Synthesis of macroreticular p-(ω-sulfonic-perfluoroalkylated)polystyrene ion-exchange resin and its application as solid acid catalyst

Zheng Huan Lin, Chuan Jin Guan, Xin Liang Feng, Cheng Xue Zhao *

Department of Chemistry, Shanghai Jiaotong University, Shanghai 200240, China

Abstract

Macroreticular p-(ω-sulfonic-perfluoroalkylated)polystyrene (FPS) resins have been synthesized at mild conditions by following suspension polymerization of styrene and divinylbenzene, perfluoroalkylation by ω-fluorosulfonylperfluorodiacyl peroxides (SFAP), alkali hydrolysis and acidification. The macroreticular FPS resins with terminal perfluorosulfonic acid group were characterized by FTIR, SEM, TGA, acidimetry and nitrogen sorption technique. The resins have higher exchange capacity and surface area than perfluorinated resin Nafion NR50, and better thermostability than nonfluorinated sulfonic resin Amberlyst 15. The influences of the type and the amount of porogen, the crosslinker degree, the chain length of perfluoroalkylating reagent as well as the extent of perfluoroalkylation on the resin's properties were investigated. The FPS resins exhibited higher activity and selectivity than several commercial cation-exchange resins in the synthesis of ionone and diindolylmethanes (DIMs).
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Keywords: Ion-exchange resin; Polystyrene; Perfluoroalkylation; Solid acids

1. Introduction

Solid acids have many advantages over liquid acids in organic catalysis. They do less harm to environment and have no corrosion or disposal of effluent problems. They are reusable and easy to be separated from liquid products. As economically and ecologically benign catalysts, their research and application have attracted much attention in chemistry and industry. There are more than 100 industrial processes using over 103 solid acids as catalysts at the end of last century [1]. The replacement of traditional homogeneous catalysts with solid acids is becoming an inevitable trend.

Solid acid can be mainly divided into eight categories: oxides (Al_2O_3, SiO_2, etc.), sulfides (CdS, ZnS, etc.), metal salts ($AlPO_4$, $CuSO_4$, etc.), zeolites (HZSM-5, HY, H-β, etc.), heteropolyacids ($H_3PW_{12}O_{40}$, etc.), natural clays (kaolin, montmorillonite K10 and KSF, etc.), supported solid acids (BF_3/Al_2O_3, SO_4^{2-}/ZrO_2, etc.) and cationic ion-exchange resins (Amberlyst-15, Nafion NR 50, etc.). Thereinto, the use of cation-exchange resins is receiving more and more interests. For their stable struc-

ture, cation-exchange resins can be used in aqueous as well as non-aqueous, polar or non-polar media, and behave high selectivity which enables them to be used in separation of the close boiling mixture and in distillation column reactor (DCR). For an example, resin catalysts are exclusively used for industrial manufacture of methyl-*tert*-butyl ether, ethyl-*tert*-butyl ether, methyl-*tert*-amyl ether and ethyl-*tert*-amyl ether [2].

Since macroreticular polystyrene (PS) resin was invented in 1960s, cationic ion-exchange resins as solid acid catalysts have been increasingly employing in organic synthesis [2,3–9]. The ion-exchange resins used in organic catalysis can be divided into two categories: macroporous PS sulfonic resins (such as Amberlyst-15) and perfluorinated sulfonic resins (such as Nafion NR50). Although exchange capacity of Amberlyst-15 is above 4.2 mmol/g, the temperature of catalytic process can not be higher than 120 °C. Very differently, Nafion NR50 is a superacid ($H_0 = \sim -12$), and has extremely good chemical resistance and thermostability, but the surface area is too low, down to 0.02 m^2/g. Though the Nafion nanocomposite with SiO_2 has greatly increased surface area, exchange capacity is rather small (0.12 mmol/g). The disadvantages of the both types of resins greatly limit their applications.

In 1983, Zhao et al. [10] discovered a new aromatic perfluoroalkylation reaction by using perfluorodiacyl peroxides

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* Corresponding author. Tel.: +86 21 54742824; fax: +86 21 54741297.
E-mail address: cxzhao@sjtu.edu.cn (C.X. Zhao).

