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Polyvinyl alcohol immobilized *N*-ethyl sulfamic acid (PVA-$NHSO_3H$) as an efficient catalyst for rapid and selective acetylation of phenols, alcohols, amines and thiols under solvent free conditions

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Abstract : PVA-$NHSO_3H$ is a highly efficient catalyst for rapid acetylation of a variety of phenols, alcohols, amines and thiols with acetic anhydrides at ambient temperature under solvent free conditions. The reaction is mild and selective with good to high yield. The catalyst works well for a large variety of simple and functionalized phenols, alcohols, amines and thiols.

Keywords : PVA-$NHSO_3H$, acetylation, phenol, alcohol, amine, thiol, acetic anhydride.

Introduction

Functional group protection strategies are central to target molecule synthesis. The protection of alcohols, phenols, amines and thiols are fundamental and useful transformation in organic synthesis. Among the various protecting groups used for the hydroxyl, phenols, amines and thiols, acetyl is used with high frequency in view of its easy introduction, being stable in the acid reaction conditions and also ease of removal by mild alkaline hydrolysis[1]. Acyl chlorides[2] and acid anhydrides[3] as the most common and cheap reagents are currently used in order to perform the acylation in presence of amine bases like triethylamine, pyridine, 4-diaminopyridine (DMAP) and 4-pyrrolidinopyridine (PPY)[4], tributylphosphine[5], etc. Lewis acid catalysts such as $COCl_2$[6], $ZnCl_2$[7a], ZnO[7b,c], $CeCl_3$[8], $ZrOCl_2.8H_2O$[9], $TaCl_5$[10a], $RuCl_2$[10b], iodine[10c], 3-nitro benzene boronic acid[11], $La(NO_3)_3.6H_2O$[12], P_2O_5/Al_2O_3[13], $NiCl_2$[14], Co^{II} salen-complex[15], melamine trisulfonic acid[16], $Sn(TPP)(BF_4)_2$[17], alkylorthoformate-$ZnCl_2$-Ac_2O[18], vanadium(IV) tetraphenylporphyrin[19], $[Ti^{IV}(salophen)(OTf)_2]$[20], *N*-acyl 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) tetraphenylborate salts[21], iron(III) tosylate[22], $Al(HSO_4)_3$[23], $NbCl_5$[24], montmorillonite K-10[25a], KSF[25b], MgBr-R_3N[25c], aminophosphine super base[25c], metal triflates[26], PS lipase and zeolites HZSM-360[27] and yttria-zirconia based Lewis acids[28] have been reported to be efficient catalysts for this reaction.

However, most of these reported methods suffer from one or more disadvantages like the use of (1) expensive, moisture sensitive and toxic catalysts in stoichiometric amounts or even in large excess to effect complete conversion of the substrate (the toxic metals as part of catalysts are not recommended for the synthesis of active pharmaceutical ingredients due to stringent requirements by regulatory agencies as the traces of these need to be controlled in the order of ppm)[29], (2) long reaction times and (3) a lack of generality. Contemporary organic synthesis is constantly striving for discovery, design and development of reagents, which provides beneficial levels of efficiency and mildness towards other protecting groups. Therefore, as part of our continuing interest in the development of new synthetic methodologies[30], we attempted to develop an efficient and rapid method for selective acetylation of phenols, alcohols, amines and thiols in the presence of a readily and cheaply available catalyst.

Results and discussion

Recently, new methods of chemical transformation were explored by running the reactions on the surface of solids that may be more desirable than a solution counterpart, because the reaction is more convenient to run, or a

high yield of product is attained. Also, solid phase catalysts generally have the following advantages : (1) easy isolation of the products and separation of catalyst; (2) in comparison with the related homogeneous reactions, they are so mild that a high yield of specific products formation are expected. In the present study, we investigated the acetylation of phenols, alcohols, amines and thiols in the presence of PVA-$NHSO_3H$, as a solid acid, under solvent free conditions (Scheme 1).

$$RXH + Ac_2O \xrightarrow[\text{Solvent free r.t.}]{\text{PVA-NHSO}_3\text{H}} RXAc$$

X = O, NH, S
R = Aryl, alkyl

Scheme 1

The reaction conditions for acetylation of phenols, alcohols, amines and thiols were optimized by using the reaction of 1/1 molar ratio of *p*-nitro phenol/acetic anhydride in the presence of different amounts of catalyst in various solvents (Table 1). In the absence of any catalyst, acetylation was not completed after 24 h (Table 1, entry 1). On the basis of data obtained from Table 1, acetylation of *p*-nitro phenol in the presence of PVA was not also progressed completely (Table 1, entry 2). To improve the performance of the reaction conditions, acetylation was carried out in the presence of solid acid PVA-$NHSO_3H$ under solvent free conditions and in different solvents (Table 1, entries 3–8). The best result was obtained by applying 0.96 mol% (0.036 g) of PVA-$NHSO_3H$ under solvent free conditions. Applying 0.48 mol% (0.018 g) of PVA-$NHSO_3H$, gave the desired product as the same as 0.96 mol %(0.036 g) of catalyst (compare entry 3 with 9), but when 0.24 mol %(0.009 g) of PVA-$NHSO_3H$ was used the corresponding product was produced in longer reaction time (Table 1, entry 10).

