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Polyvinyl trisulfonate ethylamine based solid acid catalyst for efficient glycosylation of sugars under solvent free condition

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Abstract

Heterogeneous Brønsted solid acid catalysts have the potential to decrease the environmental impact related with chemical production. Herein, we have synthesized the polyvinyl bound trisulfonate ethylamine chloride (PV-THEAC) and polyvinyl bound disulfonate ethylamine (PV-DSEA) as a Brønsted solid acid catalysts and it was effectively exhibited catalytic activity for acid catalyzed glycosylation reaction with sugar derivatives. Especially, the 0.3 equiv. PV-THEAC catalyst was found to be the most efficient and reusable catalyst for glycosylation reactions. A high density of the trisulfonic group (-OSO_3H) contributed to excellent catalytic activity during the glycosylation. Moreover, glycosylation reaction with D-mannose, D-xylose and D-glucose has been studied with alcohol. Remarkable acceleration of glycosylation using glycosyltrichloroacetimidate donor was obtained with selective production of β-glycoside.

Keyword: solid acid; trisulfonate; glycosylation; trichloroacetimidate.

1. Introduction

Homogeneous Brønsted acid catalysts such as H_2SO_4 are the remarkable catalyst for production of the fuel and it is a very important chemical for industry [1, 2]. However, the uses of these catalysts need energy-inefficient processes for recycling, separation and treatment of spent acids [3, 4]. Moreover, neutralization of homogeneous acid generates sulfate waste and thus, the acid does not succeed for requirement of catalyst that can be reused for accelerate the reaction. The development in chemistry toward green chemical processes has been activated with use of recyclable strong solid acid as replacements for such unrecyclable liquid acid catalyst [5, 6]. However, the main disadvantage to such progress is the lack of solid acids that is as active, stable and inexpensive.

Solid acid catalysts have received much attention in the green field of catalysis with advantages no pollution, easy separation and reusability [7, 8]. Thus, an ideal solid acid material for such applications should have high stability and many strong protonic acid sites [9, 10]. In this regard, researchers around the world have been committed to improving the acid density, strength and stability of solid acids [11, 12]. Although organic or inorganic solid oxide hybrids and strong acidic cation exchangeable resins such as perfluorosulfonated monomers have been studied broadly for the construction of desired solid acid [13], such materials are expensive and their activation is still much lower than that of sulfuric acid, so their convenient effectiveness is limited [14,15]. However, this work has explored by the development of solid acid catalysts such as sulfated zirconium [16, 17], Cs-exchanged heteropoly acids [14], acidic polymers [17] and zeolites [18]. In recent years, sulfonated carbon based solid acid use as the efficient catalyst for a variety of acid catalyzed reactions has been reported. This type of solid acid was usually prepared through carbonization and sulfonation reaction via renewable biomass as a carbon

source [19, 20]. These solid acids have proven their worth as a catalyst for some important chemical transformations like biodisel production and hydrolysis of the cellulose acetylation of glycerol etc [21].

In inorganic solid acid, the acid strength depends on several factors such as crystallinity, topology of structure, morphology and most importantly chemical composition. For example, microporous zeolites through its crystalline nature demonstrate stronger acid strength than mesoporous A1-MCM-42, although they are both composed of aluminosilicates [22, 23]. Moreover, polystyrene sulphonic acid resins are among the very important solid acids in industry and have been widely used in acid catalysed reactions such as etherification, olefin hydration, etherification and alkylation of phenols [24, 25]. In the case of polymer based solid acids great challenge still remain in improving the acid strength via factors beyond chemical composition, which are probably due to lack of morphology, structure controls of polymers [26]. In this paper, we report the synthesis and performance of polyvinyl bonded Brønsted trisulfonic group (-OSO_3H) solid acids as a novel, strong and stable solid acid catalyst with high density of sulfuric acid groups. A new strategy is adopted for the development of new types of solid acids: polyvinyl bound tri sulfonate ethyl amine chloride. This simple approach of polyvinyl bound trisulfonic group through triethanol amine exhibites remarkable catalytic activity for the glycosylation of unprotected sugars/ glycosyl trichloroacetimidate.

2. Experimental procedure

2.1. Material

Polyvinyl chloride (99 % pure) with average (M*w* = 48000 g/mol), diethanol amine (99 % pure), triethanol amine (99 % pure), chloromethane (99 % pure) and sodium sulfate (99 %), Amberlyst 15, sulfamic acid (99.3% pure). All substrates used for glycosylation reaction were

purchased form Aldrich and Acros with (99 %) purity and were used without further purification. glycosyltrichloroacetimidate donor was prepared by previously reported procedure in the literature using D-glucose, acetic anhydride (99 % pure) and trichloracetanitrile (99 %) chemicals [37]. TLC analysis was performed on silica-gel (SIL G/UV 254) plates to monitor the reaction.

2*.2. Characterization*

The FTIR spectra of samples were obtained by pelletizing the dried samples with potassium bromide (KBr) and recorded using a Varian 2000 (Scimitar series) spectrophotometer. A spectrum was recorded from 4000 to 500 cm^{-1} maintaining a resolution of 4 cm^{-1} with 32 scans in transmittance mode. Mass spectra for samples were obtained using Waters Micromass ZQ LC/MS 2000 (Scimitar series) spectrophotometer. Thermo gravimetric analysis (Scinco TGA *N*-100) was used to check the thermal stability of samples. The heating of samples was carried out from room temperature to 600 ^{o}C, at a heating rate of 10 ^{o}C/min under the continuous purge of nitrogen (50 mL/min), and spectra's were collected using Q600 Software (TA Instruments). The specific surface area, pore volume and pore diameter were determined based on physical adsorption of nitrogen on the solid surface of Brønsted solid acid catalyst by Brunauer–Emmett–Taller (BET) approach, using BELSORP-Max (MP) from BEL Japan. NMR spectra were recorded in $CDCl_3$ at 25 ^{o}C on either Bruker 400 (400 MHz) or Bruker 200 spectrometer (200 MHz). For ^{13}C NMR spectra, carbon chemical shifts were internally referenced to the deuterated solvent signal of $CDCl_3$ (77.16 ppm).

2.3. Typical synthesis procedure for solid acid catalyst

2.3.1. Preparation of trisulfonate solid acid catalyst (polyvinyl bound trisulfonate triethyl amine chloride)

In a typical synthesis procedure of polyvinyl bound diethanol amine (PV-DEA), a mixture of PVC (10.0 g, 160.10 mmol, 53.57 % Cl content), diethanolamine (16.81 g, 160.12 mmol) and acetonitrile (50 mL) was heated at 80 ^{o}C for 48 h in a 125 mL round bottom flask with stirring. After cooling this reaction mixture to room temperature, solid residue was collected by filtration and washed successively with water and acetone. Then, solid was dried under vacuum at 60 ^{o}C for 12 h and afforded PV-DEA as product. The loading of diethanol amine attached to PVC was 3.89 mmol/g determined by nitrogen content from elementary analysis. 88 % of Cl was reacted through the calculation. The chloroethanol (160.12 mmol, 17.35 g) with PV-DEA (10.0 g) and acetonitrile (40 mL) were added into a round bottom flask and mixture was heated at 80 ^{o}C for 24 h. After which the reaction mixture was cooled down to room temperature. The liquid phase was poured off and solid residue was washed with acetone. Then, solid was dried under vacuum at 60 ^{o}C and obtained polyvinyl triethanol amine chloride (PV-THEAC).

The PV-THEAC (5 g, 80 mmol) and chlorosulphonic acid (27.88 g, 240 mmol) were added into a round bottom flask and this reaction mixture was vigorously stirred for 48 h. After that, solid residue was collected by filtration and washed separately with water and acetone. The formation of PV-TSEAC was confirmed by sulpher contained using elemental analysis and IR. Elemental Analysis: PV-DEA calcd: N 8.41 %, C 43.25 %, H 7.80 %, observed; N 7.35 %, C 48.25 %, H 7.45 %. PV-THEAC calcd: N 6.63 %, C 45.49 %, H 8.50 %, observed; N 5.58 %, C 45.48 %, H 8.85 %. PV-TSEAC calcd: N 3.63 %, C 21.28 %, H 3.99 %, S 21.30 %, observed; N 3.23 %, C 45.48 %, H 8.85 %, S 60.30 %. PV-DSEA calcd: N 3.63 %, C 25.70 %, H 4.28 %, S 15.42 %, observed; N 3.27 %, C 30.45 %, H 3.13 %, S 15.81 %.