[FAP, $(R_fCOO)_2$]. Since then, this reaction has been widely used in the synthesis of fluorinated materials for various purposes [11–13]. Recently, Zhao et al. [14] have synthesized two new perfluorodiacyl peroxides (SFAP) bearing further convertible ω-fluorosulfonyl group, namely, perfluoro[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (SFAP-0) and perfluoro{2-[2-(2-fluorosulfonyl)ethoxy]propoxy}propionyl peroxide (SFAP-1). By using SFAP, a new cation-exchange resin with ω-sulfonic-perfluoroalkyl group similar to the functional group in Nafion has been synthesized [15]. This work is preparation and characterization of macroreticular p-(ω-sulfonic-perfluoroalkylated)polystyrene (FPS) resin and its application as solid acid catalyst in cyclization of pseudoionone and synthesis of diindolylmethanes (DIMs).
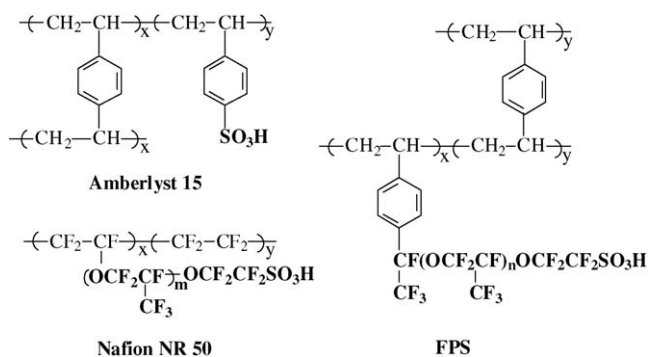
2. Experimental

2.1. Materials

Divinylbenzene (80% tech. grade, Shandong Dongda Chemical Industrial Co.) and styrene (Sinopharm Chemical Reagent Co.) were washed with 5% aq. NaOH and several portions of deionised water. The F113 (CCl_2FCClF_2) solution of SFAP (SFAP-0 or SFAP-1) was prepared according to the reported procedure [24] and kept under freezing condition before use. Toluene, heptane, polystyrene, poly(vinyl alcohol) (PVA, M_w 85,000–146,000, 87–89% hydrolysed), methylene chloride and all other solvents were used as received. Benzoyl peroxide (BPO) was purified by recrystallization from chloroform by adding methanol. Other reagents used in catalysis studies were purified before use and were purchased from Sinopharm Chemical Reagent Co.

For comparative purposes other solid acids were used in catalytic experiments. These catalysts were purchased from commercial sources and dried at 60 °C under vacuum overnight before use.

2.2. Characterization

BET surface area, pore diameter and BJH cumulative pore volume were obtained using a Micromeritics instrument (ASAP Micromeritics 2000). Fourier transform infrared spectroscopy (FTIR) was carried out using Perkin-Elmer 930 spectrometer, using the KBr pellet technique. The morphological characteristics were observed with an optical microscope (LEICA-

DMLP) and a scanning electron microscope (Hitach S-2150). The thermogravimetric studies were performed on a TGA 7 (Perkin-Elmer). Exchange capacity was determined by acidimetry. Nuclear magnetic resonance was performed using Varian Mercury 400 spectrometer. Melting points were determined by XT-4 apparatus and are uncorrected.

2.3. Preparation of macroreticular PS resin

The copolymerization process was carried out in a 500 ml three-neck flask fitted with mechanical stirrer, thermometer and refluxing condenser. The stabilizer PVA (1 g) was dissolved in water (200 ml) in the flask immersed in a water bath maintained at 80 °C. After cooled to room temperature, the organic phase (50 ml) composed by monomers mixture, porogen and BPO was then added rapidly to the aqueous solution at stirring speed of 400 rpm. The temperature was then raised at 80 °C. After 5 h, the polymer beads were filtered, washed with hot distilled water, and extracted with acetone in Soxhlet thimble for 24 h. Then, the beads were dried at 50 °C under vacuum to constant weight and then sieved. The fraction in the range of (60–40 mesh) was collected.

2.4. ω-Sulfonic-perfluoroalkylation of macroreticular PS resin

The macroreticular PS beads (5 g) prepared (see Section 2.3) were swelled in methylene dichloride (20 ml) overnight in a glass reactor fitted with a magnetic stirrer. At 0 °C, 0.4M F113 solution of FAP (FAP-S_0 or FAP-S_1) was added to the beads suspension under stirring. After 40 h, the beads were filtered and washed two to three times with $NaHCO_3$, water and ethanol. Then the beads were hydrolyzed in excess 30% aq. NaOH at 80 °C for 4 h. After washing with water to neutral, the beads were immersed in excess of 5N aq. HCl at room temperature for 24 h, then washed with water to neutral and dried at 50 °C under vacuum to constant weight to obtained the resulted FPS resins.

2.5. Catalysis studies

Cyclization of pseudoionone was carried out in a two-neck flask. To a solution of pseudoionone (0.2 ml) in cyclohexane (5 ml) a solid catalyst (0.1 g) was added under stirring at 80 °C. Remaining pseudoionone and all products were determined by an Agilent 6890N GC equipped with a FID detector.

