585, 1,515, 1,458, 1,360, 1,325, 1,290, 1,260, 1,230, 1,162, 1,140, 1,020, 990, 842, 808 cm^{-1}; ^1H NMR (DMSO-d6, 300 MHz) $\delta = 1.36$ (s, 9H), 2.60 (t, $J = 7.0$ Hz, 2H), 3.09 (t, $J = 7.0$ Hz, 2H), 3.70 (s, 3H), 3.73 (s, 3H), 6.68 (d, $J = 8.25$ Hz, 1H), 6.76 (s, 1H), 6.84 (d, $J = 8.25$ Hz, 2H) ppm; ^{13}C NMR (DMSO-d6, 75 MHz) $\delta = 28.69$, 35.49, 42.12, 55.73, 77.89, 112,26, 112.83, 120.83, 132.29, 147.58, 149.00, 155.95 ppm.



Scheme 1 Preparation of NSPVPC

25b: White solid; m.p. 80–82 °C; IR (KBr): $v = 3{,}414$, 3,395, 2,980, 2,920, 1,680, 1,600, 1,508, 1,360, 1,320, 1,295, 1,260, 1,172, 1,000, 858, 761, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.50$ (s, 9H), 3.28 (t, $J = 5.6$ Hz, 2H), 3.39 (m, 2H), 4.02 (br s, 1H), 4.90 (br s, 1H), 6.64 (d, $J = 8.0$ Hz, 2H), 6.74 (dd, $J = 7.2$ and 7.6 Hz, 1H), 7.21 (dd, $J = 7.6$ and 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 28.4$, 40.11, 44.37, 79.58, 112.76, 117.54, 129.34, 148.06, 156.47 ppm.

26b: Colorless solid, m.p; 50–52 °C IR (neat): $v = 3{,}490$, 3,300, 2,994, 2,930, 1,696, 1,680, 1,540, 1,520, 1,362, 1,300, 1,250, 1,170, 1,080, 1,040 cm^{-1}; ^1H NMR (DMSO-d6, 300 MHz) $\delta = 1.12$ (s, 6H), 1.35 (s, 9H), 3.28 (s, 2H), 4.72 (bs, 1H), 6.11 (s, 1H) ppm; ^{13}C NMR (DMSO-d6, 75 MHz) $\delta = 23.98$, 28.72, 53.51, 68.18, 77.67, 154.86 ppm.

Results and discussion

In recent years, introduction of new methods and reagents for the functional group transformations became an important part of our ongoing research program [4, 33]. In continuation of these studies, we have found that poly(4-vinylpyridine) [PVP] as a cheap and commercially

