

# Preparation, characterization and catalytic activity of polystyrene with pendent perfluoroalkylsulfonylimide groups

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## Abstract

The new type of polystyrene with pendent perfluoroalkylsulfonylimide groups polymer (PPFSI or P-SO<sub>2</sub>NHSO<sub>2</sub>R<sub>f</sub>, where P is the polymer chain, R = -CF<sub>3</sub>, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>) was prepared by chemical modification of chlorosulfanated poly(styrene-co-divinylbenzene) resins with perfluoroalkylsulfonylamides R<sub>f</sub>SO<sub>2</sub>NH<sub>2</sub>. Acid strength of the PPFSI was tested by the Hammett indicator method, acid contents of the PPFSI were determined by acid–base titration and the nature of chemical modification for the PPFSI was evaluated by IR, TGA and SEM. The results indicated that the PPFSI was a strongly acidic polymer, which could be tolerant of high temperature, and an effective catalyst for direct condensation of carboxylic acids and alcohols.

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**Keywords:** Strongly acidic polymer; Perfluoroalkylsulfonylamides R<sub>f</sub>SO<sub>2</sub>NH<sub>2</sub>; Catalyst; Esterification

## 1. Introduction

Conventional Lewis acid catalysts are now facing a challenge especially in relation to Today's environmental concerns [1,2]. A wide variety of novel Lewis acid catalysts such as metal triflate and triflimide have been developed and a series of reactions such as Friedel–Craftes acylation [3,4], Diels–Alder [5], and esterification [6,7] are effectively catalyzed by these catalysts. Although some of these catalysts are to be recovered and reused, the separation of the catalysts from the reaction system has to be accomplished by processes like distillation or extraction. For the ease of workup and separation, a lot of efforts have been done. Great progress has been made in solid acid catalysts such as clay, zeolite, sulfonated metal oxides, sulfonated polymer and polymer-supported catalysts [8–13]. Each of these solid acid catalysts offers unique properties that can influence the catalytic activity. However, these solid acid catalysts have also some disadvantages. Supported catalysts are in trouble with

'leaching' that leads to loss of activity [14]. Although zeolites catalysts have higher activity, reactions always give a variety of undesired by-product due to the higher temperature. Ion exchange resins are limited in application because they are thermally unstable above 120 °C in the acid form [15].

Attractive alternatives to materials containing sulfonic acid groups are those containing sulfonimide groups. The high acid strength of sulfonimide has been well documented [16]. Recently, DesMarteau et al. have prepared perfluorinated polymeric membranes containing perfluoroalkylsulfonylimide groups as solid polymer electrolytes [17,18]. Feiring et al. reported the synthesis of a novel styrene monomer bearing a pendent perfluoroalkylsulfonylimide group and copolymers with a variety of olefinic monomers as potential electrolytes for lithium battery applications [19]. To the best of our knowledge, there is no report on the polymer containing side perfluorosulfonylimide groups in catalysis domain.

Recently, Yamamoto and co-workers reported a polystyrene-bound tetrafluorophenylbis(triflyl)methane as an organic-solvent-swallowable and strong Brønsted acid catalyst and the high catalytic activity was achieved in a series of reactions [20]. In this paper, we report a new type

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of strongly acidic polymer. After polymer modification via fluorofunctionalization, the  $\text{SO}_2\text{-NH-SO}_2$  units are introduced and expected to show 'super' acidities due to the powerful electron-withdrawing effect of perfluoroalkylsulfonyl group ( $-\text{SO}_2\text{CF}_3$ ,  $-\text{SO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ ) whose anion is highly delocalized [21,22]. Moreover, fluorinated polymer potentially offers additional benefits of the enhancement thermal and chemical stability compared with the sulfonated polystyrene [23]. On the other hand, the highly hydrophobic nature of polymer catalysts was reported to play a very important role in activity for some reaction systems [24,25]. The esterification reaction was selected as the model reaction to evaluate the catalytic activity of the PPFSI.

## 2. Experimental

### 2.1. Materials and methods

All solvents used for synthesis and esterification reaction were of analytical grade made in china and pretreated before use. D4020 and NKC-9 were purchased from Nankai Chemical Plant. Nafion NR50 was obtained from Wako Pure Chemical Industries Ltd. (Japan). All products were purified by column chromatography using ZCX-II (200–300 mesh).