In synthesis of diindolylmethanes (DIMs), to 10 mol% catalyst was added indole (2.0 mmol), aldehyde (1.0 mmol) or N-benzylidene aniline (2.0 mmol, synthesized according to the literature [25]) and 5 ml of CH_2Cl_2 as solvent. Then the mixture was stirred for 24 h at room temperature. The catalyst was filtered and washed with ethanol or ethyl acetate three times. The combined solution was evaporated under reduced pressure. The residue was purified via column chromatography (silica gel, petroleum ether:ethyl acetate = 4:1) to give product. DIM 4: mp 70–72 °C, 1H NMR ($CDCl_3$, 400 MHz): $\delta 0.91$ (t, 3H, $J = 7.2$ Hz), 1.35 (m, 6H), 2.25 (m, 2H), 4.49 (t, 1H, $J = 7.2$ Hz), 6.94 (d, 2H, $J = 2$ Hz), 7.08 (t, 2H, $J = 7.5$ Hz), 7.18 (t, 2H,

$J = 7.5$ Hz), 7.30 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.78 (brs, 2H, NH). IR (KBr) ν (cm^{-1}): 3412, 3051, 2922, 1638, 1614, 735. DIM **5**: mp 89–91 °C, 1H NMR: δ5.89 (s, 1H), 6.69 (d, 2H, $J = 3.2$ Hz), 7.00 (t, 2H, $J = 8$ Hz), 7.17 (t, 2H, $J = 8$ Hz), 7.30 (m, 9H), 7.93 (brs, 2H, NH). IR (KBr) ν (cm^{-1}): 3412, 3046, 1637, 746.

3. Results and discussion

Via electron-transfer induced perfluoroalkylation of macroreticular PS with SFAP, followed by hydrolysis and acidification, the target resin FPS was synthesized (Scheme 1). Zhao et al. have proposed the reaction mechanism as follows [10,11]:

The peroxide SFAP accepted an electron from the electron-rich phenyl ring in PS and turned into an anion radical which

underwent extremely rapid collapse into a perfluoroacyloxy radical $R_fCOO^\bullet$ and a perfluorocarboxylate anion R_fCOO^-. Then $R_f^\bullet$ generated in very fast decarboxylation of $R_fCOO^\bullet$ attacked phenyl ring of PS$^{+\bullet}$ cation radical to form a δ-complex. The δ-complex lost a proton to give ω-fluorosulfonylperfluoroalkylated polystyrene. Followed by alkali hydrolysis and acidification, the FPS resin was finally obtained.