Table 1. Acetylation of *p*-nitro phenol in the presence of PVA-$NHSO_3H$ under different reaction conditions[a]

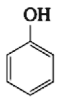
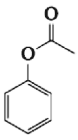
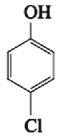
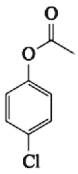
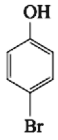
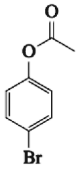
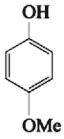
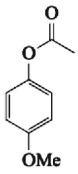
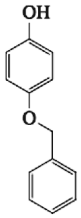
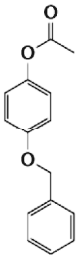
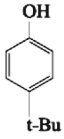
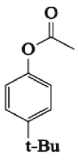
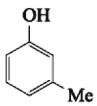
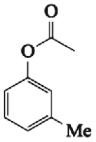
Entry	Solvent	Catalyst (mol%)	Temp. (°C)	Time (min)	Conversion (%)
1	None	None	r.t.	24 (h)	50
2[b]	None	0.05 (0.036 g)	r.t.	24 (h)	85
3	None	0.96 (0.036 g)	r.t.	4	100
4	CH_2Cl_2	0.96 (0.036 g)	r.t.	5	100
5	Toluene	0.96 (0.036 g)	r.t.	10	100
6	CH_3NO_2	0.96 (0.036 g)	r.t.	10	100
7	CH_3CN	0.96 (0.036 g)	r.t.	20	100
8	Ethanol	0.96 (0.036 g)	r.t.	24 (h)	25
9	None	0.48 (0.018 g)	r.t.	4	100
10	None	0.24 (0.009 g)	r.t.	20	100

[a]1/1 molar ratio of reactants was applied in all of reactions. [b]The reaction was performed in the presence of PVA.

Encouraged by our initial studies, we tested the feasibility, generality, and versatility of the protocol using a series of structurally different phenols, alcohols, amines and thiols (commercially available) under these optimized conditions (Table 1, entry 9). A combinatorial library of acetylated phenols, alcohols, amines and thiols was smoothly prepared in high yields, and the results are summarized in Table 2.

Phenol and phenols bearing electron-releasing substituents and halogens, in the presence of PVA-$NHSO_3H$ were acetylated efficiently and the acetylated products were obtained instantaneously (Table 2, entries 1–7). Phenols with electron-withdrawing substituents as the same as naphthols were acetylated in a few minutes (Table 2, entries 8–11). It means that PVA-$NHSO_3H$ as an efficient catalyst forwarded the acetylation reactions with high performance irrespective the electron density of phenol rings. In order to gain more insight into the general applicability of this method, we also studied the possibility of applying this method to alcohols. As shown in Table 2, this method is very suitable for acetylation of primary, secondary, tertiary and benzylic alcohols (Table 2, entries 12–18). On the basis of the results obtained from Table 2, PVA-$NHSO_3H$ catalyzed the acetylation of aliphatic and benzylic alcohols in a few minutes. We also applied this method for acetylation of aromatic and aliphatic amines (Table 2, entries 19–27). When aniline, anilines with electron-rich rings, benzyl amine , substituted benzyl amines and aliphatic amines (primary and secondary amines) were treated with acetic anhydride in the presence of PVA-$NHSO_3H$, the corresponding products were obtained instantaneously as the same as phenols. *p*-Nitro aniline with an electron-poor ring was acetylated in 10 min (Table 2, entry 25). When we applied our method to thiols, the reaction furnished their corresponding acetylated thiols quickly with high yields (Table 2, entries 28–29). In all of the above mentioned reactions the acetylated products were obtained in high yields.

Table 2. Acetylation of various phenols, alcohols, amines and thiols with acetic anhydrides in the presence of PVA-$NHSO_3H$ under solvent free condition

Entry	Substrate	Product	Time (min)	Conversion (%)
1			Instantaneously	100
2			Instantaneously	100
3			Instantaneously	100
4			Instantaneously	100
5			Instantaneously	100
6			Instantaneously	100
7			Instantaneously	100

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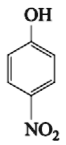
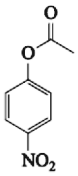
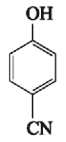
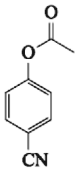
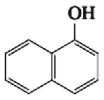
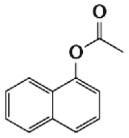
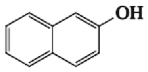
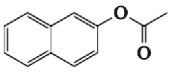
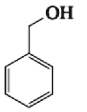
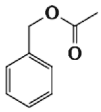
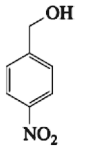
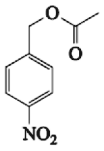
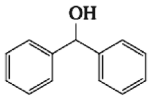
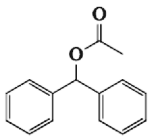
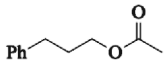
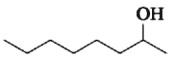
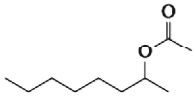
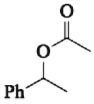
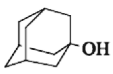
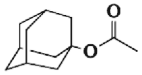
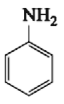
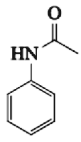
8			4	100
9			4	100
10			5	100
11			8	100
12			Instantaneously	100
13			20	90
14			5	100
15			5	100
16			5	100
17			Instantaneously	100
18			5	100
19			Instantaneously	100