IR spectra were recorded on a Bruker Vertex 70 Fourier Transform instrument (the variable temperature cell P/N 20610 solids Holder, 50–200 °C). TG and SEM analyses were performed on Perkin-Elmer TG97 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. GC analysis was carried out using a FuLi 9790 chromatograph equipped with a flame ionization detector.

### 2.2. Preparation of the PPFSI

The synthesis route of the PPFSI is shown in Scheme 1.

#### 2.2.1. Preparation of polystyrylsulfonyl chloride

To 1 g of macroporous polystyrene beads crosslinked with 5% DVB (D4020, 1 g, 9.52 mequiv. of phenyl ring) was added to a 1,2-dichloroethane (35 ml) solution of chlorosulfonic

acid (11.11 g, 95.2 mmol) and the mixture was stirred at 80 °C for 2 h. The polymer was then filtered on a frit, washed successively with chloroform, THF, THF–Water (1:1), and THF. After drying in vacuo, the polymer was then treated with large amount of thionyl chloride and small amount of pyridine for 16 h at reflux temperature in Ar atmosphere, immediately poured into ice-water when cooled to room temperature, washed with deionised water until the filtrate was neutral, and then dried in vacuo at 60 °C for 24 h, to give 2.71 g of polystyrylsulfonyl chloride polymer (yield 81.1% relative to the aromatic rings in polystyrene; loading of  $-\text{SO}_2\text{Cl}$  = 2.85 mmol/g,  $\text{SO}_2\text{Cl}$  groups content is determined by argentometry). IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3067, 2928 ( $-\text{CH}$ ); 1598, 1484, 1452 ( $-\text{C}_6\text{H}_5$ ); 1372, 1174 ( $-\text{SO}_2\text{Cl}$ ).

#### 2.2.2. Preparation of $\text{C}_4\text{F}_9\text{SO}_2\text{NH}_2$

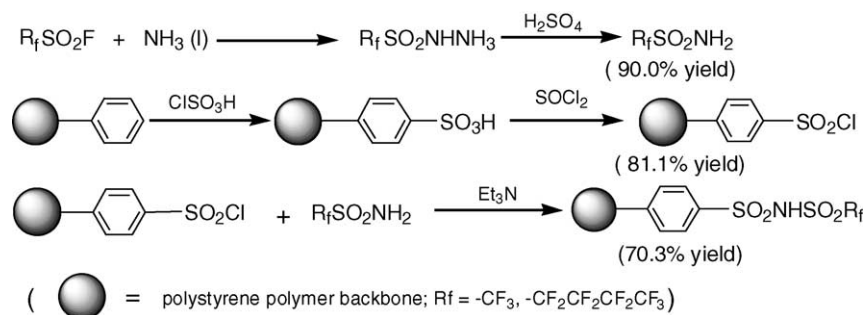
$\text{CF}_3\text{SO}_2\text{NH}_2$  and  $\text{C}_4\text{F}_9\text{SO}_2\text{NH}_2$  were prepared according to the literature [22,26,27].

#### 2.2.3. Preparation of $P\text{-SO}_2\text{NHSO}_2\text{F}_9\text{C}_4$

Triethylamine (5 ml, 0.033 mol) was carefully added dropwise into the mixture of polystyrylsulfonyl chloride resin (5 g, loading of  $-\text{SO}_2\text{Cl}$  = 2.85 mmol/g) and  $\text{C}_4\text{F}_9\text{SO}_2\text{NH}_2$  (28.5 mmol) in 50 ml of 1,2-dichloroethane, heated at 60 °C for 48 h with stirring under an atmosphere of argon, filtered, washed successively with  $\text{CHCl}_3$ , HCl,  $\text{H}_2\text{O}$ , and dried in vacuo at 80 °C for 24 h. A 7.32 g of polymer was obtained (yield was estimated to be 70.3% base on titration and reclaiming  $\text{R}_f\text{SO}_2\text{NH}_2$ ). IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3427, 1632 (N–H); 1601, 1479, 1452 ( $-\text{C}_6\text{H}_5$ ); 1367, 1172 ( $-\text{SO}_2-$ ); 1218 (C–F).

### 2.3. Measurement of acid strength and contents for PPFSI

The acid strength of the PPFSI was characterized by the Hammett indicator method [10]. The PPFSI was pretreated by being evacuated at 393 K for 2 h, then cooled to room temperature and allowed to contact the vapor of the Hammett indicator. The acid strength was determined by observing the color change of the indicator adsorbed on the surface of the PPFSI. The anthraquinone ( $H_0 = -8.2$ ), *p*-nitrotoluene ( $H_0 = -11.35$ ) and 4-chloronitrobenzene ( $H_0 = -12.70$ )



Scheme 1.