3.1. Physical characterization of the resins

The porosity of macroreticular PS beads (PS1, PS2) and their fluorinated resins (FPS1, FPS2) employing toluene/*n*-heptane as binary porogen was analyzed by nitrogen sorption technique. As shown in Table 1, perfluoroalkylation brought about the resins significant changes in surface area, pore volume and pore diameter distribution. The BJH pore diameter
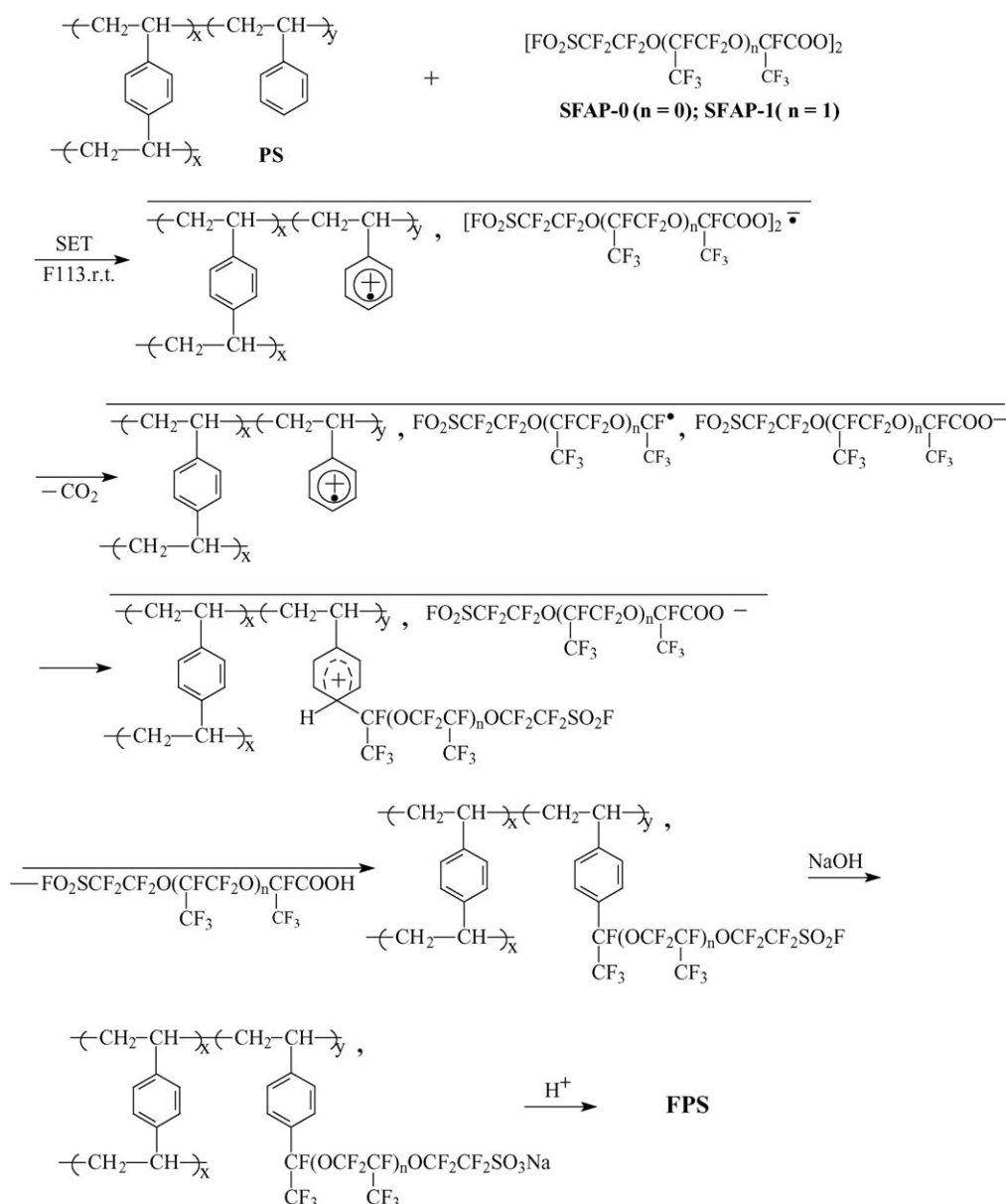
Scheme 1.

Table 1
Porosity characteristics of PS beads (PS1, PS2) and FPS resins (FPS1, FPS2)[a]

Resin	Crosslink degree (mol%)	Porogen[b] (wt%)	BET surface area (m²/g)	BJH pore volume (cm³/g)	BJH pore diameter (Å)	Pore size (Å)
PS1	23	30Tol/70Hep	128	0.64	187	10–300
FPS1[c]	23	30Tol/70Hep	59	0.31	188	10–220
PS2	36	50Tol/50Hep	361	0.83	151	10–400
FPS2[c]	36	50Tol/50Hep	107	0.44	146	10–300

[a] Perfluoroalkylation conditions: molar ratio, SFAP-0:PS = 1:0.6, temperature at 0 °C, time for 40 h.

[b] Tol = toluene; Hep = *n*-heptane.

[c] The exchange capacity of FPS1 and FPS2 is 1.5, 1.3 mmol/g, respectively.
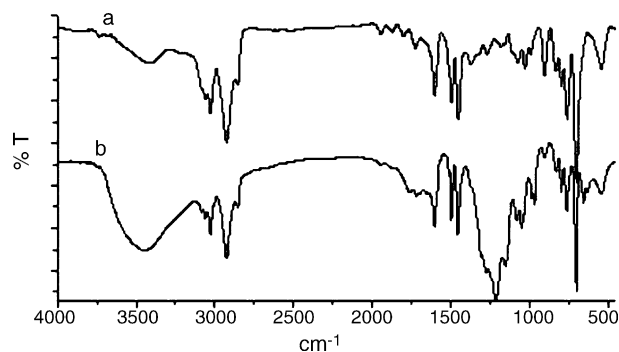

Fig. 1. FTIR spectra of macroreticular resins PS2 (a) and FPS2 (b).

data clearly show that the fluorinated resins are mesoporous in nature.

The FTIR spectra of FPS2 resin (Fig. 1) shows strong bands characteristic of the fluorinated groups: $\nu(CF_3)$ at 1312 cm^{-1}, $\nu(CF_2)$ at 1271 and 1213 cm^{-1}. The lack of carbonyl absorption discloses the absence of ring-ω-fluorosulfonylperfluoro-acyloxylation.