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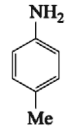
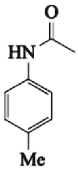
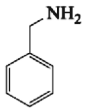
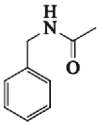
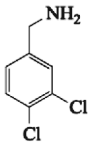
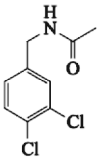
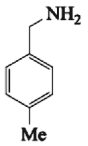
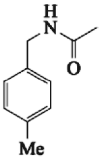
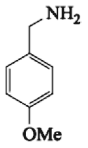
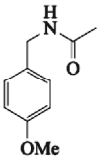
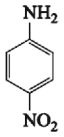
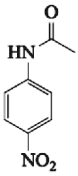
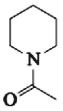
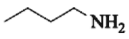
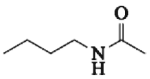
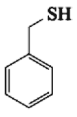
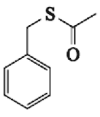
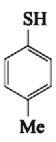
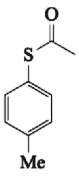
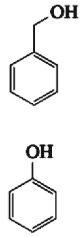
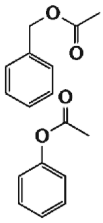
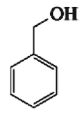
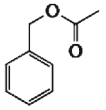
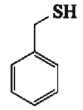
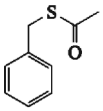
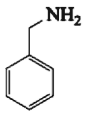
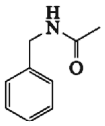
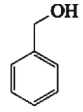
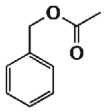
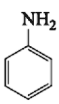
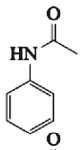
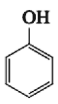
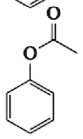
20			Instantaneously	100
21			Instantaneously	100
22			Instantaneously	100
23			Instantaneously	100
24			Instantaneously	100
25			10	100
26			Instantaneously	100
27			Instantaneously	100
28			5	90
29			5	90

To see the applicability and limitation of this new method, we studied the acetylation of phenols, alcohols, amines and thiols in the presence of some other functional groups in binary mixtures (1 : 1) using the same amount of PVA-$NHSO_3H$ as before. The most important point about the selectivity of this reaction is that alcohol can be acetylated with excellent selectivity in the presence of phenol and thiol (Table 3, entries 1, 2). This method also acetylated amine with excellent selectivity in the presence of alcohol, phenol and thiol (Table 3, entries 3–5). In a binary mixture of phenol and thiophenol, phenol was quantitatively acetylated while thiophenol remained intact (Table 3, entry 6). Similarly, this method showed selectivity for the acetylation of primary alcohol in the presence of secondary and tertiary ones and also acetylation of secondary alcohol in the presence of tertiary alcohol (Table 3, entries 7–9). Primary alcohol was acetylated in 90% yield while only 10% conversion was observed for secondary and tertiary alcohol. Secondary alcohol in the presence of PVA-$NHSO_3H$ was acetylated completely while tertiary alcohol remains intact too.

In our experiments, the completion of the reaction

Table 3. Acetylation of different binary mixtures with acetic anhydride in the presence of PVA-$NHSO_3H$

Entry	Binary mixture	Product	Time (min)	Conversion (%)
1			20	100
				0
2			30	100
				0
3			10	100
				0
4			30	100
				0

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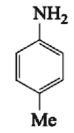
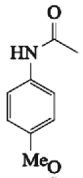
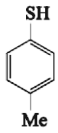
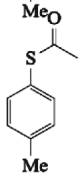
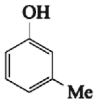
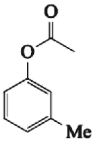
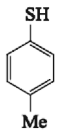
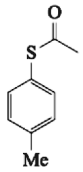
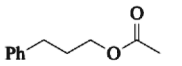
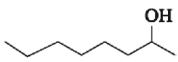
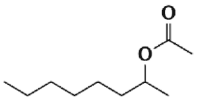
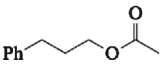
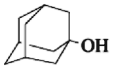
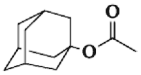
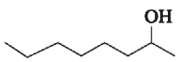
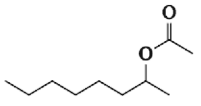
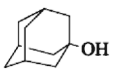
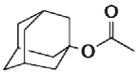
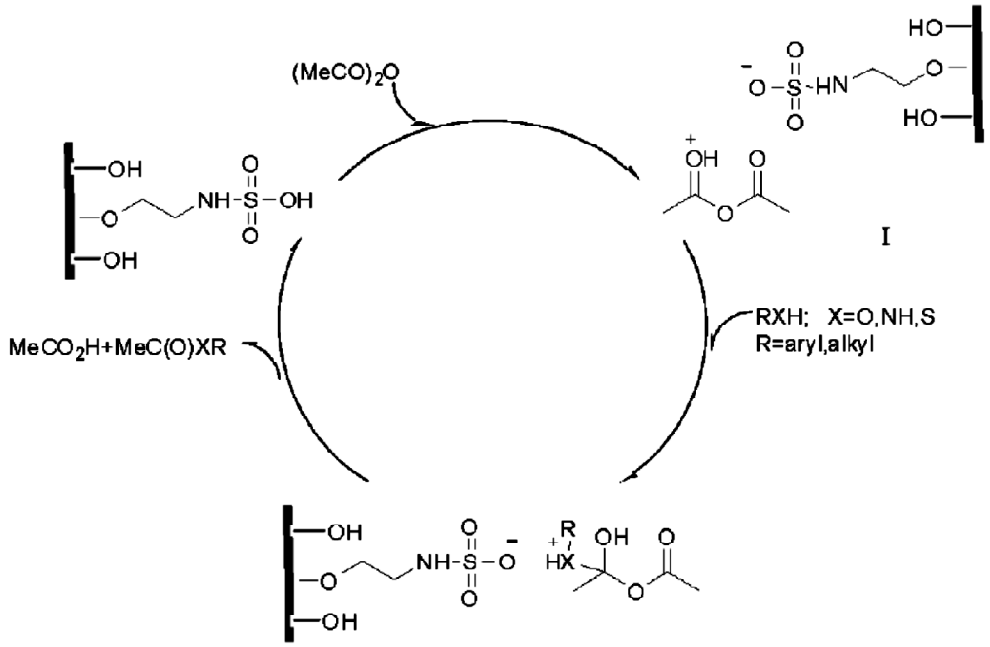
5			15	100
				0
6			20	100
				0
7			15	90
				10
8			10	90
				10
9			15	90
				10