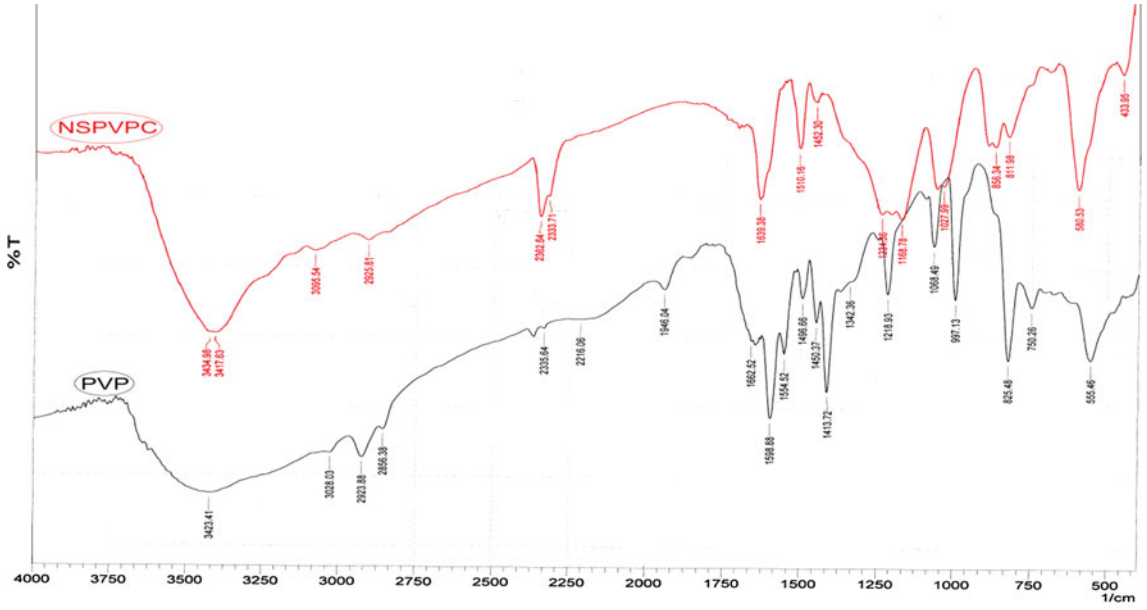


Fig. 1 FTIR spectra of NSPVPC (*up*) and PVP (*down*)

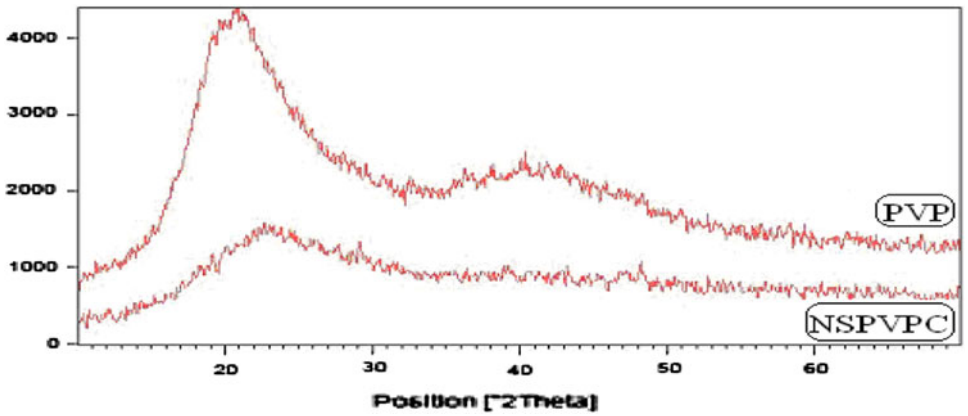


Fig. 2 XRD patterns of PVP (*up*) and NSPVPC (*down*)

available reagent reacts with chlorosulfonic acid to give *N*-sulfonic acid poly(4-vinylpyridinium) chloride [NSPVPC] at room temperature. The reaction is easy and clean, and needs no special work-up procedure (Scheme 1).

Catalyst characterization

IR analysis

Figure 1 presents the FTIR spectra of PVP and NSPVPC. As shown in this figure, the presence of an extra sulfonic acid group on the pyridine nitrogen in NSPVPC increases the number of vibrational modes and brought completely different FTIR spectrum [23–25]. In the case of NSPVPC, the broad band between 3,250 and 3,750 cm^{-1} that centered at 3,419.56 cm^{-1} can be attributed to the –OH stretching of the $–SO_3H$ group. NSPVPC exhibited other characteristic absorption bands at 1,234.36, 1,168.78, 1,027.99 and 856.34 cm^{-1}, which are assigned to the asymmetric and symmetric SO_2 stretching, S–OH bending and symmetric S–N stretching vibrations, respectively [26–28]. On the other hand, in the IR spectra of NSPVPC, the bands at 1,554.52 and 1,450.37 cm^{-1}