2.3.2. General procedure for glycosylation

A mixture of unactivated, unprotected sugars/glycosyl trichloroacetimidate donor (1 mmol), alcohol (5 mmol) and 15 wt % PV-TSEAC was stirred at 60 ^{o}C for 4 h. After consumption of glycosyl donor from TLC, reaction mixture was diluted with ethyl acetate and the catalyst was separated by filtration. The filtrate was evaporated in a rotary evaporator and further purified by column chromatography to obtain the desired glycosides.

Propargyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (a)

White solid; Yield 97 %; R_f = 0.3 (EtOAc-Pet ether = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.01 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H), 2.48 (t, *J* = 2.2 Hz, 1H), 3.71-3.75 (m, 1H), 4.11-4.17 (m, 1H), 4.26-4.30 (m, 1H), 4.37 (d, *J* = 2.7 Hz, 2H), 4.78 (d, *J* = 7.8 Hz, 1H), 5.0-5.04 (m, 1H), 5.11 (t, *J* = 10.0 Hz, 1H), 5.25 (t, *J* = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.5, 20.6, 29.6, 55.8, 60.3, 61.6, 68.1, 70.8, 71.8, 72.6, 75.4, 78.0, 98.0, 169.3, 169.4, 170.2, 170.6; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{22}O_{10}Na$ 409.11, found 407.12.

2-propyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (c)

White crystals; M.p-87^{0}c ; Yield 97%; R_f = 0.2 (EtOAc-Pet ether = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.84 (dddd, 1H, *J* = 17.1 Hz, 10.5 Hz, 6.1 Hz, 5.0 Hz) 5.27 (dq, 1H, *J* =17.1 Hz, 1.6 Hz), 5.25-5.18 (m, 1H), 5.21 (app t, 1H, *J* = 9.3 Hz), 5.09 (app t, 1H, *J* = 9.6Hz), 5.02 (dd, 1H, *J* = 9.4 Hz, 7.9 Hz), 4.55 (d, 1H, *J* = 7.9 Hz), 4.32 (ddt, 1H, *J* = 13.2Hz, 5.0 Hz, 1.6 Hz), 4.25 (dd, 1H, *J* = 12.2 Hz, 4.7 Hz), 4.12 (dd, 1H, *J* = 12.2 Hz, 2.5Hz), 4.08 (ddt, 1H, *J* = 13.2 Hz, 6.1 Hz, 1.3 Hz), 3.67 (ddd, 1H, *J* = 9.8 Hz, 4.7 Hz, 2.5Hz), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H); 13C NMR (63 MHz, CDCl3): δ170.2, 169.9, 169.1, 168.9, 133.1, 117.2, 99.3, 72.6, 71.5, 71.0, 69.7, 68.2, 61.7, 20.4,20.32, 20.26 (2C); HRMS (ESI+): *m/z* calcd. for [C17H24O10Na] 411.12, found 411.12.

2-butene-1-ol 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (d)

White solid; Yield 94 %; R_f = 0.3 (EtOAc-Pet ether = 1:1);^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.01 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 3.69-3.70 (m, 1H), 4.15-4.21 (m, 3H), 4.24 (d, *J* = 4.5 Hz, 1H), 4.28 (t, *J* = 5.9 Hz, 1H), 4.32 (bs, 1H), 4.35-4.39 (m, 1H), 4.58 (d, *J* = 7.7 Hz, 1H), 4.98-5.03 (m, 1H), 5.09 (t, *J* = 9.6 Hz, 1H), 5.21 (t, *J* = 9.6 Hz, 1H), 5.6-5.67 (m, 1H), 5.83-5.89 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.6, 20.7, 20.73, 58.5, 61.9, 64.3, 68.4, 71.2, 71.7, 72.7, 99.2, 126.7, 133.3, 169.4, 169.4, 170.3, 170.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{26}O_{11}Na$ 441.13, found 441.10.

1-decyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (e)

White solid; Yield 98%; R_f = 0.6 (EtOAc-Pet ether = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, 3H), 1.24 (m, 18H), 1.5-1.59 (m, 2H), 2.0 (s, 3H), 2.2 (s, 3H), 2.4 (s, 3H), 2.8 (s, 3H), 3.43-3.49 (m, 1H), 3.67-3.71 (m, 1H), 3.84-3.89 (m, 1H), 4.11-4.14 (m, 1H), 4.26 (dd, *J* = 7.8 and 4.6 Hz, 1H), 4.49 (d, *J*=7.8, 1H), 4.97 (dd, *J*=8, 1.4 Hz, 1H), 5.08 (t, *J*=9.7, 9.5 Hz), 5.2 (t, *J*=9.5, 9.2 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 20.5, 22.5, 25.7, 29.2, 29.5, 31.7, 61.8, 68.3, 70.2, 71.2, 71.5, 72.7, 100.7, 169.3, 169.4, 170.3, 170.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{25}H_{42}O_{10}Na$ 525.26, found 524.80.

2-isopropyl-5-methyl cyclohexyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (f)

White solid ; Yield 94%; R_f = 0.5 (EtOAc-Pet ether= 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.73 (d, *J* = 4.6 Hz, 3H), 0.85 (s, 3H), 0.89 (d, *J* = 1.7Hz, 3H), 0.91-0.93 (m, 2H), 1.14-1.41 (m, 4H), 1.55-1.72 (m, 5H), 2.01 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H),3.25-3.45 (m, 1H), 3.63-3.76 (m, 1H), 4.07-4.28 (m, 2H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.97 (dd, *J* =9.7 and 3.6 Hz, 1H), 5.07 (dd, *J* = 8.9 and 2.2 Hz, 1H), 5.21 (t, *J* = 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ15.4, 15.9, 20.5, 20.6, 20.7, 20.9, 21.0, 22.3, 22.8, 25.0, 31.4, 31.6, 34.0, 34.1, 40.8, 42.8, 47.4, 48.0,

62.4, 68.7, 68.9, 71.5, 71.6, 73.0, 79.1, 83.1, 98.7, 101.9, 169.3, 169.5, 170.4, 170.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{38}O_{10}Na$ 509.23, found 508.80.

1-adamantanylmethayl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (g)

White solid; Yield 97%; R_f = 0.6 (EtOAc-Pet ether = 1:1);^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48-1.52 (m, 3H), 1.58-1.74 (m, 12H), 2.02 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.97 (d, *J* = 9.4 Hz, 1H), 3.51 (d, *J* = 9.4 Hz, 1H), 3.63-3.71 (m, 1H), 4.16 (dd, *J* = 9.4 Hz, 1H), 4.28 (dd, *J* = 7.7 and 4.5 Hz, 1H), 4.43 (d, *J* = 7.7 Hz, 1H), 5.01 (dd, *J* = 9.4 and 4.8 Hz, 1H), 5.09 (t, *J* = 9.47 Hz, 1H), 5.21 (t, *J* = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.6, 20.68, 20.7, 28.0, 33.8, 37.0, 39.2, 61.9, 68.4, 71.2, 71.6, 72.7, 80.9, 101.7, 169.2, 169.4, 170.3, 170.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{25}H_{36}O_{10}Na$ 519.22, found 519.01.

(Z)-octadec-9-enyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (h)

White solid; Yield 82 %; R_f = 0.3 (EtOAc-Pet ether = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, 3H), 1.26 (bs, 24H), 1.5-1.67 (m, 4H), 2.01 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 3.44-3.5 (m, 1H), 3.67-3.72 (m, 1H), 3.85-3.90 (m, 1H), 4.14 (dd, *J* = 9.7 and 2.4 Hz, 1H), 4.5 (d, *J* = 8 Hz, 1H), 4.99 (dd, *J* = 7.8 and 1.4 Hz, 1H), 5.1 (t, *J* = 9.7 Hz, 1H), 5.21 (t, *J* = 9.5 Hz, 1H), 5.34-5.37 (m, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 20.1, 20.68, 21.7, 28.0, 33.8, 37.5, 39.2, 61.9, 68.4, 71.2, 71.6, 72.7, 80.9, 103.7, 169.2, 169.4, 170.5, 170.1.

Benzoyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (i)

Yield 93%; R_f = 0.2 (EtOAc-Pet ether = 1:2);1H NMR (400 Hz, CDCl3): d=8.07 (d, 2H,J = 7.2 Hz), 7.61 (t, 1H, J = 7.6 Hz), 7.47 (t, 2H, J = 7.6 Hz), 5.94 (d, 1H,J = 8.0 Hz), 5.55 (dd, 1H, J1= 8.4 Hz, J2= 10.4 Hz), 5.50 (d, 1H,J= 3.2 Hz), 5.21 (dd, 1H, J1= 3.6 Hz, J2= 10.8 Hz), 4.24e4.14 (m, 3H),2.20 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H) ppm. 13C NMR (125 Hz, CDCl3): d= 170.1, 170.0, 169.7, 169.3, 164.4, 133.8, 130.0, 128.6, 128.4, 92.6, 71.6, 70.5, 67.7,

66.8, 60.9, 20.42, 20.35 ppm. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{24}NaO_{11}$ 475.11. found 474.80.

Cyclohexyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside (j)

White solid ; Yield 93%; R_f = 0.2 (EtOAc-Pet ether = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24-1.26 (m, 4H), 1.38-1.48 (m, 2H), 1.64-1.77 (m, 3H), 1.83-1.86 (m, 1H), 1.99 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 3.58-3.63 (m, 1H), 3.64-3.69 (m, 1H), 4.10 (dd, *J* = 11.9 and 2.3 Hz, 1H), 4.25 (dd, *J* = 11.9 and 4.5 Hz, 1H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.95 (dd, *J* =9.6 and 8.2 Hz, 1H), 5.07 (t, *J* = 9.6 Hz, 1H), 5.19 (t, *J* = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.6, 20.65, 20.68, 20.7, 23.5, 23.6, 25.4, 31.5, 33.1, 62.0, 68.5, 71.4, 71.5, 72.8, 78.0, 99.3, 169.2, 169.4, 170.3, 170.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{30}O_{10}Na$ 453.1737, found 452.20.

3. Results and discussion

3.1. FT-IR analysis and Acidity determination of solid acid catalyst

The fourier transform infrared spectra of PV-THEAC, PV-DEA and PVC are shown in figure 1. The absorption bands in pure polyvinyl chloride are identified by the vibration band at 750 cm^{-1}, 1398 cm^{-1} and 3137 cm^{-1} for C-Cl, C-C as well as C-H respectively. When diethanol amine bound to polyvinyl Chloride, the C-Cl vibration band at 750 cm^{-1} is disappeared. In additon, the C-N, -OH and C-O vibrabration band at 1247 cm^{-1}, 3409 cm^{-1} and 957 cm^{-1} appeared in the FT-IR spectra (Fig. 1A). Moreover, polyvinyl chloride bound to triethanol amine is identified by a vibration band at 1247 cm^{-1}, 957 cm^{-1} and 3409 cm^{-1} for C-N, C-O as well as –OH functionlised groups respectively [27]. The spectra for PV-TSEAC and PV-DSEA has a

vibration band at 1169 cm^{-1} and 1038 cm^{-1}, which are associated with the stretching frequency of O=S=O and SO_3^- stretching mode in SO_3H group correspondingly (Fig. 2).

Yang and Kou et al determined Lewis and Brønsted acidity of solid acid by monitoring the shift of IR absorption bands at 1438 cm^{-1} and 1540 cm^{-1} in pyridine [28]. Generally, the pyridine adsorbed complexes shows two major absorption peaks at 1438 cm^{-1} and 1548 cm^{-1} analogous to Lewis and Brønsted acidity, respectively. This method implies that the presence band occurring at 1437 cm^{-1} to pure pyridine is shifted near to 1450 cm^{-1} that indicates pyridine is coordinated to Lewis acid sites. While, the new band appeared near 1541 cm^{-1} is an indication of pyridinium ions resulting from presence of Brønsted acidic sites. In this regard, result of pyridine adsorption spectra of PV-TSEAC, PV-DSEA catalyst and pure pyridine are shown in Fig .3. It can be seen that PV-TSEAC and PV-DSEA catalyst has shown the new vibration band at position 1541 cm^{-1}, which confirms the prepared solid acids are strictly Brønsted acidic. Furthermore, evidence for Brønsted acidity is the presence of protonated pyridine band for individual N–H bending and C–C stretching modes in both catalyst spectra.

3.2. TGA and BET analysis of solid acid catalyst

TGA thermograms of PV-TSEAC and PV-DSEA are shown in figure 4. It is described that both catalysts are stable up to 100 ^oC. In case of PV-TSEAC catalyst, 55 % continuous weight loss was recorded from 100 to 305 ^oC. Indeed, this weight loss corresponds to the three –OSO_3H groups from the PV-TSEAC. Afterward, the second weight loss observed from 305 ^oC to 500 ^oC that is because of polyvinyl chloride decomposition which was previously reported in literature [29]. The TGA of PV-DSEA signify a continuous weight loss of approximately 54 % from 100 ^oC to 300 ^oC due to the corresponding loss of –OSO_3H groups and the second weight

loss form 300 ^{o}C to 600 ^{o}C corresponds to the decomposition of polyvinyl chloride. Based on the result of the TGA analysis, it can be confirmed that of PV-TSEAC and PV-DSEA are stable up to 100 ^{o}C, therefore it can used in a wide veriets of acid catalyzed reaction.

Figure 5a and 5b show nitrogen adsorption desorption isotherms of PV-TSEAC and PV-DSEA. The nitrogen adsorption desorption isotherms of PV-TSEAC and PV-DSEA exhibited a well defined type-II isotherm pattern. This shows a evidence for monolayer-multilayer adsorption up to the high P/P_o. Moreover, the existence of the H_5 type hysteresis loop start from the relative pressure P/P_o at 0.26, which indicates that macropores are present on the outer surface of the catalyst. The pore size of the PV-TSEAC and PV-DSEA are shown to be 95.28 nm and 95.21 nm respectively. Moreover, the BET surface area of PV-TSEAC and PV-DSEA was recorded as 2 m^2/g. However; this result suggests a homogeneous distribution of the chelating group ($-OSO_3H$) in the macroporous polymer framework, which probably provide good density of acidic sites and activity for acidic reaction.

3.2. Catalytic activity

Fischer glycosylation always propose a useful way for the preparation of simple alkyl or aryl glycosides from the unprotected, unactivated reducing sugars. Moreover, the Fischer glycosylation reaction has been enhanced using heterogeneous solid acid catalysis [7, 8]. We sought to explore the catalytic activity of ours as prepare catalyst as a probable heterogeneous Brønsted acid catalyst for glycosylation reactions using different sugar derivate. In the preliminary set of reactions, unprotected D-glucose (1 equiv.) was allowed to react with 1-octanol (5 equiv.) under solvent and catalyst free condition at 60 °C and reaction progress monitored continuously, there was no any reaction up to 8h (scheme 3). Afterward, same reaction was conducted in 0.3 equiv. of PV-TSEAC and PV-DSEA catalyst under solvent free

condition at 60 °C. After 4 h, total utilization of the D-glucose was verified by TLC for PV-TSEAC catalyst, whereas in 6h total utilization of the D-glucose was observed for the PV-DSEA catalyst. The reaction mixture was then separated from the catalysts by filtration, purified by column chromatography and subjected to ^{1}H NMR. In ^{1}H NMR spectra it was observed that the reaction of D-glucose with 1-octanol using PV-TSEAC afforded high (96 %) yield of glycoside product (Table 1). While, the PV-DSEA catalyst provided only 88% yield of glycoside. These results indicate that the prepared catalysts are active for glycosylation of glucose and between the PV-TSEAC and PV-DSEA catalyst; PV-TSEAC catalyst shows the highest activity for glycosylation reaction of glucose. Therefore, we considered PV-TSEAC as a Brønsted acid catalyst for further catalytic study.