Table 1  
Acid strength of the PPFSI

Catalysts	Indicator and $H_0$		
	Anthraquinone	<i>p</i> -Nitrotoluene	4-Chloronitrobenzene
	-8.2	-11.35	-12.70
P-SO <sub>2</sub> NHSO <sub>2</sub> CF <sub>3</sub>	+	±	-
P-SO <sub>2</sub> NHSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	+	+	-

(+) Colour changed clearly; (-) colour unchanged; (±) colour changed unclearly.

were used as indicators and benzene was used as the solvent.

Acid contents of the PPFSI were determined by acid–base titration. To a suspension of the PPFSI in H<sub>2</sub>O–EtOH (1:1) was added a standard NaOH solution. After the mixture was stirred for 2 h, 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 the PPFSI was determined by several parallel experiments.

#### 2.4. General procedure for esterification

The PPFSI (0.1 equiv. H<sup>+</sup> relative to the carboxylic acid) was added to a mixture of carboxylic acid (5 mmol) and alcohols (15 mmol). The mixture was heated and stirred at given temperature for 6 h. After the resulting mixture was cooled to room temperature, filtered and washed with ether. The organic layer was washed with saturated Na<sub>2</sub>CO<sub>3</sub> solution, extracted with ether (3 × 3 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The products were purified by silica-gel chromatographic separation. The products were analyzed by gas chromatography, and characterized by IR and <sup>1</sup>H NMR.

### 3. Results and discussion

#### 3.1. Acidic contents and acidic strength of PPFSI

The acid loading of P-SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub> and P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> was found to be 3.10 and 3.21 mmol/g by several parallel experiments, respectively. The acid strength of solid acids can be measured by using an indicator method, IR spectroscopy of base molecules, temperature-programmed desorption (TPD) of base molecules, or microcalorimetry. Each method has its advantages and disadvantages [28]. The acid strength of PPFSI determined with the Hammett indicators is listed in Table 1, which shows that P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> shows higher acid strength than P-SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub>.

#### 3.2. FT-IR analysis of the PPFSI

A typical spectrum is shown in Fig. 1. For comparison, the FT-IR spectra of chlorosulfonyl polymer (a) and the PPFSI (b) are shown in Fig. 1. The introduction of chlorosulfonyl group into the crosslinked polystyrene was not very easy because of

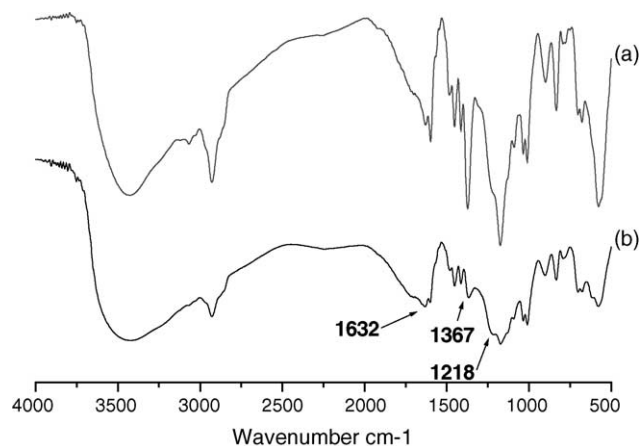


Fig. 1. FT-IR of chlorosulfonyl polymer (a) and the PPFSI (b).