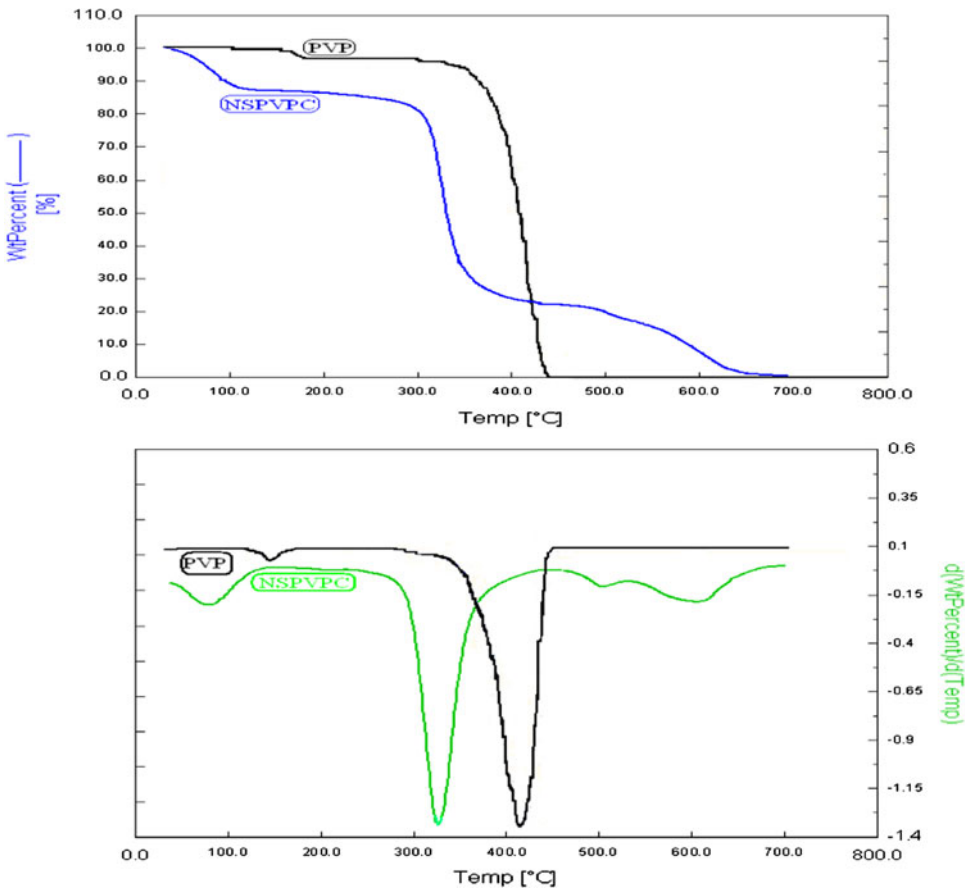


Fig. 3 TGA curves (*up*) for PVP and NSPVPC and DTA curves (*down*) for PVP and NSPVPC

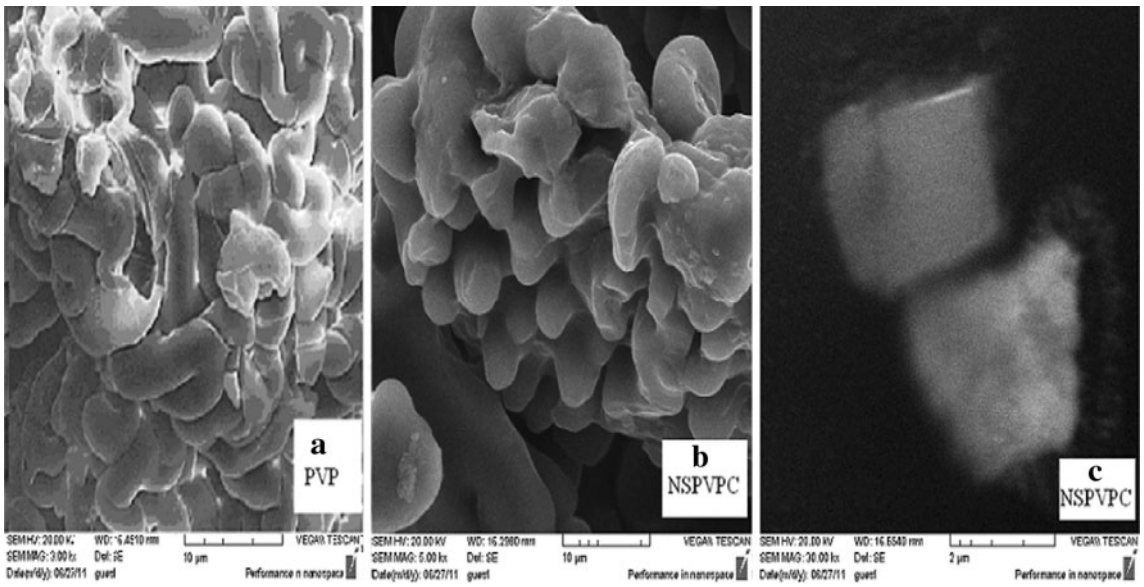


Fig. 4 SEM images for PVP (**a**) and NSPVPC (**b** and **c**)