Stereochemical control of glycosylation is the most recent area of synthesis to be entirely resolved. In this context, we initiated an investigation to see if the Brønsted acid catalyst could be used for stereochemical outcome of a glycosylation reaction. Glycosyl trichloroacetimidates is one of the most reliable, applicable classes of glycosyl donors and it is easily activated by catalytic quantities of Brønsted acid [30]. Therefore, we sought to investigate glycosylation of glycosyltrichloracetimidate donor (scheme 4) using PV-TSEAC as Brønsted acid catalyst. When a glycosyltrichloroacetimidate donor (1) was used for glycosylation under a solvent free condition, an excellent yield of β-glycoside as the major product was obtained (Table 2). Probably, β-glycoside product selectivity was obtained via reaction proceeds through S_N2 reaction (nucleophilic attack of –OR from β side) which depends on good leaving groups and solvent free reaction conditions that was previously reported [31]. In this fashion, we observed that glycosylation of glycosyltrichloroacetimidate donor (1) with cyclohexanol in presence of PV-TSEAC catalyst at 60 °C led to formation of β-cyclohexyl glycoside as 93 % yield (Table 2

entry j). Thus, reaction conditions have been generalized by treating a set of alcohols with glycosyltrichloroacetimidate donor (1) and very good yield of β-alkyl glycoside were obtained . A series of primary alcohol such as 1-pentanol and 1-decanol also demonstrated 94 %, 98 % (Table 2 entry b & e) yields of β-alkyl glycoside under similar conditions via PV-TSEAC Brønsted acidic catalyst. Moreover, from cyclic alcohols such as 2-isopropyl-5-methyl cyclohexanol and cyclohexanol were obtained excellent yields of 2-isopropyl-5-methyl cyclohexyl glycoside and cyclohexyl glycoside respectively (Table 2 entry f & j). In case of a Aromatic and secondary alcohol also obtained an excellent stereoselective yield of β-glycoside product. The NMR spectral analysis of acetylated products revealed the formation of the products as β-anomers. Moreover, activity of the catalyst was also demonstrated using the O-bezylated glycosyl donor 2 (scheme 3). Donor 2 in presence of PV-TSEAC catalyst was tested with propyl alcohol acceptor, which provided a high yield with 94 % selectivity of β-glycoside product (Table 2 entry k). On the other hand, the noteworthy activating power of PV-TSEAC catalyst was futher established via disaccharide synthesis. We examined the reactivity of acceptor 4 with donor 2 and donor 1. In these case as well, the coupling reaction occurred smoothly under mild conditions and afforded desired β-linked disaccharide (Table 2 entry l & m).

Additionally, glycosylation reactions using other monosaccharide such as D-mannose, D-xylose and D-galactose were also allowed to react with 1-octanol under similar condition using PV-TSEAC Brønsted acidic catalyst. As expected, these reactions also proceeded smoothly and provided 95 %, 88 % and 91 % yield of glycoside product from D-mannose, D-fructose and D-xylose respectively (Table 3). The acid density in PV-TSEAC is the vital aspect for glycosylation through formation and breakage of hydrogen bond interaction [32]. The ratio of

the anomeric products was determined by comparing the integral values of the peaks in ^{1}H NMR and ^{13}C NMR spectra. A comparative study of the catalytic performance of the PV-TSEAC with other catalysts is shown in Table 4. In comparative studies, the PV-TSEAC catalyst obtained a high yield of product as that of sulfamic acid and triflic acid catalyst. Under the same optimal conditions commonly used acid catalyst as an amberlyst 15 and sulfonated zirconia has been screened and result afforded clearly shows that PV-TSEAC as the excellent catalyst for glycosylation reaction. Moreover, comparing the Hammett acidity of these catalysts using 2, 4 dinitroaniline as an indicator on UV-spectroscopy. Hammett acidity (H_o) of the sulfomic acid (-4.64), HOTf (-4.73), sulfonated zirconia (-4.67) and amberlyst 15 catalysts (-4.59) are comparatively lower than that PV-TSEAC catalyst (-5.18) (Table 5). Hence, we can demonstrate that PV-TSEAC is the best heterogeneous Brønsted acid catalyst for glycosylation reaction.

Reusability is a very significant factor in the case of solid acid catalyst. Innovative accomplishment of new ecofriendly, mild, advanced and reusable catalyst for glycosylation is one of the major ambitions of this study. To study the reusability of the catalyst it was collected at the end of reaction, wash three times with distilled water and reused. The catalytic activity of recycled PV-TSEAC catalyst was studied under similar condition with 1-octanol and D-glucose for five successive cycles (Fig. 6). Excellent yield of 1-octayl glycoside was obtained for up to five cycles without any significant loss of activity. Hence, the catalyst is capable of five recycles without any loss of catalytic activity.

4. Conclusion

In conclusion, new Brønsted solid acid catalysts as PV-TSEAC and PV-DSEA were synthesized via sulfonate group fictionalization on polyvinyl polymer. We characterized the sulfonate group (–OSO_3H) moiety on polyvinyl polymer by FT-IR spectroscopy and elemental analysis. TGA analysis also showed the stability of the catalyst is up to 100 ^oC and distribution of –OSO_3H group was proved by BET analysis. The synthesized PV-TSEAC catalyst showed excellent catalytic activity for glycosylation reaction with alcohol and sugar derivatives. We also investigated β-glycoside selectivity using glycosyltrichloracetimidate donor as reactant. From the result, we can conclude that high density of –OSO_3H group contributed to the catalytic activity of the catalyst during glycosylation. Overall result revealed that synthesized PV-TSEAC catalyst exhibited excellent activity for glycosylation reaction.

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Scheme captions

Scheme 1. Synthesis procedure of PV-TSEAC and PV-DSEA solid acid catalyst.

Scheme 2. Structure of PV-DSEA and PV-TSEAC.

Scheme 3. Reaction of D-glucose with 1-octanol in presence of catalyst at 60 ^{o}C.

Scheme 4. Reaction of glycosyltrichloroacetimidate donor with alcohol in presence of PV-TSEAC catalyst.

Scheme 5. Different glycosyl donor and acceptor used for glycosylation of sugars using PV-TSEAC as the catalyst.

Table captions

Table 1. Fischer glycosylations under predictable reflux conditions.

Table 2. Catalytic activity of synthesized PV-TSEAC for glycosilytion from glycosyltrichloroacetimidate donor in various alcohols.

Table 3. Catalytic activity of synthesized PV-TSEAC for glycosilytion using different sugar derivatives with cyclohexanol.

Table 4. Comparison of catalytic activity of different catalyst for glycosylation of D-glucose using 1-octanol at 60 ^{o}C.

Table 5. Comparison of Hammett acidity functions of different acids with PV-TSEAC catalyst.

Figure captions

Figure 1. FT-IR analysis of PVC (A) polyvinyl bound diethanol amine (B), polyvinyl bound triethanol amine chloride (C).

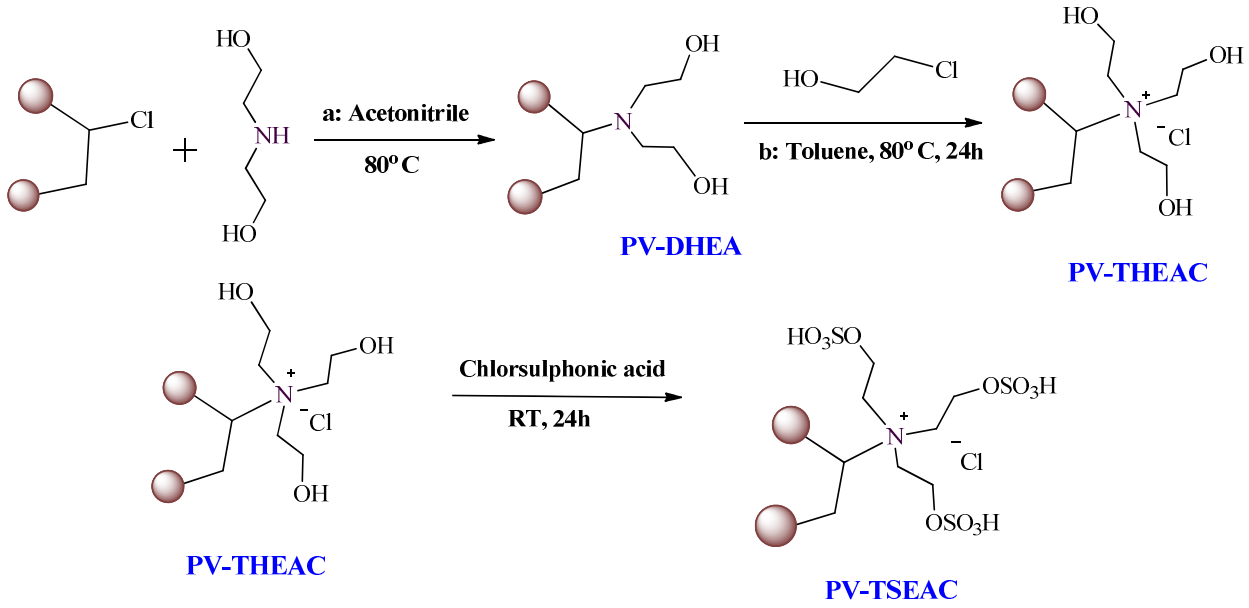
Figure 2. FI-IR spectra of PV-TSEAC (A) and PV-DSEA (B) that shows -OSO_3H group vibration band.