was confirmed by the disappearance of phenols, alcohols, amines or thiols on TLC followed by the disappearance of OH or NH_2 stretching frequencies of phenols, alcohols and amines in the FTIR spectra. Also, formation of acetylated phenols and alcohols was confirmed by the appearance of two absorption bands at 1768–1710, 1743–1727 and 1224–1196, 1274–1228 cm^{-1} due to carbonyl groups and C–O bonds of corresponding esters respectively. FT-IR spectra of acetylated amines show absorption bands at 3294–3278 and 1566–1550 cm^{-1} attributed to NH stretching and bending vibrations respectively. Also, carbonyl groups and C–N bonds of acetylated amines were con-

firmed by appearance of two other absorption bands at 1683–1634 and 1288–1232 cm^{-1}. In FT-IR spectra of acetylated thiols, absorption bands of carbonyl groups and C-S bond were also revealed at 1744–1691 and 949–957 cm^{-1}.

A plausible mechanism for the reaction methodology under current development is shown in Scheme 2. Initially protonation of acetic anhydride by PVA-$NHSO_3H$ forms **I** which accelerates the nucleophilic attack of RXH (X = O, NH, S) to carbonyl group. This idea is supported by performing the reaction in the absence of PVA-$NHSO_3H$. Without any catalyst, the acetylation reaction is not completed even after long period of time (Table 1, entries 1-2). The acetylation reaction takes place rapidly to form the intermediate **II**. Cleavage of **II** leads to fast extrusion of acetic acid and release PVA-$NHSO_3H$ which re-enters to the catalytic cycle. Nevertheless, at this time there is no experimental evidence for **I** and **II** acting in this manner, and further studies to elucidate the details of the mechanism are ongoing.



Scheme 2

Conclusion

In this study, our group introduce PVA-$NHSO_3H$ as a solid acid which could be easily prepared from available and low cost reagents. PVA-$NHSO_3H$ was characterized by FT-IR spectroscopy, elemental analysis data and thermogravimetric technique and also applied as an efficient catalyst in acetylation of phenols, alcohols, amines and thiols at room temperature under solvent free condition. This method is applicable to a range of phenols, alcohols, amines and thiols. It has also been shown that, the yields are high and reaction completion time is immediately or within a few minutes. The catalyst is readily available and environmentally friendly. Selectivity, short reaction time, excellent yields, safe process and simple workup make this method an attractive and useful contribution to the present methods of acetylation of phenols, alcohols, amines and thiols.

Experimental

The products were purified by column chromatography and TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on a Brucker Avance 400 MHz instruments in $CDCl_3$. Mass spectra were recorded with a

Shimadzu GC-MS-QP5050 and CH7A Varianmat Bremem instruments at 70 eV; in *m/z* (rel %). Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) were performed on a Shimadzu Thermogavimetric Analyzer (TG-50) under air atmosphere. All of the products were known compounds and characterized by the FT-IR spectroscopy, mass spectrometry and comparison of their melting points with known compounds.

Preparation of PVA-NH_2 :

Commercially available polyvinyl alcohol with average of molecular weight of 72000 (0.5 g) was mixed with 10 mL of ethanol amine at 80 °C. After 18 h magnetically stirring, methanol (40 mL) was added to the reaction mixture. The solid was filtered off and washed with methanol (5× 50). The pale yellow precipitate was refluxed with methanol (100 mL) for 18 h. The hot mixture was filtrated and dried in a stove at 50 °C for 24 h.

Preparation of PVA-$NHSO_3H$:

To a magnetically stirring suspension of PVA-NH_2 (0.5 g, 0.135 mmol) in dry CH_2Cl_2 (5 mL) at room temperature, chlrorosulfonic acid (0.015 g, 0.135 mmol) was added drop by drop over a period of 30 min at room temperature. After complete evolution of HCl, the reaction mixture was filtered and washed with dry CH_2Cl_2 (20 mL). The dark brown precipitate was dried in a stove at 50 °C for 24 h.

Characterization of PVA-$NHSO_3H$:

FT-IR spectroscopy :

The catalyst structure was defined by FT-IR spectroscopy. Fig. 1 illustrates the FT-IR spectra of the PVA, PVA-NH_2 and PVA-$NHSO_3H$.

FT-IR spectra of PVA-NH_2 shows two absorption bands at 3549 and 3338 cm^{-1} due to N-H stretching of immobilized NH_2 on poly vinyl alcohol. In the low frequency region, the presence of the weak N–H bending vibration at 1668 cm^{-1} confirms the incorporation of amino groups. The peak of the C–N stretching vibration is normally observed in the range of 1250–1020 cm^{-1}.