The TGA (Fig. 2) of macroreticular PS2 resin shows that less than 5% weight lost before 400 °C. This low weight loss was due to removal of the residual moisture. At higher temperature, polymer chain began to collapse. Very differently, the FPS2 resin appeared a significant weight loss at 190 °C, mainly due to desulfonation.

The microstructure of the resins has been observed by SEM (Fig. 3). The porous PS beads appeared smooth, regular surface
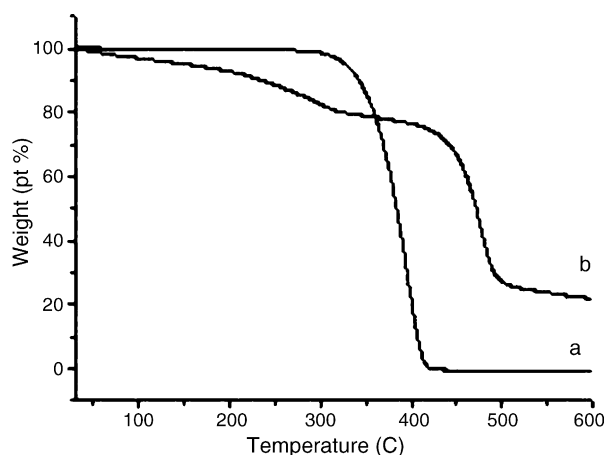

Fig. 2. TGA of macroreticular resins PS2 (a) and FPS2 (b).

and complex irregular pore structure (Fig. 3a and b). After perfluoroalkylation (Fig. 3c and d), the surface became rough, and the internal pore volume became less. And these observations are also proved by BJH determination.

3.2. Effect of synthetic conditions on the properties of macroreticular FPS resins

The porous structure and the properties of the modified resins can be varied by changing synthetic conditions mainly including crosslink degree, type of porogen, chain length of the perfluoroalkylating agent, and extent of perfluoroalkylation. By changing these factors, a series of FPS resins was prepared.

Divinylbenzene was used as crosslinker in suspension polymerization. Its amount (denoted with the nominal crosslink degree for convenience) is vital for the construction of porous structure [16]. As shown in Table 2, average molecular weight of macroreticular FPS increases with the increase in crosslink degree for larger molecular weight of divinylbenzene than that of styrene. On the other hand, proton exchange capacity and fluoroalkylation ratio of the FPS resins decrease with the increase in crosslink degree. This is because that the bigger crosslink degree results in PS beads' smaller pore diameter, greater steric hindrance or less accessibility of FAP to the benzene rings. However, if crosslink degree is too low, the rigidity of the PS beads is poor. Irregularly shaped and weak beads are vulnerable to mechanical attrition and easy to collapse. Actually, FPS3, FPS4 and FPS5 beads broke down into powders during the modification process. Therefore, crosslink degree should be moderate in order to balance the mechanical strength and exchange capacity.