Figure 3. Acidity determination by IR spectroscopy based on pyridine: Pyridine (A), PV-TSEAC (B), PV-TSEAC with Pyridine (C) and PV-DSEA with Pyridine (D).

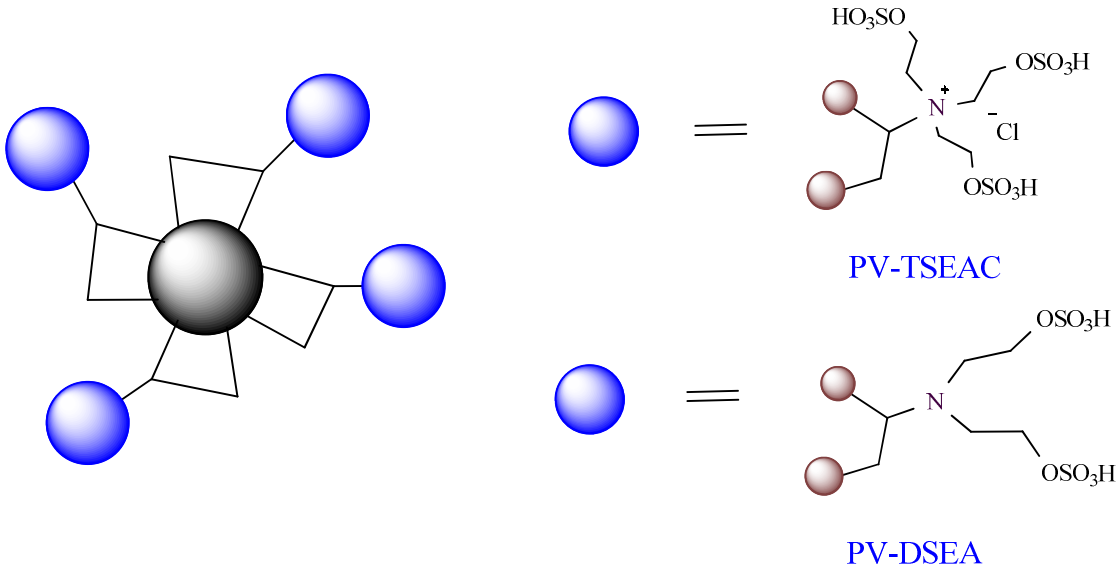
Figure 4. Thermogravimetric analysis of synthesized PV-TSEAC and PV-DSEA solid acid catalyst.

Figure 5. BJH cure (A) and Pore size distribution cure (B) for synthesized PV-TSEAC and PV-DSEA solid acid catalyst.

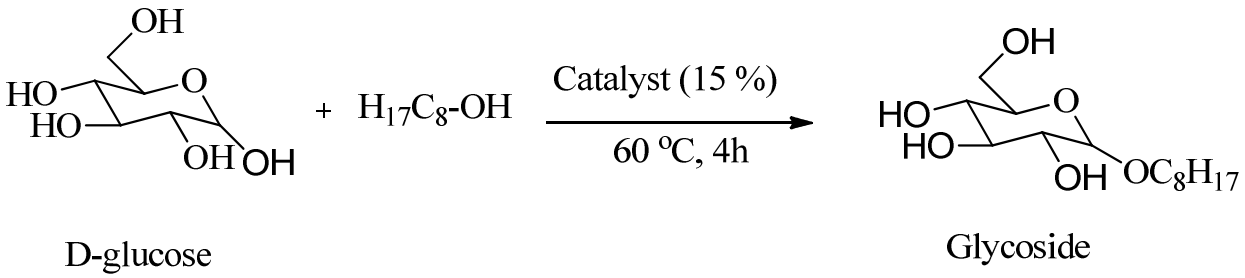
Figure 6. Reusability of PV-TSEAC catalyst for glycosylation reaction using D-glucose and 1-octanol at 60 ^{o}C for 4 h.


Cl
HO
NH
HO
a: Acetonitrile
80° C
OH
N
OH
PV-DHEA
HO
Cl
b: Toluene, 80° C, 24h
HO
OH
N
Cl
OH
PV-THEAC
HO
OH
N
Cl
OH
PV-THEAC
Chlorsulphonic acid
RT, 24h
HO3SO
OSO3H
N
Cl
OSO3H
PV-TSEAC

Scheme 1

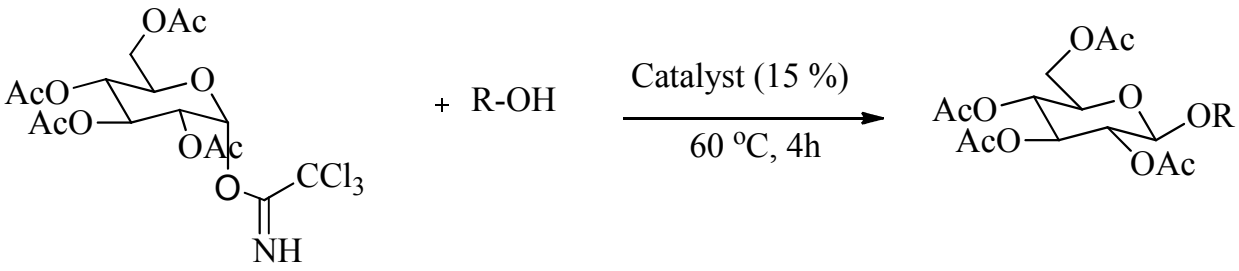


Scheme 2



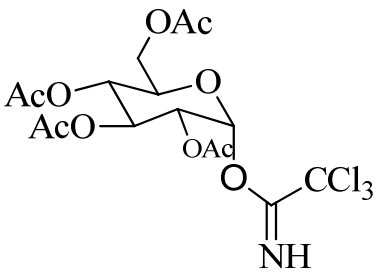
D-glucose Glycoside

Scheme 3

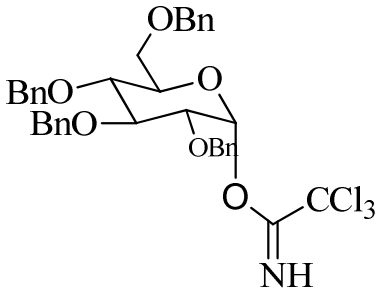

OAc
AcO
AcO
O
OAc
O
CCl3
NH
+ R-OH
Catalyst (15 %)
60 °C, 4h
OAc
AcO
AcO
O
OR
OAc
β-glycoside

3

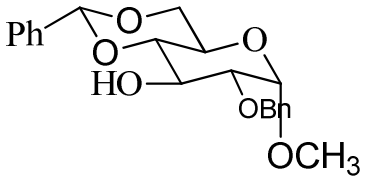
Scheme 4


OAc
AcO
AcO
O
OAc
O
CCl3
NH

1


OBn
BnO
BnO
O
OBn
O
CCl3
NH

2


Ph
O
O
O
HO
OBn
OCH3

3

Scheme 5

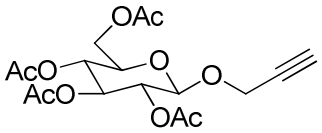
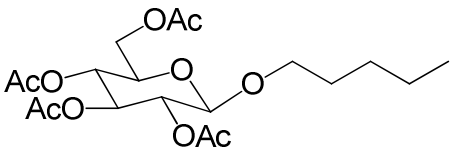
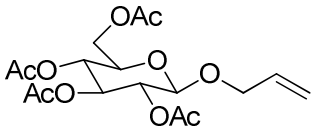
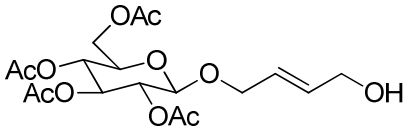
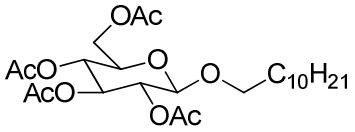
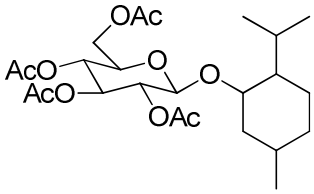
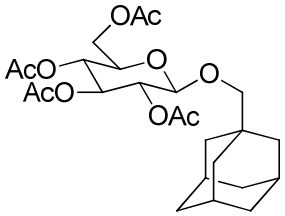
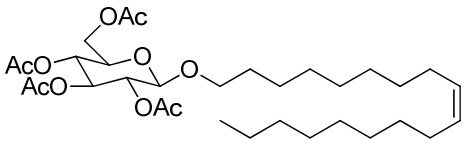
Table 1

Entry	Heating time [h]	Reactant [%]	Yield [%]
[a]1	8	100	0
2	1	< 22	40
3	2	10	60
4	3	< 6	90
5	4	0	96
[b]6	6	0	88

All reactions are carried out using PV-TSEAC catalyst with D-glucose and 1-octanol under solvent free condition at 60^{o}C. [a] Reaction was carried out catalyst free condition with other same condition**.** [b] reaction was carried out with PV-DSEA catalyst under same condition.