The structure of PVA-$NHSO_3H$ was confirmed by appearance of a broad absorption band from 3600–3000 cm^{-1} and 3398 cm^{-1} due to OH vibration stretching of sulfonic acid and NH vibration frequency of sulfonamide respectively. Also, presence of SO_2 was established by presence of asymmetric and symmetric vibration frequencies of SO_2 at 1320 and 1174 cm^{-1} respectively. The S–N stretching vibration is observed at 578 cm^{-1}.

Thermogravimetric analysis (TGA) :

Thermogravimetric studies of pure PVA, PVA-NH_2 and PVA-$NHSO_3H$ at heating rate 10 °C/min was appeared in Figs. 2-4. It can be seen that both PVA and PVA-NH_2 exhibited a three-step degradation patterns. As PVA contain a small quantity of physically adsorbed water, the first stage of degradation represents the loss of physically adsorbed water and splitting or volatilization of small molecules or monomers (weight loss 4.6%, from 21–180 °C). On the other hand above 120 °C elimination of water could be resulted formation of C–C double bond, which consequently leads to formation of polyene. The second stage (weight loss 54.5%, from 181–305 °C) corresponds to side chain decomposition. The higher value of weight loss in second stage was attributed to chemical degradation of some C–C bonds of polymer backbone. In

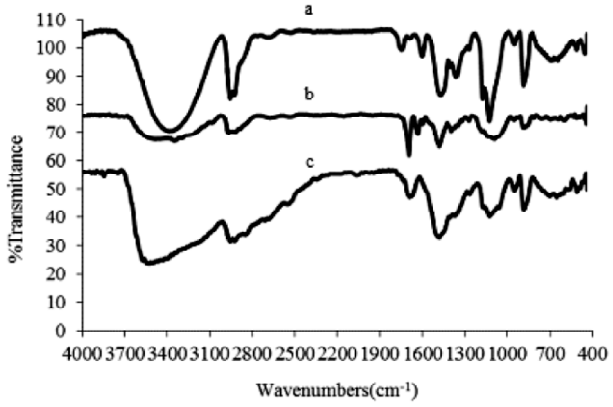


Fig. 1. FT-IR spectra of (a) PVA, (b) PVA-NH_2, (c) PVA-$NHSO_3H$.

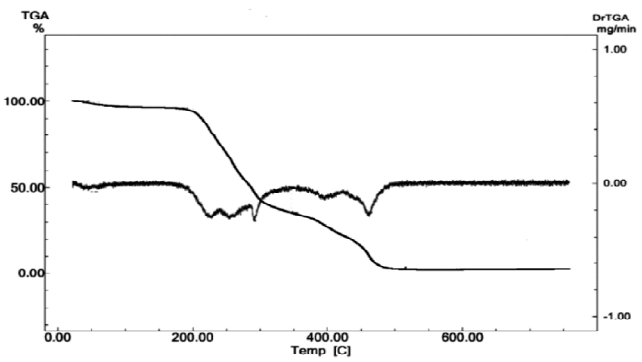


Fig. 2. TGA/DTG thermograms of PVA.

the third stage (weight loss 36.3%, 306–474 °C) the complete decomposition of the main chain of polymer was occurred[31,32].

Similarly, TGA/DTG thermograms of PVA-NH_2 exhibited three distinct weight loss stages. As can be seen, every stage of weight loss was occurred in higher temperature than PVA, this confirmed the modification of the PVA by chemical introduction of ethanolamine, which raised the thermal stability of polymer. The first step (weight loss 3.7%, 25–228 °C) attributed to evaporation of moisture, methanol, ethanolamine and easily degraded components. The mentioned components are strongly bonded to polymer backbone via hydrogen bonding with immobilized NH_2 group on polymer chain. Water elimination was also occurred at higher temperature than PVA. The major mass loss took place in the second step (weight loss 57.3%, 229–442 °C) and was followed by a further mass loss in the third step (34.9%, 443–605 °C). The second stage represents chemical degradation of side chain (C–C side chain bond and aminoethyl group). The third step of weight loss was predominantly the characteristic degradation of polymer structure (breaking down and cracking of polymer backbone).

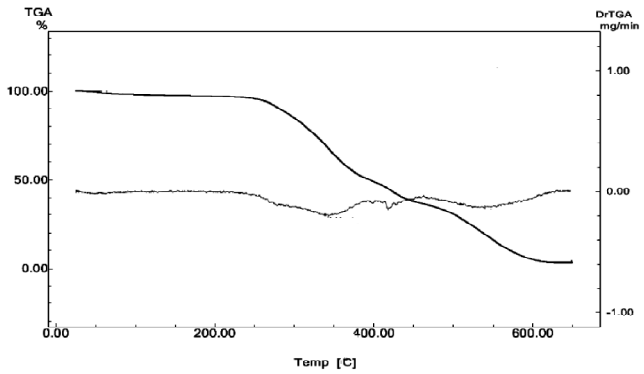


Fig. 3. TGA/DTG thermograms of PVA-NH_2.

The results of thermogravimetric analysis are in good agreement with those of the chemical elemental analyses, revealing that 0.271 mmol of ethanolamine was incorporated into the 1.000 g of PVA-NH_2 framework.

The thermogravimetric analysis (TGA/DTG) curves of the PVA-$NHSO_3H$ exhibited a three steps degradation pattern. The first step (weight loss 7.66%, 22–92 °C) was attributed to evaporation of moisture. The higher value of weight loss in the second step (weight loss 55.2%, 93–474 °C) demonstrated the existing of easily degraded components which are strongly bonded to PVA chain via hydrogen bonding with pendent OH and immobilized NH group on polymer chain, water elimination and also, chemical degradation of side chain. The weight loss in the third step (weight loss 34.61%, 475–660 °C) represents chemical degradation of C–C bonds of the main chain of PVA-$NHSO_3H$ which occurred in higher temperature than PVA and PVA-NH_2.