In suspension polymerization the solvating power of the porogen to polymer has a critical effect on the porous structure of macroporous copolymers [17] According to solvating power, the porogens can be classified into three types: solvating porogens (e.g., toluene), nonsolvating porogens (e.g., *n*-heptane) and linear polymers or mixtures thereof. As can be seen from the results reported in Table 3, the influence of porogen is more complicated than that of crosslink degree. The polymerization with solvating porogen could not yield porous beads at low crosslink degree (such as FPS13 and FPS17). The exchange capacity of FPS resins (FPS12, and FPS14) made by employing sole porogen was lower than that of resins by employing mixed porogens. Among mixed porogens, the binary one 30Tol/70Hep was the best. The resin exhibited in the case of FPS19 has regular shape and relatively high exchange capacity up to 1.27 mmol/g. This is
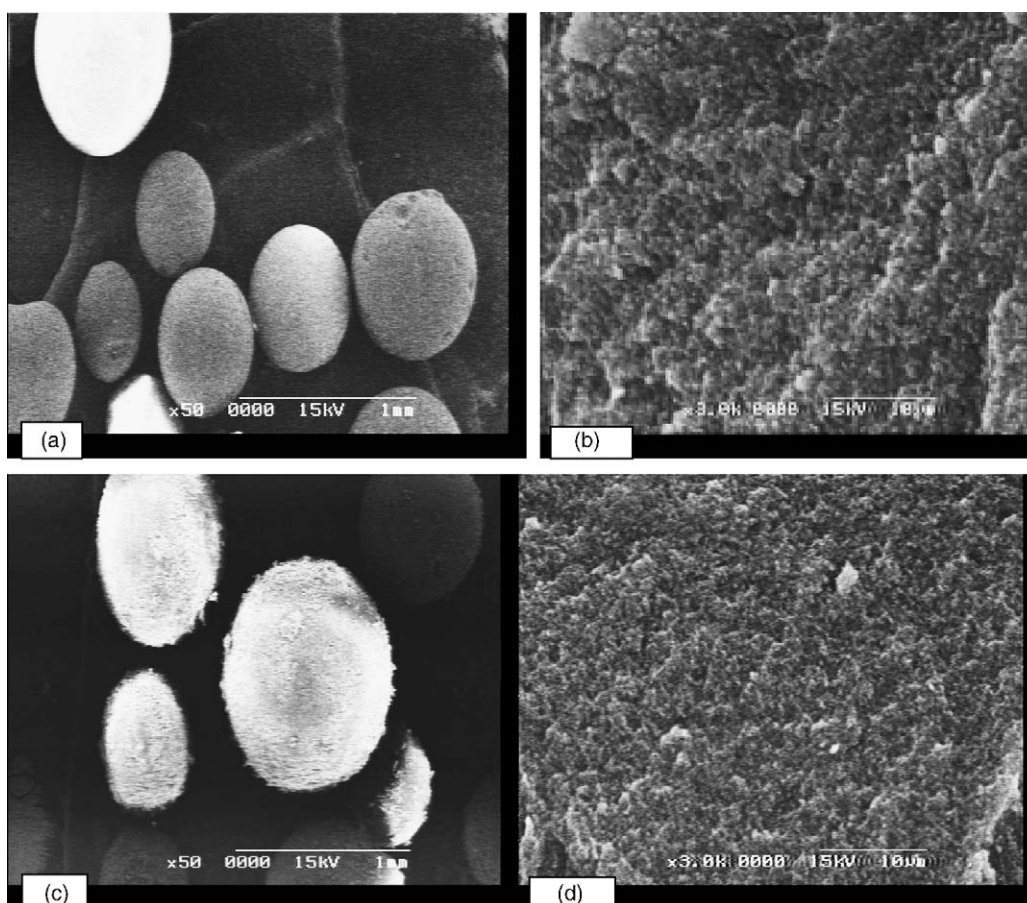
Fig. 3. SEM pictures of macroreticular PS1 beads (a and b) and FPS1 resin (c and d).

probably because the mixed porogens behave the chief merits of both the solvating porogen leading to high specific surface area, and the nonsolvating porogen favoring in high porous volume [17].

Table 4 shows the effect of the chain length of perfluoroalkylating agent on the property of macroreticular FPS resins. The exchange capacity of the resin using peroxide SFAP-1 ($n = 1$) with longer perfluoroalkyl chain is significantly lower than that of the resin produced from peroxide SFAP-0 ($n = 0$). It is because that the longer perfluoroalkyl chain reduces the accessibility of the peroxide to the benzene ring of the polymer substrate. The thermostability of FPS18-1, FPS19-1, FPS20-1 and FPS21-1 is also lower than that of FPS18, FPS19, FPS20 and FPS21, respectively. This can be explained that the compatibility of the longer molecular chains introduced by peroxide SFAP-1 with the polymer backbone is reduced.

Table 2
Exchange capacity and perfluoroalkylation ratio of macroreticular FPS resins with different crosslink degrees[a]

Resin	Crosslink degree (mol%)	Average molecular weight[b]	Exchange capacity (mmol/g)	Fluoroalkylation ratio (%)[c]	Shape of fluorinated resin[d]
FPS3	6	105.6	2.01	54	P
FPS4	10	106.6	1.88	45	P
FPS5	15	107.9	1.81	42	P
FPS6	20	109.2	1.59	33	P/S
FPS7	25	110.5	1.47	29	S
FPS8	30	111.8	1.26	22	S
FPS9	35	113.1	1.19	21	S
FPS10	40	114.4	1.16	20	S
FPS11	50	117.0	1.10	19	S

[a] *Synthetic conditions*: *n*-heptane was employed as porogen; molar ratio, SFAP-0:PS = 1:0.6; perfluoroalkylated temperature, 0 °C; perfluoroalkylated time, 40 h.
[b] Average molecular weight of two structural unit in macroreticular PS.
[c] Ratio of the number of perfluoroalkylated phenyl ring over the total number of phenyl ring in PS (conversion from exchange capacity).
[d] P = powder; S = sphere; P/S, there are powder and spheres in resins.