resulting –SO<sub>2</sub>Cl and –SO<sub>3</sub>H groups at the same time with the chlorosulfonic acid as sulfonation agent [29]. Sulfonated polymer was treated with thionyl chloride to obtain a desired chlorosulfonyl polymer (a). It can be clearly seen from Fig. 1 that the characteristic absorption bands of –SO<sub>2</sub>Cl group ( $\nu_{as}$  1367 cm<sup>-1</sup>;  $\nu_s$  1172 cm<sup>-1</sup>) in Fig. 1(a) almost disappeared in Fig. 1(b). Peaks at 1601 cm<sup>-1</sup>, 1452 and 1413 cm<sup>-1</sup> can be assigned to the skeletal vibration bands of the benzene ring. Symmetric C–F stretching vibration at 1218 cm<sup>-1</sup> looked that very weak because of band overlap [30]. In Fig. 1, the characteristic absorption of N–H at 3424 cm<sup>-1</sup> was covered up by water peak from the samples or the KBr pellets, which was confirmed by the variable temperature cell P/N 20610 that can allow the study of band variation over a wide temperature range (see Fig. 2). Fig. 2 demonstrates that, above the 120 °C, and the water of the PPFSI and KBr pellet was eliminated and the PPFSI showed bands at 3427 and 1632 cm<sup>-1</sup> for  $\nu_{(N-H)}$  stretching and  $\delta_{(N-H)}$  bending vibrations, respectively, which was in accord with the literature [31,32]. Furthermore, no band at 3424 cm<sup>-1</sup> was observed for the chlorosulfonyl polymer above 120 °C. The bands of the PPFSI

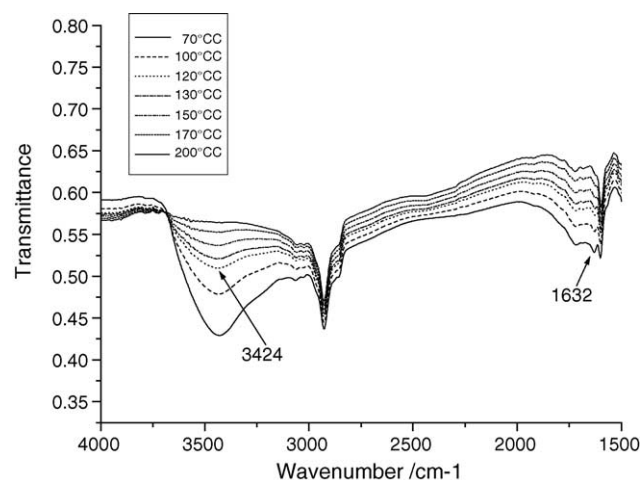


Fig. 2. FT-IR of PPFSI over 70–200 °C temperature.

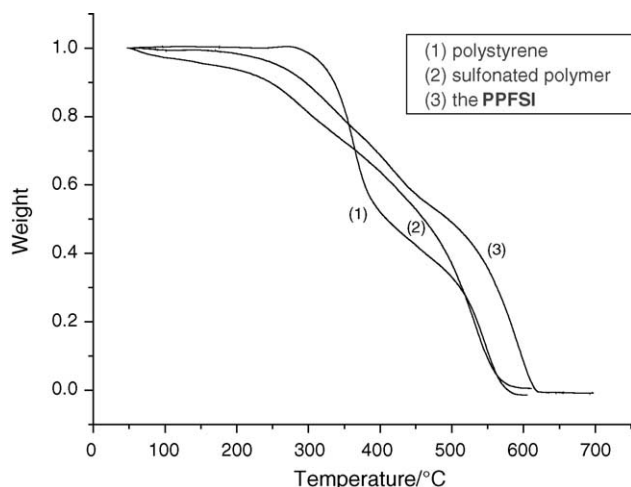


Fig. 3. TGA of polystyrene (1), sulfonated polymer (2) and the PPFSI (3).

at  $1632$  and  $3424\text{ cm}^{-1}$  above  $170\text{ }^{\circ}\text{C}$  almost disappeared due to the decomposition of the perfluoroalkylsulfonylimide group.

### 3.3. TG analysis of PPFSI

The thermal stability of the PPFSI was investigated by thermogravimetric analysis (TGA) and the result is shown in Fig. 3. No obvious weight loss was observed between 50 and

$280\text{ }^{\circ}\text{C}$  for polystyrene (1). The thermogram of the PPFSI (3) showed no clear weight loss up to  $170\text{ }^{\circ}\text{C}$ , and about 1% weight loss from 130 to  $170\text{ }^{\circ}\text{C}$  which could be attributed to the loss of crystalline water or small organic molecules. The perfluoroalkylsulfonylimide group of the PPFSI began to decompose at  $170\text{ }^{\circ}\text{C}$ , resulting in a 39.5% weight loss in the temperature region of  $170\text{--}450\text{ }^{\circ}\text{C}$ . This result is consistent with the variable temperature FT-IR spectra shown in Fig. 2. At a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere, the weight loss was drastic above  $250\text{ }^{\circ}\text{C}$  and completed at  $550\text{ }^{\circ}\text{C}$ , which may be attributed to the decomposition of the polymer backbone. It is evident that compared with the sulfonated polymer (2), the PPFSI achieved a significant improvement in thermal stability. These results indicate that the PPFSI can be used safely below  $170\text{ }^{\circ}\text{C}$ .