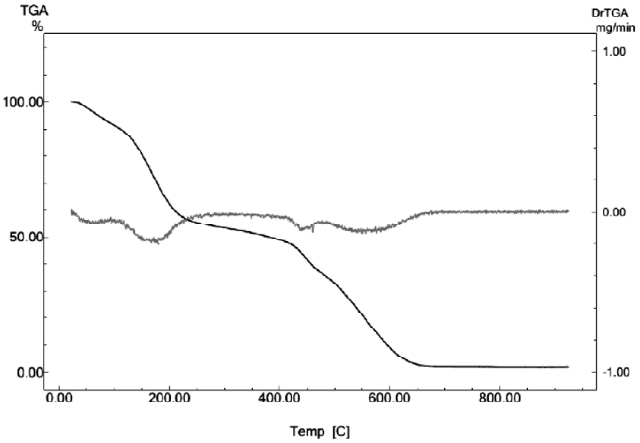


Fig. 4. TGA/DTG thermograms of PVA-$NHSO_3H$.

Considering the TGA/DTG thermograms and the results obtained from back-titration of PVA-$NHSO_3H$, which are in good agreement with each other, reveals that total immobilized -NH_2 groups on PVA was functionalized as *N*-ethyl sulfamic acid. When the prepared PVA-$NHSO_3H$ was placed in an aqueous NaCl solution (1 *M*, 25 mL), the pH dropped instantaneously to ≈1.26, indicating an ion exchange between sulfamic acid protons and sodium ions. The ion exchange capacity was found to be 0.27 mmol/g of sulfamic acid groups.

Typical procedure for acetylation of p-nitro phenol :

p-Nitro phenol (0.139 g, 1 mmol) and PVA-$NHSO_3H$ (0.018 g) were mixed thoroughly and treated with acetic anhydride (0.102 g, 1 mmol) at room temperature. The progress of reaction was monitored by TLC using *n*-hexane/ethylacetate (10 : 1) as eluent. After completion of the reaction, the obtained mixture was diluted with ethylacetate (10 mL) and then neutralized by saturated $NaHCO_3$ (10 ml). The organic layer was separated and

dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude product was purified by thin layer chromatography. *p*-Nitro phenyl acetate was obtained with 98% yield.

Phenyl acetate (**1**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{33}$: 3045, 2962, 2847, 2721, 1710 (C=O), 1595, 1499, 1473, 1367, 1224 (C–O), 1168, 1070, 1023, 887, 810, 752, 690, 538, 507 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ : 7.46–7.35 (3H, m, Ph), 7.24–7.08 (2H, m, Ph), 2.40 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 169.5 (C=O), 150.6, 129.4, 125.8, 121.5, 21.1; EIMS *m/z* (rel. int.) : 134 [M^+] (4).

4-Chlorophenyl acetate (**2**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{34}$: 3092, 3072, 2929, 2851, 1764 (C=O), 1589, 1494, 1431, 1370, 1264, 1198 (C–O), 1163, 1089, 1013, 909, 828, 800, 718, 642, 600, 505 cm^{-1}; EIMS *m/z* (rel. int.) : 171 [M^+] (22).

4-Bromophenyl acetate (**3**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{35}$: 3092, 3064, 2929, 2851, 1761 (C=O), 1580, 1484, 1433, 1368, 1196 (C–O), 1163, 1102, 1067, 1011, 935, 907, 841, 793, 709, 674, 592, 501 cm^{-1}; EIMS *m/z* (rel. int.) : 215 [M^+] (22).

4-Methoxyphenyl acetate (**4**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{35}$: 3056, 3005, 2956, 2908, 2839, 1761 (C=O), 1600, 1506, 1464, 1442, 1369, 1299, 1249, 1218 (C–O), 1193, 1102, 1033, 1012, 933, 905, 842, 815, 760, 738, 703, 632, 594, 525, 461 cm^{-1}; EIMS *m/z* (rel. int.) : 166 [M^+] (40).

4-(Benzyloxy)phenyl acetate (**5**) : m.p. 104–108 °C (Lit. 104–108 °C)[36]; FT-IR (KBr) $\bar{\upsilon}$: 3154, 3068, 3034, 2938, 2880, 2847, 1754 (C=O), 1593, 1504, 1452, 1375, 1297, 1221 (C–O), 1193, 1105, 1014, 945, 908, 846, 818, 747, 696, 594, 529, 508 cm^{-1}; EIMS *m/z* (rel. int.) : 242 [M^+] (2).

4-(tert-Butyl)phenyl acetate (**6**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{37}$: 3042, 2963, 2907, 2870, 1822, 1765 (C=O), 1602, 1510, 1464, 1410, 1393, 1367, 1268, 1203 (C–O), 1170, 1110, 1044, 1016, 942, 911, 852, 837, 799, 748, 697, 610, 594, 550, 512 cm^{-1}; EIMS *m/z* (rel. int.) : 192 [M^+] (70).

m-Tolyl acetate (**7**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{38}$: 3032, 2953, 2924, 2854, 1768 (C=O), 1613, 1588, 1488, 1459, 1369, 1208 (C–O), 1143, 1084, 1016, 942, 906, 874, 785, 747, 689, 665, 597, 534, 443 cm^{-1}; EIMS *m/z* (rel. int.) : 150 [M^+] (10).