Table 3
Exchange capacity and perfluoroalkylation ratio of macroreticular FPS resins with different porogens[a]

Resin	Porogen (wt%)	Crosslink degree (mol%)	Beads appearance[b]	Exchange capacity (mmol/g)	Perfluoroalkylation ratio (%)
FPS 12	100Hep	23	O, R	0.78	11
FPS 13	100Tol	23	T	–	–
FPS 14	100Tol	39	D, R	0.63	9
FPS 15	20PS/80Tol	23	O, R	0.88	13
FPS16	20PS/40Tol/40Hep	23	O/D, R/IR	0.96	15
FPS17	50Tol/50Hep	23	T/D, R	–	–
FPS18	50Tol/50Hep	30	O, R	1.09	18
FPS19	30Tol/70Hep	23	O/D, R	1.27	22

[a] *Synthetic conditions*: molar ratio, SFAP-0: PS = 1:2.5; perfluoroalkylated temperature, 0 °C; perfluoroalkylated time, 20 h.
[b] O, opaque (macroreticular bead); T, transparent (gel-type bead); D, diaphanous (mixed morphology); R, regular; IR, irregular.

Table 4
The effect of the chain length of FAP on the property of FPS resins[a]

Resin	Crosslink degree (mol%)	Porogen (wt%)	Perfluoroalkylating reagent	Exchange capacity	T_1 (°C)[b]
FPS18	30	50Tol/50Hep	SFAP-0	1.09	143
FPS19	23	30Tol/70Hep	SFAP-0	1.27	174
FPS20	13	20PS/80Tol	SFAP-0	0.96	171
FPS21	36	50Tol/50Hep	SFAP-0	0.95	133
FPS18-1	30	50Tol/50Hep	SFAP-1	0.69	134
FPS19-1	23	30Tol/70Hep	SFAP-1	0.76	166
FPS20-1	13	20PS/80Tol	SFAP-1	0.25	168
FPS21-1	36	50Tol/50Hep	SFAP-1	0.62	118

[a] *Synthetic conditions*: molar ratio, SFAP-0: PS = 1:2.5; perfluoroalkylated temperature, 0 °C; perfluoroalkylated time, 20 h.
[b] The beginning temperature of desulfonation.

As shown in Fig. 4, to add more SFAP-0 certainly increased the exchange capacity and perfluoroalkylation ratio of the resulted resins. At lower molar ratio between SFAP-0 and PS, the addition of exchange capacity and perfluoroalkylation ratio was more, while at higher molar ratio, the addition was relatively less. More SFAP-0 underwent thermo-decomposition and inducing decomposition forming radical coupling product R_f–R_f at high molar ratio. As a result, the perfluoroalkylation degree of FPS was not deep.
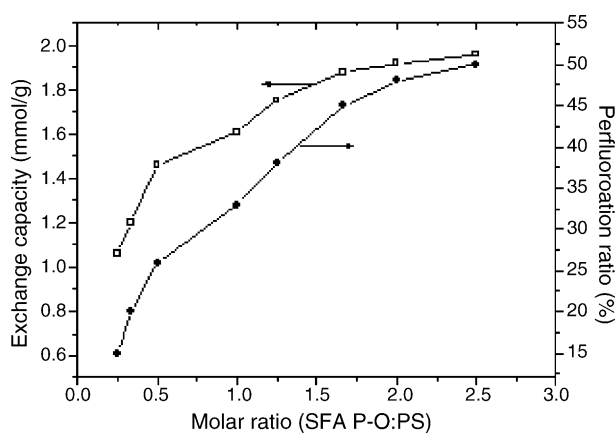

Fig. 4. Exchange capacity and perfluoroalkylation ratio of macroreticular FPS resins using *n*-heptane as porogen with 10% crosslink degree (mol%) at different molar ratio between SFAP-0 and PS (perfluoroalkylated temperature, 0 °C; perfluoroalkylated time, 40 h).

3.3. FPS catalyzed cyclization of pseudoionone

The novel fluorinated resin was applied to the cyclization of pseudoionone **1** (Scheme 2) to produce ionone. Ionone is one of the most important perfumes. Ionone has two isomers **2** and **3**. Thereinto, α-ionone **2** has violet odor and is widely used in the synthesis of perfumers and cosmetics; β-ionone **3** is a main precursor of Vitamin A and β-carotene.

The conversion of pseudoionone and yield of ionone under the catalysis of FPS1 and FPS2 are given in Table 5 with a comparison with that result by using Amberlyst 36 (Rohm & Hass) and Nafion NR50 (Aldrich). The yield of ionone by using Amberlyst 36 (49.17%, 3 h) was higher than other catalysts, because there are more acid sites on its surface. The FPS resins behaved best activity in those catalysts, a quantitative conversion reached up in only 1 h. Moreover, the selectivity of α-ionone **2** was obviously higher than the case of Amberlyst 36 (about 75%). Such high efficiency of FPS resin is due to its particular structure and strong acidity for the perfluoroalkyl environment and high electron-withdrawing character of α-CF_2 group. Nafion NR50 was found no good in the reaction because of its low surface area.
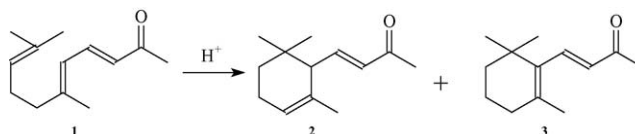
Scheme 2.