1

2 **Table 2**

Entry	Alcohol	Product	Time [h]	Yield [%]	β ratio
a	Propargyl alcohol		3.5	97	96
b	1-pentanol		3	94	98
c	2-propenol		4.2	97	98
d	2-butene-1,4-diol		4	94	99
e	1-decanol		4	98	96
f	2-isopropyl-5-methyl cyclohexanol		3.5	94	98
g	1-adamantane methanol		3	96	90
h	(Z)-octadec-9-enol		4.3	82	96

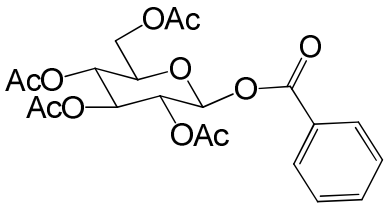
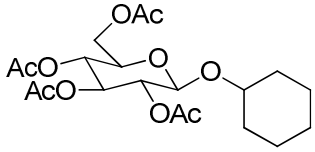
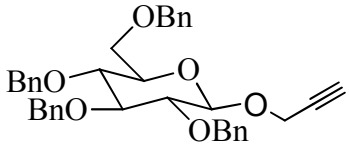
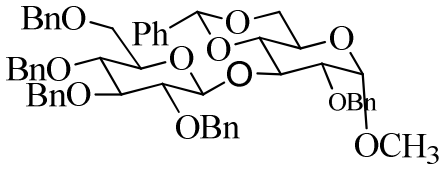
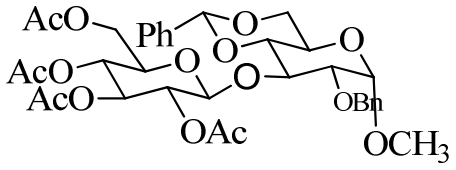
i	Benzoic acid		4	88	90
j	cyclohexanol		2.5	93	99
K	Propargyl alcohol		3.5	95	94
l	(2R,4aR,6S,7R,8S,8aS)-8-Hydroxy-6-methoxy-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxin-7-yl benzoate		3.8	88	91
m	(2R,4aR,6S,7R,8S,8aS)-8-Hydroxy-6-methoxy-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxin-7-yl benzoate		3.5	86	90

Table 3

Carbohydrate	Alcohol	Time [h]	Yield [%]	α:β
D-Glucose	1-octanol	3.5	97	<25:>75
D-Mannose	1-octanol	3.6	95	<45:>55
D-Fructose	1-octanol	4	88	<23:>77
D-Xylose	1-octanol	4	91	<18:>82

Table 4

Entry	Catalyst	Catalyst load	Time [h]	Yield [%]	Refs.
1	$Sc(OTf)_3$	0.1 equiv.	24	55	34
2	Sulfamic acid	0.2 equiv.	5	81	35
3	TfOH	0.2 equiv.	5	77	36
4	$BF_3.OEt_2$	1.0 equiv.	16	52	37
5	PV-TSEAC	0.3 equiv.	4	97	In this study
6	Amberlyst 15	0.3 equiv.	4	65	In this study
7	Sulfated Zirconia	0.3equiv.	4	78	In this study

Table 5

Acid	A_{max}	[I] (%)	[IH+] (%)	H_0 (±0.05)
Sulfonted Zirconia	0.65	41.8	58.1	- 4.67
Sulfamic acid	0.66	43.2	56.7	- 4.64
HOTf	0.58	38.2	61.7	- 4.73
Amberlyst 15	0.71	46.4	53.5	- 4.59
PV-TSEAC	0.30	19.6	80.3	- 5.18

Indicator: 2, 4 dinitroaniline ($pK(I)_{aq}$ = - 4.53)

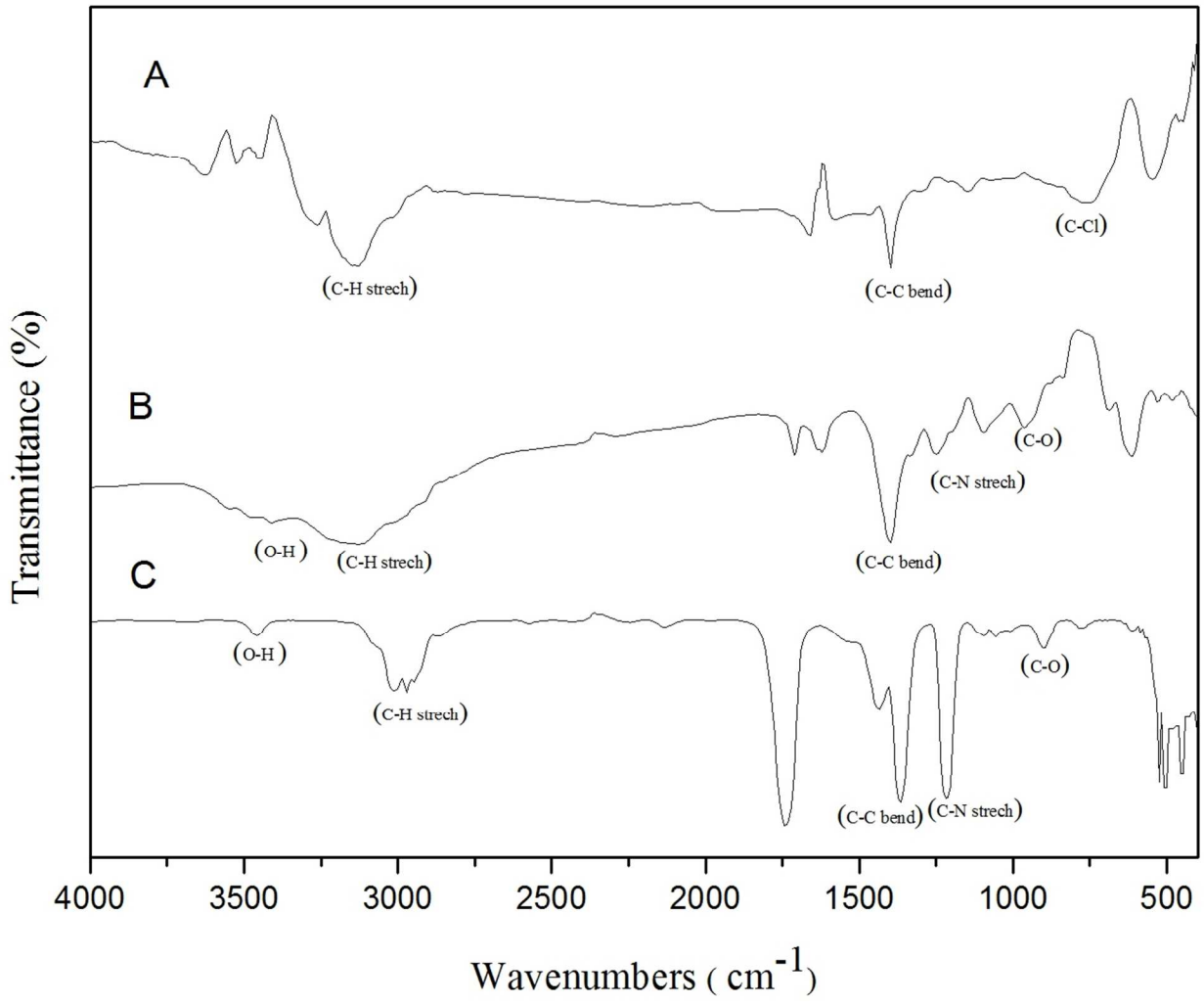

A
(C-H strech)
(C-C bend)
(C-Cl)
B
(O-H)
(C-H strech)
(C-C bend)
(C-N strech)
(C-O)
C
(O-H)
(C-H strech)
(C-C bend)
(C-N strech)
(C-O)
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Figure 1