Table 1 Acid strength of NSPVPC

Catalysts	Indicator and H_0		
	Anthraquinone	*p*-Nitrotoluene	4-Chloronitrobenzene
	−8.2	−11.35	−12.70
NSPVPC	+	±	−

+, Color changed clearly; −, color unchanged; ±, color changed unclearly

disappeared and a band at 1,639.38 cm^{-1}, related to the sulfonated pyridine ion, appeared. Thus, the treatment of PVP with chlorosulfonic acid results in sulfonation of pyridine unit of polymer. Furthermore, the appearance of band originating from the pyridinium ion indicates that chlorosulfonic acid acted at the sulfonating agent. Thus, the incorporation of Cl^- species in the form of counterions may be expected.

Powder X-ray diffraction

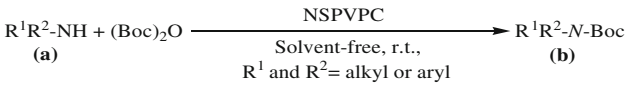
X-ray diffraction (XRD) studies were performed for PVP and NSPVPC and the obtained diffractograms are displayed in Fig. 2. (It should be noted that PVP and NSPVPC were dried at 100 °C before analysis.) As shown in this figure, the incorporation of $ClSO_3H$ led to some changes in the diffractogram of PVP. In the diffractogram of PVP, two broad reflexes centered at 2θ around 21° and 41.5° appeared. After modification of PVP by $ClSO_3H$, the position of the first peak (2θ around 23°) was changed and its intensity was reduced, and the broad peak at 2θ around 41° disappeared. These observations imply that the crystalline size of PVP is decreased after reaction with $ClSO_3H$.

Thermal analysis

Figure 3 provides the TGA and DTGA (differential thermogravimetry) curves of poly(4-vinylpyridine) and catalyst under nitrogen. The TGA curve of PVP displayed a weight loss below 100 °C which is corresponding to the loss of the physically adsorbed water and bonded H_2O within the gallery of PVP. The polymer underwent complete degradation in the range of 325–413 °C. NSPVPC is degraded mainly by a four-stage process. The first weight loss which is observed in the range of 30–100 °C ($T_{max} = 78.6$), attributed to the loss of moisture contents. The second weight loss, started at 320 °C (320–340 °C, $T_{max} =$ 325.6 °C) can be due to the thermal decomposition of the pendant sulfonic groups. This is involved with a total overall weight loss of 77.8 % of the catalyst. The sulfonated PVP moiety undergoes intermolecular bonding interactions in the solid state, leading to the formation of a rigid network structure which requires higher temperature for decomposition. This is confirmed by the third (490–510 °C, $T_{max} = 500.0$ °C) and fourth (590–680 °C, $T_{max} = 610.0$ °C) decomposition stages. The DTGA–TGA data show that the catalyst is stable to 285 °C.

SEM analysis

The SEM micrographs of PVP and NSPVPC showed that with chemical modification, the primary structure of PVP was changed (Fig. 4). As seen in SEM images, the aggregation of particles was retarded by loaded $ClSO_3H$ groups. Both size reductions and retardation of aggregation resulted in an increase in the surface area of the catalyst. This



Scheme 2 *N*-Boc protection of amines

Table 2 The effect of different amounts of NSPVPC on the reaction of aniline with di-*tert*-butoxypyrocarbonate $(Boc)_2O$

Entry	Catalyst (mg)	Time (min)	Yield (%)[b]
1	2	10	78
2	4	5	92
3	6	5	92
4	8	5	92

Reaction conditions: aniline (Table 3, entry 1) (1 mmol), di-*tert*-butoxypyrocarbonate $(Boc)_2O$ (1 mmol), room temperature, solvent-free

[b] Determined by GC-MS

increased the catalytic activity of the catalyst in reaction. In the third SEM image with 30,000× magnification, the pendant sulfonic groups are observed on the sulfonated PVP polymer.