### 3.4. SEM characterization of polystyrene and PPFSI

The SEM micrographs of polymers are shown in Fig. 4.

From the SEM micrographs (Fig. 4), magnified 5000 times, it was found that the pore size of the PPFSI (b) became smaller compared with the polystyrene (a) due to anchoring organic groups to the polymer beads surface. The SEM micrographs of polymer bead fragment (c) and (d) showed that with chemical modification the primary structure of polystyrene changed not only at polystyrene spheres surface but also in the polystyrene spheres interior [23].

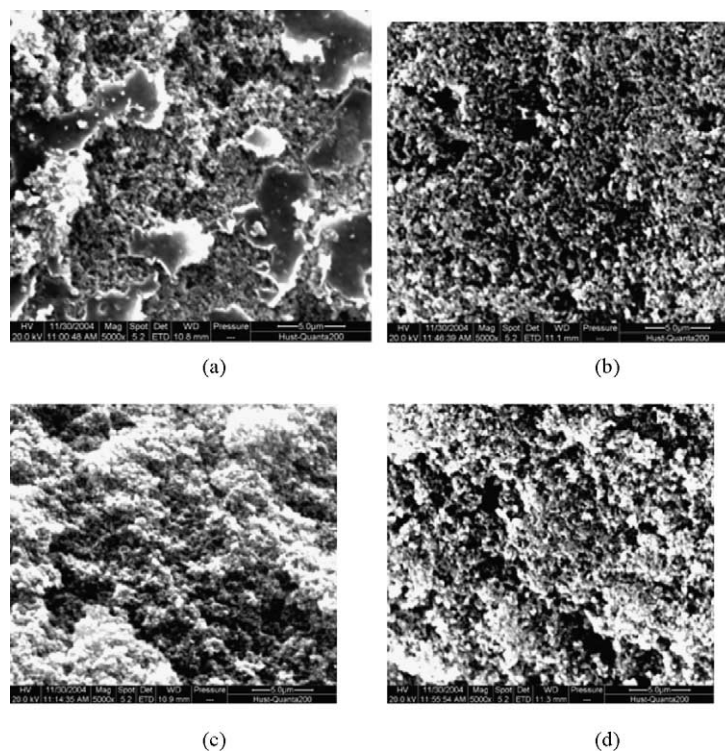


Fig. 4. SEM micrographs of polymer bead surface (magnification of 5000): (a) polystyrene (b) the PPFSI; SEM micrographs of polymer bead fragment (magnification of 5000): (c) polystyrene (d) the PPFSI.

Table 2

The results of catalytic esterification using P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> as catalyst<sup>a</sup> RCO<sub>2</sub>H + HOR<sub>1</sub> →<sup>catalyst(0.10 equiv.)</sup> RCO<sub>2</sub>R<sub>1</sub>

Entry	R	R'	Conditions	Yield <sup>b</sup> (%)
1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	6 h, 100 °C	81.5
2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> –	6 h, 100 °C	85.3
3	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	<i>n</i> -C <sub>4</sub> H <sub>9</sub> –	6 h, 100 °C	96.5
4	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	CH≡CCH <sub>2</sub> –	6 h, 100 °C	91.5
5	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	<i>t</i> -C <sub>5</sub> H <sub>11</sub> –	6 h, 100 °C	30.4
6	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	<i>n</i> -C <sub>3</sub> H <sub>7</sub> –	6 h, 100 °C	80.2
7	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	<i>i</i> -C <sub>3</sub> H <sub>7</sub> –	11 h, 60 °C	57.2
8	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> –	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	6 h, 120 °C	87.5
9	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> –	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –	6 h, 120 °C	93.4
10	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> –	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> –	6 h, 120 °C	95.4

<sup>a</sup> Reaction conditions: catalyst (3.21 mmol/g, 0.10 equiv. relative to carboxylic acids), carboxylic acids (5 mmol), alcohols (15 mmol), stirred at given temperature.

<sup>b</sup> Isolated yield.