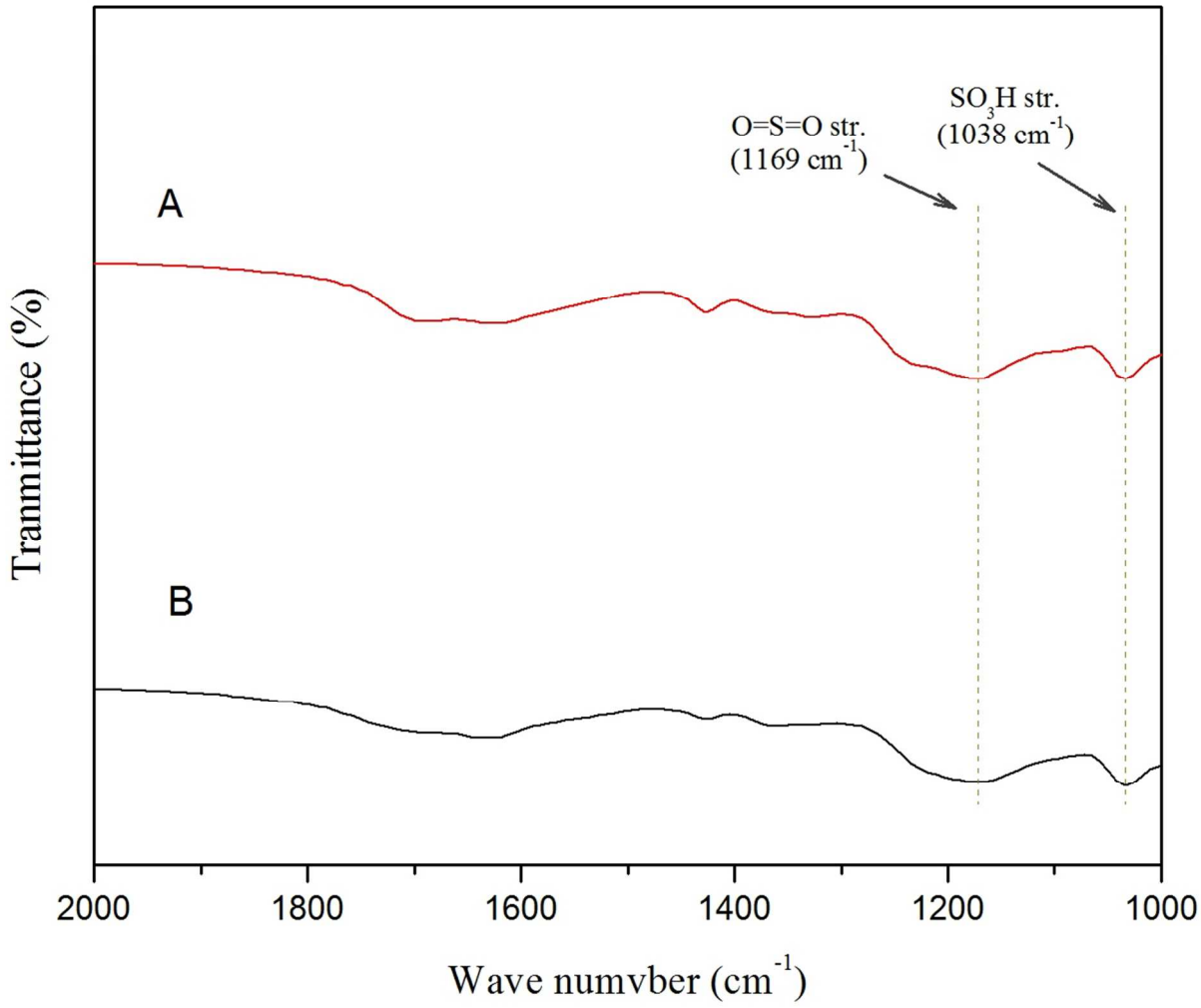

O=S=O str.
(1169 cm-1)
SO3H str.
(1038 cm-1)
A
B
Tranmittance (%)
2000
1800
1600
1400
1200
1000
Wave numvber (cm-1)

Figure 2

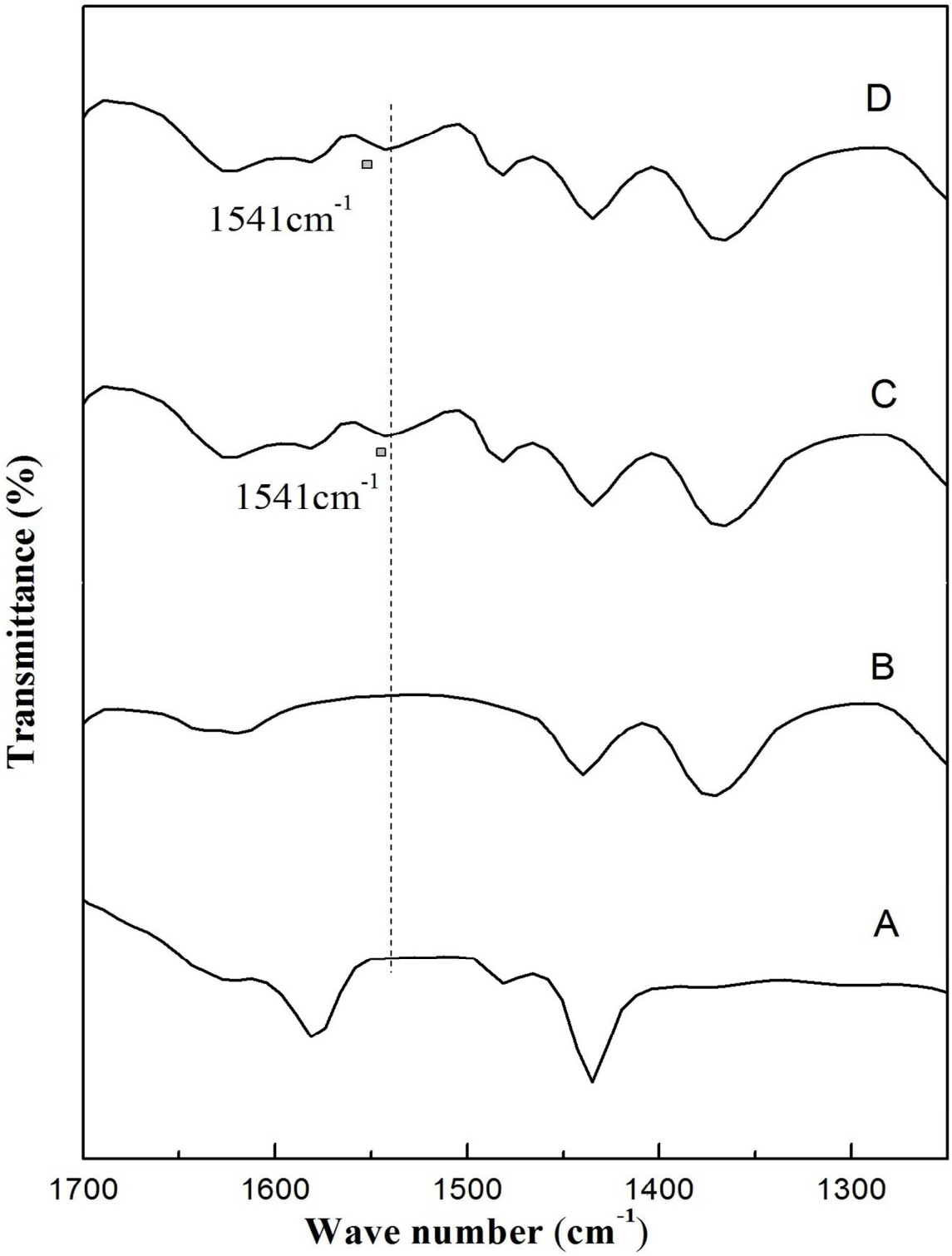

D
1541cm-1
C
1541cm-1
B
A
Transmittance (%)
1700
1600
1500
1400
1300
Wave number (cm-1)