Acidity of the catalyst

The acid strength of NSPVPC was determined by the Hammett indicator method [29]. Using this method, the catalyst was pretreated by evacuating at 398 K for 2 h, then cooled to room temperature and allowed to contact with the vapor of the Hammett indicator. The acid strength was determined by observing the color change of the indicator adsorbed on the surface of NSPVPC. Anthraquinone ($H_0 = -8.2$), *p*-nitrotoluene ($H_0 = -11.35$) and 4-chloronitrobenzene ($H_0 = -12.70$) were used as indicators and benzene was used as the solvent (Table 1).

Acid contents of NSPVPC were determined by acid–base titration. In this method, a standard solution of NaOH was added to a suspension of the catalyst in H_2O–EtOH (1:1). Then the mixture was stirred for 2 h, and a 0.01 % solution of phenolphthalein in EtOH was added to the suspension as an indicator. The solution was titrated with a standard HCl solution. The acid loading of NSPVPC was found to be in the range of 1.9 and 2.1 mmol g^{-1} by several parallel experiments.

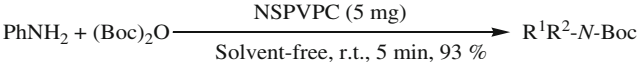
N-Boc protection of amines

The structure of NSPVPC assured us to accept that this reagent can act as an efficient catalyst in reactions that need acidic reagents to speed up. Our investigations clarified that this prediction is correct and the *N*-Boc protection of amines efficiently promoted in the presence of NSPVPC (Scheme 2).

In order to optimize the reaction conditions, we conducted the *N*-Boc protection of aniline (1 mmol) with di-*tert*-butoxypyrocarbonate [$(Boc)_2O$] (1 mmol) using different amounts of NSPVPC in the absence of solvent at room temperature. The results are shown in Table 2. On the basis of this Table, the best result can be obtained under the conditions showed in Scheme 3. To illustrate the efficiency of NSPVPC, the *N*-Boc protection of aniline was also carried out in the absence of the catalyst and in the presence of poly(4-vinylpyridine). The results are shown in Table 3. Obviously, the sulfonation of PVP is important for the reaction.

After optimization of the reaction conditions, various aromatic, aliphatic and heterocyclic amines were subjected to the *N*-Boc protection with $(Boc)_2O$ under the selected conditions. The results are summarized in Table 4. Obviously, the present method is quite general and found to be very effective for the *N*-Boc protection of the above-mentioned amines. The reaction conditions is mild enough not to induce any damage to moieties like methoxy group (Table 4, entries 8, 24) which often undergo cleavage in the presence of strong acids or certain Lewis acids. Under the selected conditions, aromatic amines bearing electron withdrawing substituents such as 4-nitroaniline (Table 4, entry 7) gave low yields at long times. Mention must be made here that –OH and –SH functionalities are not protected under the same reaction conditions. Therefore, the method shows selectivity and is very useful for the chemoselective *N*-Boc protection of amines in the presence of the above-mentioned functional groups (Table 4, entries 2, 3, 26 and 27).

We have also found that NSPVPC can be easily recovered by filtration, washing with EtOAc and drying at 60 °C. The reusability of this reagent is exemplified by the *N*-Boc protection of aniline in the presence of recycled



Scheme 3 *N*-Boc protection of aniline

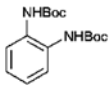
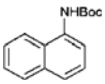
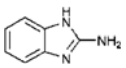
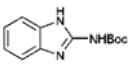
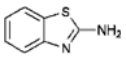
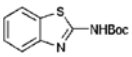
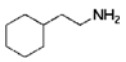
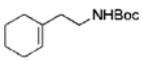
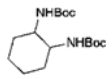
Table 3 *N*-Boc protection of aniline in the absence of catalyst and in the presence of poly(4-vinylpyridine) and NSPVPC

Entry	Catalyst (5 mg)	Time (min)	Yield (%)[b]
1	–	360	Trace
2	Poly(4-vinylpyridine)	25	50
3	NSPVPC	5	93

Reaction conditions: aniline (1 mmol), di-*tert*-butoxypyrocarbonate $(Boc)_2O$ (1 mmol), room temperature, solvent-free