4-Nitrophenyl acetate (**8**) : m.p. 77–78 °C (Lit. 77–78 °C)[34]; FT-IR (KBr) $\bar{\upsilon}$: 3113, 3084, 3027, 3027, 2937, 2847, 2439, 1760 (C=O), 1615, 1592, 1526, 1487, 1442, 1349, 1294, 1209 (C–O), 1105, 1008, 918, 865, 751, 701, 583, 493, 420 cm^{-1}; EIMS *m/z* (rel. int.) : 181 [M^+] (50).

4-Cyanophenyl acetate (**9**) : m.p. 52–54 °C (Lit. 52–55 °C)[39]; FT-IR (KBr) $\bar{\upsilon}$: 3105, 3078, 3050, 2228 (CN), 1928, 1756 (C=O), 1602, 1502, 1433, 1371, 1285, 1225, 1208 (C–O), 1174, 1040, 1017, 916, 857, 825, 810, 746, 697, 647, 615, 592, 548, 475, 454 cm^{-1}; EIMS *m/z* (rel. int.) : 161 [M^+] (15).

1-Naphthyl acetate (**10**) : m.p. 48–49 °C (Lit. 48–49 °C)[40]; FT-IR (KBr) $\bar{\upsilon}$: 3061, 2959, 2929, 2860, 1768 (C=O), 1725, 1598, 1577, 1509, 1462, 1369, 1264, 1204 (C–O), 1155, 1077, 1042, 1013, 916, 869, 796, 772, 745, 704, 552 cm^{-1}; EIMS *m/z* (rel. int.) : 186 [M^+] (2).

2-Naphthyl acetate (**11**) : m.p. 70–72 °C (Lit. 70–72 °C)[41]; FT-IR (KBr) $\bar{\upsilon}$: 3051, 2925, 1755 (C=O), 1629, 1600, 1511, 1466, 1371, 1220 (C–O), 1153, 1137, 1012, 931, 824, 759, 737, 480 cm^{-1}; EIMS *m/z* (rel. int.) : 186 [M^+] (40).

Benzyl acetate (**12**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{35}$: 3090, 3066, 3034, 2953, 2928, 2854, 1956, 1743 (C=O), 1586, 1497, 1455, 1380, 1362, 1228 (C–O), 1080, 1026, 965, 902, 836, 749, 698, 643, 612, 577, 502, 448 cm^{-1}; EIMS *m/z* (rel. int.) : 150 [M^+] (20).

4-Nitrobenzyl acetate (**13**) : m.p. 76–78 °C (Lit. 76–78 °C)[42]; FT-IR (KBr) $\bar{\upsilon}$: 3111, 3077, 2923, 2850, 1738 (C=O), 1604, 1518, 1449, 1378, 1344, 1298, 1254, 1236 (C–O), 1107, 1048, 967, 921, 859, 836, 803, 741, 665, 604, 530, 462, 412 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ : 8.22 (2H, d, *J* 8.8 Hz, Ph), 7.52 (2H, d, *J* 8.8 Hz, Ph), 5.20 (2H, s, CH_2), 2.15 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 170.2 (C=O), 146.6, 142.2, 128.0, 124.1, 66.1, 20.7; EIMS *m/z* (rel. int.) : 195 [M^+] (100).

Benzhydryl acetate (**14**) : Liquid; FT-IR (neat) $\bar{\upsilon}^{43}$: 3084, 3063, 3032, 2929, 2855, 1741 (C=O), 1601, 1495, 1452, 1370, 1229 (C–O), 1185, 1078, 1021, 973, 865, 744, 699, 647, 607, 548 cm^{-1}; EIMS *m/z* (rel. int.) : 226 [M^+] (2).

3-Phenylpropyl acetate (**15**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[44] : 3062, 3027, 2954, 2860, 1739 (C=O), 1602, 1496, 1453, 1366, 1242 (C–O), 1036, 947, 747, 700, 606 cm^{-1}; EIMS *m/z* (rel. int.) : 178 [M^+] (0).

Octan-2-yl acetate (**16**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[45] : 2958, 2928, 2857, 1739 (C=O), 1462, 1372, 1244 (C–O), 1123, 1021, 949, 609 cm^{-1}.

1-Phenylethyl acetate (**17**) : Liquid; FT-IR (neat) $\bar{\upsilon}$: 3062, 3028, 2959, 2927, 2858, 1727 (C=O), 1600, 1580, 1491, 1461, 1380, 1274 (C–O), 1202, 1123, 1073, 1039, 1010, 957, 899, 744, 699, 606, 541 cm^{-1}; EIMS *m/z* (rel. int.)[46] : 164 [M^+] (4).

1-Adamantanyl acetate (**18**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[35] : 2912, 2853, 2676, 2655, 1781, 1732 (C=O), 1456, 1367, 1274, 1245 (C–O), 1187, 1104, 1060, 1016, 968, 933, 864, 749, 731, 605, 547, 449 cm^{-1}; EIMS *m/z* (rel. int.) : 194 [M^+] (10).

N-Phenylacetamide (**19**) : m.p. 112–114 °C (Lit. 112–114 °C)[47]; FT-IR (KBr) $\bar{\upsilon}$: 3289 (NH), 3256, 3194, 3135, 3059, 2962, 2924, 2853, 2798, 1665 (C=O), 1599, 1557 (NH bending), 1500, 1434, 1368, 1322, 1263 (C–N), 1041, 963, 906, 753, 694, 606, 533, 510 cm^{-1}; EIMS *m/z* (rel. int.) : 135 [M^+] (32).