Figure 3

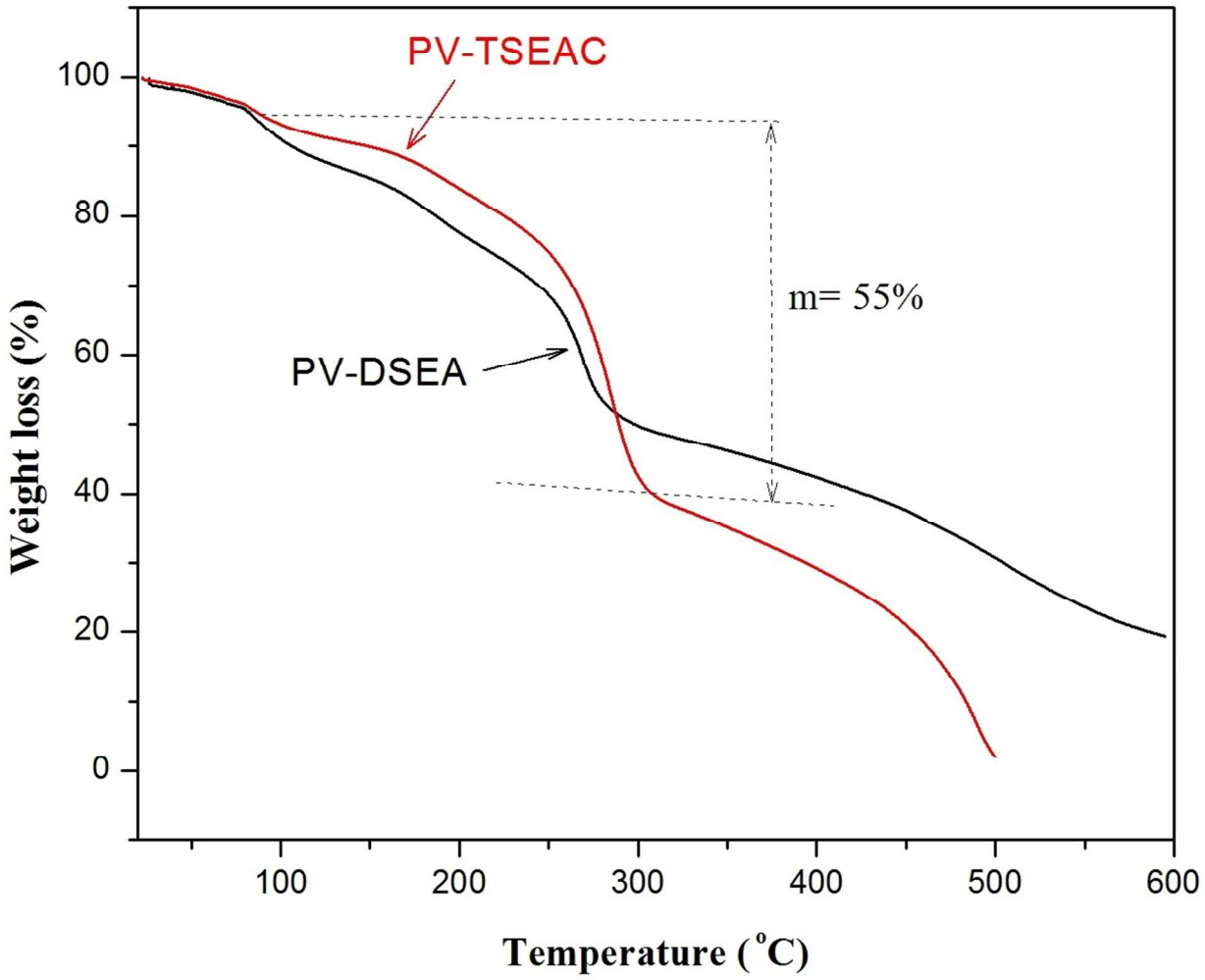

PV-TSEAC
PV-DSEA
m= 55%
Weight loss (%)
Temperature (°C)
100
80
60
40
20
0
100
200
300
400
500
600

Figure 4

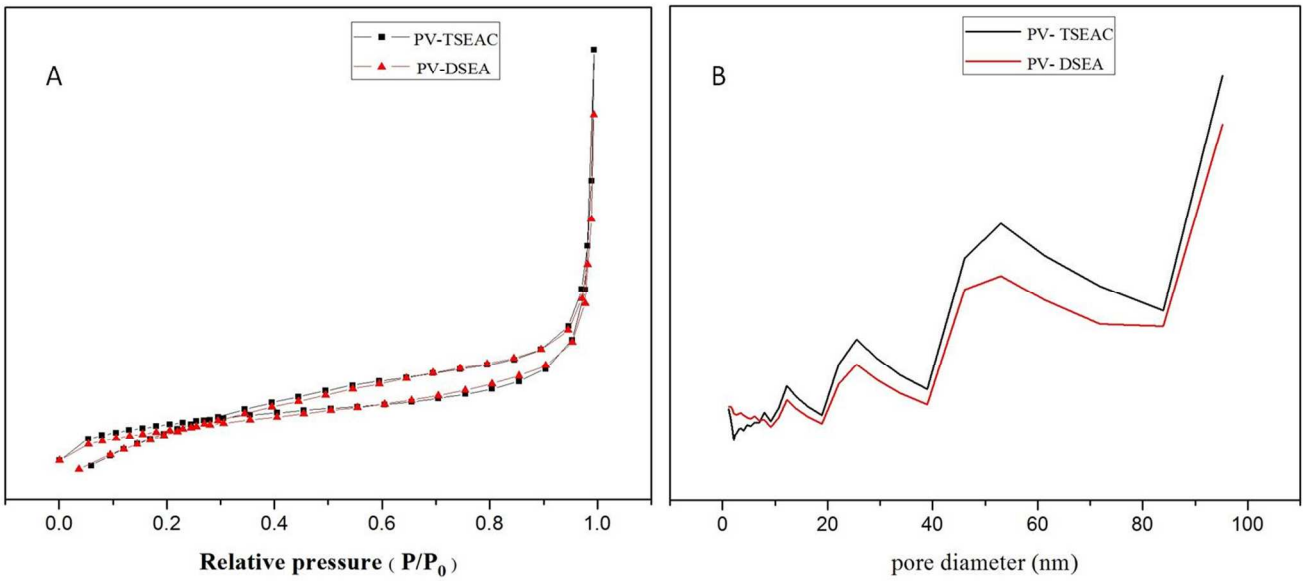

A
PV-TSEAC
PV-DSEA
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure (P/P0)
B
PV- TSEAC
PV- DSEA
0
20
40
60
80
100
pore diameter (nm)

Figure 5

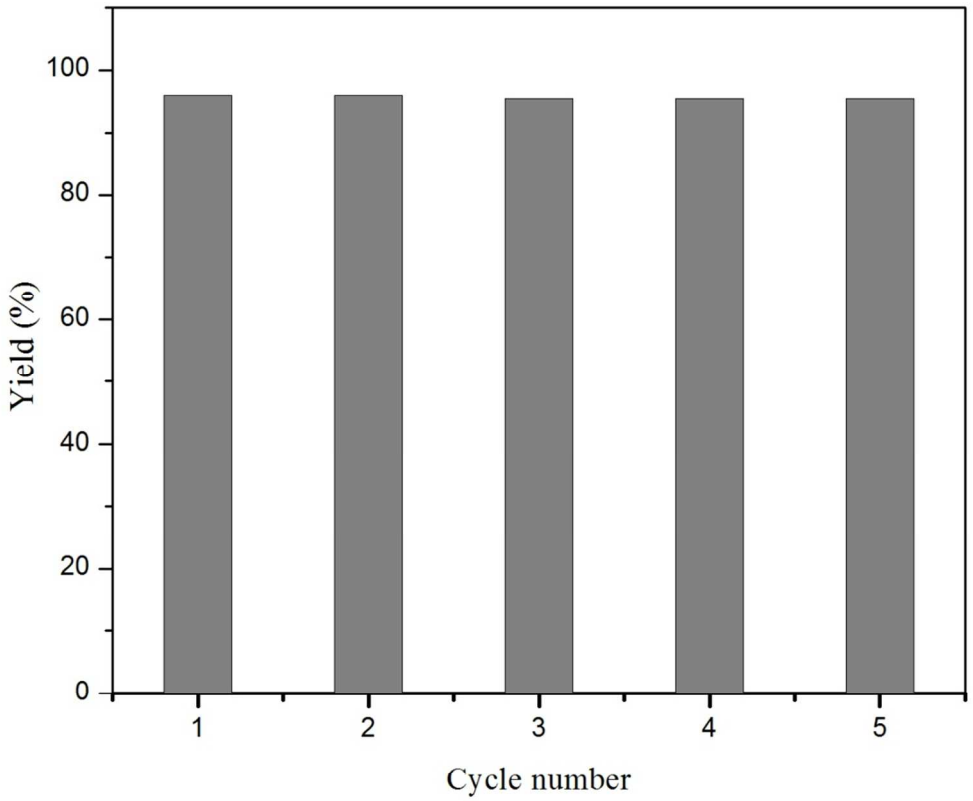


Figure 6

Graphical abstract