[a] Determined by GC-MS

Table 4 *N*-Boc protection of various amines in the presence of NSPVPC

Entry	Substrate	Product	Time (min)	Yield (%)
1	$PhNH_2$	PhNH-Boc	5	93
2	$2\text{-}HOC_6H_4NH_2$	$2\text{-}HOC_6H_4NH\text{-}Boc$	11	92
3	$4\text{-}HSC_6H_4NH_2$	$4\text{-}HSC_6H_4NH\text{-}Boc$	22	90
4	$3\text{-}ClC_6H_4NH_2$	$3\text{-}ClC_6H_4NH\text{-}Boc$	50	89
5	$4\text{-}BrC_6H_4NH_2$	$4\text{-}BrC_6H_4NH\text{-}Boc$	25	95
6	$4\text{-}MeC_6H_4NH_2$	$4\text{-}MeC_6H_4NH\text{-}Boc$	14	94
7	$4\text{-}NO_2C_6H_4NH_2$	$4\text{-}NO_2C_6H_4NH\text{-}Boc$	180	64
8	$3\text{-}MeOC_6H_4NH_2$	$3\text{-}MeOC_6H_4NH\text{-}Boc$	30	91
9			25	90
10			30	87
11			2	92
12			1	90
13			15	84
14	$PhCH_2NH_2$	$PhCH_2NH\text{-}Boc$	1	96
15	$4\text{-}MeC_6H_4CH_2NH_2$	$4\text{-}MeC_6H_4CH_2NH\text{-}Boc$	4	97
16	$PhCH_2CH_2CH_2NH_2$	$PhCH_2CH_2CH_2NH\text{-}Boc$	15	91
17	Cyclohexyl-NH_2	Cyclohexyl-NH-Boc	1	96
18	Cyclohepyl-NH_2	Cycloheptyl-NH-Boc	10	95
19			10	80
20	$(Cyclohexyl)_2NH$	$(Cyclohexyl)_2N\text{-}Boc$	30	85
21	(Cyclohexyl)NHMe	(Cyclohexyl)*N*(Boc)Me	15	88
22	Et_2NH	$Et_2N\text{-}Boc$	15	94
23			2	92[a]
24	$3,4\text{-}(MeO)_2C_6H_3CH_2CH_2NH_2$	$3,4\text{-}(MeO)_2C_6H_3CH_2CH_2NH\text{-}Boc$	10	80
25	$PhNHCH_2CH_2NH_2$	$PhNHCH_2CH_2NH\text{-}Boc$	1	96
26	$Me_2C(NH_2)CH_2OH$	$Me_2C(NH\text{-}Boc)CH_2OH$	2	86
27	$HOCH_2CH_2NH_2$	$HOCH_2CH_2NH\text{-}Boc$	5	92

The products were characterized by the used spectroscopic data and melting point. These data closely matched with the reported data [30–34]
Isolated yield

[a] 2 mmol of *t*-butyl dicarbonate was used

solid acid catalyst, which gave the requested product in 93, 92, 92 and 90 % yields after four runs. The average time for four consecutive runs was 5.7 min and 100 % conversion for all, which clearly demonstrates the practical recyclability of the catalyst (Fig. 5).

Conclusion

In conclusion, we have developed a simple, efficient and chemoselective protocol for the *N*-Boc protection of various amines using NSPVPC as a novel heterogeneous

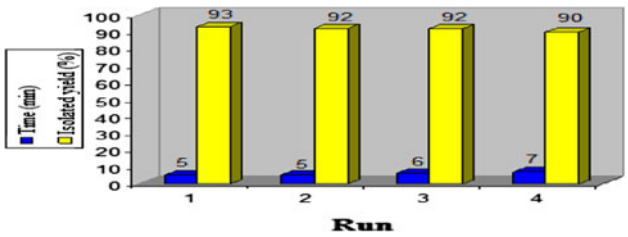


Fig. 5 Reusability of NSPVPC

catalyst. The protocol is highly chemoselective offering potential in different applications. The methodology also has several other advantages such as high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, cost efficiency and effective reusability of the catalyst, use of inexpensive catalyst with lower loading and simple experimental procedure. Further work to explore this novel catalyst in other organic transformations is in progress.

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