Table 3

Recycling results of P-SO<sub>2</sub>NHSO<sub>2</sub>F<sub>9</sub>C<sub>4</sub> in the model reaction of phenylacetic acid and butyl alcohol<sup>a</sup> PhCH<sub>2</sub>COOH + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH  $\xrightarrow[0.10 \text{ equiv.}]{\text{Catalyst}}$  PhCH<sub>2</sub>COOH<sub>9</sub>C<sub>4</sub>

Cycle	Yield <sup>b</sup> (%)
1	97.6 (96.3)
2	94.3
3	95.4
4	96.5
5	95.2

Value in parentheses is the isolated yield.

<sup>a</sup> Reaction conditions: catalyst (3.21 mmol/g, 0.10 equiv. relative to carboxylic acid), phenylacetic acid (5 mmol), butyl alcohol (15 mmol), stirred at 120–125 °C for 4 h.

<sup>b</sup> Yields of products were determined by GC using *n*-decane as internal standard.

### 3.5. Catalytic activity of the PPFSI

To assess the catalytic activities of the PPFSI, the direct esterifications of carboxylic acids and alcohols using the PPFSI as catalysts were investigated. The results are shown in Table 2.

As is apparent from Table 2, the PPFSI showed very good catalytic activity for primary alcohols (entries 1–4 and 8–10 in Table 2). But for a tertiary alcohol (entry 5 in Table 2) and a secondary alcohol (entry 7 in Table 2) the yield were not satisfactory under similar experimental conditions. More

importantly, this novel fluorinated strongly acidic polymer could tolerate higher temperature than the sulfonated polymer and readily separated from the reaction mixture by simple filtration.

In order to check whether the PPFSI could be reused at higher temperature the esterification reaction of phenylacetic acid and *n*-butyl alcohol was investigated and the results are list in Table 3.

Table 3 demonstrates that the PPFSI possesses excellent recycling stability and can be reused more than five times successively at 120–125 °C without any loss of its activity.

Table 4 lists the results of catalytic esterification of phenylacetic acid and butyl alcohol over different solid-state acids.

It can be found that there is almost no difference in the catalytic activity between P-SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub> and P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>, but the PPFSI has higher catalytic activity than the classical resins such as NKC-9 and Nafion NR50. The order of catalytic activities is: P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> ≥ P-SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub> > NKC-9 > Nafion NR50. Although Nafion NR50 has strong acidity, the surface area of the resin in this form is very small (typically 0.02 m<sup>2</sup>/g or less), and most of active sites are buried within the polymers. These sites are inaccessible or poorly accessible under typical reaction conditions, resulting in lower catalytic activities. The recent development of high surface area Nafion–Silica nanocomposites provides the opportunity to solve these issues [33].

Table 4

Comparison of different solid-state catalysts<sup>a</sup>

Catalyst	Acidic loading (mmol/g)	Hammett acidic strength <sup>b</sup> H <sub>0</sub>	Functional group	Yield <sup>c</sup> (%)
P-SO <sub>2</sub> NHSO <sub>2</sub> CF <sub>3</sub>	3.104	–8.2 to –11.35	–SO <sub>2</sub> NHSO <sub>2</sub> CF <sub>3</sub>	95.7
P-SO <sub>2</sub> NHSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	3.206	–8.2 to –12.70	–SO <sub>2</sub> NHSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	96.5
NKC-9	4.74	–3.0	–SO <sub>3</sub> H	74.5
Nafion NR50	0.89	–12	–CF <sub>2</sub> CF <sub>2</sub> SO <sub>3</sub> H	58.3

<sup>a</sup> Reaction conditions: catalyst (0.10 equiv. relative to carboxylic acid), phenylacetic acid (5 mmol), butyl alcohol (15 mmol), stirred at 100 °C for 6 h.

<sup>b</sup> The acidic strength (H<sub>0</sub>) of P-SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub> and P-SO<sub>2</sub>NHSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> was determined by Hammett indicator method in this range, and the acidic strength of NKC-9 and Nafion NR50 was cited from the literature [11].

<sup>c</sup> Yields of products were determined by GC using *n*-decane as internal standard.

#### 4. Conclusions

In summary, a new type of fluorinated strongly acidic polymer has been prepared and characterized. Its catalytic activity and recycling ability have been investigated for direct esterification of carboxylic acids with alcohols. The characterization and experimental results indicated that the PPFSA was a strongly acidic polymer, which could be tolerant of higher temperature, and an effective catalyst for direct condensation of carboxylic acids and alcohols.

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