N-(p-Tolyl)acetamide (**20**) : m.p. 140–142 °C (Lit. 138–142 °C)[48]; FT-IR (KBr) $\bar{\upsilon}$: 3294 (NH), 3256, 3188, 3124, 3067, 2922, 2853, 1898, 1734, 1663 (C=O), 1606, 1550 (NH bending), 1510, 1453, 1400, 1364, 1320, 1262 (C–N), 1180, 1119, 1039, 1012, 990, 961, 937, 820, 752, 618, 604, 508 cm^{-1}; EIMS *m/z* (rel. int.) : 149 [M^+] (60).

N-Benzylacetamide (**21**) : m.p. 60–62 °C (Lit. 60–62 °C)[49]; FT-IR (KBr) $\bar{\upsilon}$: 3294 (NH), 3086, 3023, 2925, 2852, 1643 (C=O), 1554 (NH bending), 1493, 1448, 1368, 1289, 1232 (C–N), 1155, 1078, 1027, 1001, 906, 748, 693, 616, 574, 501, 449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 7.40–7.23 (5H, m, Ph), 5.97 (1H, brs, NH), 4.41 (2H, d, *J* 5.8 Hz, CH_2), 2.00 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 169.4 (C=O), 137.9, 128.5, 126.9, 126.7, 43.3, 23.2; EIMS *m/z* (rel. int.) : 149 [M^+] (72).

N-(3,4-Dichlorobenzyl)acetamide (**22**) : m.p. 95–96 °C (Lit. 95–97 °C)[50]; FT-IR (KBr) $\bar{\upsilon}$:3279 (NH), 3079, 2925, 2871, 2852, 1644 (C=O), 1551 (NH bending), 1471, 1456, 1398, 1373, 1348, 1288 (C–N), 1255, 1209, 1128, 1097, 1030, 990, 885, 817, 731, 708, 689, 665, 620, 595, 571, 482, 453, 432 cm^{-1}; EIMS *m/z* (rel. int.) : 218 [M^+] (10).

N-(4-Methylbenzyl)acetamide (**23**) : m.p. 111–112 °C (Lit. 111–112 °C)[51]; FT-IR (KBr) $\bar{\upsilon}$:3288 (NH), 3077, 3027, 2923, 2853, 1644 (C=O), 1554 (NH bending), 1515, 1460, 1374, 1288 (C–N), 1221, 1093, 1019, 804, 732, 601, 545, 477 cm^{-1}; EIMS *m/z* (rel. int.) : 163 [M^+] (62).

N-(4-Methoxybenzyl)acetamide (**24**) : m.p. 95–96 °C (Lit. 94–96 °C)[52]; FT-IR (KBr) $\bar{\upsilon}$: 3292 (NH), 3092, 3015, 2952, 2928, 2834, 1634 (C=O), 1554 (NH bending), 1512, 1440, 1367, 1293, 1254 (C–N), 1231, 1173, 1109, 1030, 810, 757, 605, 557, 519, 436 cm^{-1}; EIMS *m/z* (rel. int.) : 179 [M^+] (10).

N-(4-Nitrophenyl)acetamide (**25**) : m.p. 212–214 °C (Lit. 212–214 °C)[53]; FT-IR (KBr) $\bar{\upsilon}$: 3309, 3278 (NH), 3220, 3158, 3094, 1683 (C=O), 1619, 1597, 1566 (NH bending), 1501, 1404, 1348, 1302, 1267 (C–N), 1180, 1113, 1005, 967, 849, 749, 692, 600, 496, 440 cm^{-1}; EIMS *m/z* (rel. int.) : 180 [M^+] (2).

1-Acetylpiperidine (**26**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[54] : 3278, 2938, 2856, 2697, 2677, 2508, 2157, 1649 (C=O), 1638, 1443, 1432, 1361, 1365, 1326, 1281(C–N), 1267, 1251, 1239, 1163, 1147, 1129, 1055, 1027, 987, 955, 894, 854, 716, 605, 590, 540, 466 cm^{-1}; EIMS *m/z* (rel. int.) : 127 [M^+] (80).

N-Butylacetamide (**27**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[55] : 3289 (NH), 3088, 2970, 2934, 2874, 1655 (C=O), 1558, 1467, 1465, 1453, 1439, 1374, 1368, 1296 (C-N), 1228, 1153, 1096, 1040, 1004, 997, 991, 738, 604, 494 cm^{-1}; EIMS *m/z* (rel. int.) : 115 [M^+] (50).

S-Benzyl thioacetate (**28**) : Liquid; FT-IR (neat) $\bar{\upsilon}$[35] : 3084, 3062, 3029, 2924, 2853, 1691 (C=O), 1601, 1495, 1453, 1413, 1353, 1244, 1133, 1103, 1072, 1027, 957 (C–S), 805, 769, 701, 626, 565, 473, 424 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 7.30–7.29 (4H, m, Ph), 7.25–7.24 (1H, m, Ph), 4.13 (2H, s, CH_2), 2.34 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 195.0 (C=O), 137.7, 128.9, 128.7, 127.3, 33.5, 30.3; EIMS *m/z* (rel. int.) : 166 [M^+] (20).

S-p-Tolylethanethioate (**29**) : Liquid; FT-IR (neat)

$\bar{\upsilon}^{35}$: 3027, 2953, 2923, 2855, 1903, 1707 (C=O), 1601, 1493, 1453, 1352, 1298, 1116, 1094, 1018, 949 (C–S), 807, 710, 643, 610, 527, 469 cm^{-1}; EIMS *m/z* (rel. int.) : 166 [M^+] (90).

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