Table 5
The yield of ionone (**2** and **3**) and conversion of pseudoionone (**1**) catalyzed by cationic ion-exchange resins

Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion of **1** (%)	Yield of ionone (%)	
					α-Ionone **2**	β-Ionone **3**
FPS1	Cyclohexane	80	0.5	75.51	5.53	0
			1	100	21.84	0
FPS2	Cyclohexane	80	0.5	90	25.52	0
			1	100	18.68	0
Amberlyst 36	Cyclohexane	80	0.5	28.11	17.31	5.5
			1	65.40	22.56	7.52
			3	96.35	35.40	13.77
Nafion NR50	Benzene	80	2	3.34	0	0
Nafion NR50	Chloroform	60	4	2.92	0	0

In addition, we have tested the activity of FPS2 resin at low temperature and its reusability. The conversion of pseudoionone **1** is 100% at 70 °C after 1.5 h and 84.16% at 60 °C after 4 h. So FPS resin behaved some reactive activity at low temperature. In the repeated experiment the used FPS2 resin after washed with ethanol was added in fresh pseudoionone. It took 1.5 h for the conversion of pseudoionone to reach 100%, when the yield and the selectivity of α-ionone **2** were 10.12% and 100%, respectively. Obviously, there was slightly deactivation in the catalytic reaction.

3.4. FPS catalyzed condensation of indole and aldehyde

Indole and their derivatives are used as antibiotic in the field of pharmaceuticals [18] Thereinto, diindolylmethanes (DIMs) is a kind of compounds with health-promoting properties which arise from a beneficial shift in the balance of the sex hormones, estrogen and testosterone [19] Traditionally, DIMs can be synthesized by condensation reactions of indoles with carbonyl compounds. Protic acids [20] as well as Lewis acids [21] are known to promote these reactions. Thus we are interested in exploring the use of FPS resins in the synthesis of DIM **4** with indole and hexanal (Scheme 3).

Table 6 gives the yield of DIM **4** under FPS1 resin and other commercial catalysts. Obviously, FPS1 was found the most effective among all the catalysts tested with the yield of DIM **4** reaching 99% after 12 h. At the same time, the yields of DIM **4** catalyzed by Amberlyst-15, 35 (Rohm & Hass) and Yb-Nafion were only 47%, 56% and 30% respectively. After 24 h, the yields under Amberlyst-15, 35 and KSF (Fluka) both exceeded 85%, but the catalyst loading was 20 mmol%. In repeated experiment, FPS1 resin was simply filtered, washed with ethanol for three

Table 6
The yield of DIM **4** catalyzed by various solid acids

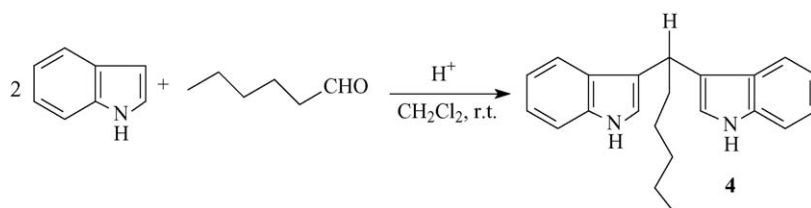| Catalyst	Catalyst loading (mol%)	Time (h)	Yield[a] of DIM **4** (%)
FPS1	10	12	99
Amberlyst-15	10	12	47
Amberlyst-35	10	12	56
Yb-Nafion	10	12	30[b]
Amberlyst-15	20	24	92
Amberlyst-35	20	24	90
KSF	20	24	85
None	–	24	0

[a] Isolated yield.
[b] Literature value [22].

times and dried at 60 °C under vacuum overnight. In six runs, the yields of DIM **4** were 95%, 97%, 99%, 98%, 97% and 98%, respectively. Thus FPS1 could effectively catalyze the reaction after repeated using seven times without loss of activity.

3.5. FPS catalyzed reaction of indole and imine

It was reported that indolyl amines as the major products and DIMs as byproducts were got when the reactions of indole with imines catalyzed by lanthanide triflates [23] Base on the reaction of indole with *N*-benzylidene aniline, we compared the catalytic activities of different catalysts. It is interesting to find that the DIM **5** were got as the only products (Scheme 4). It may be due to the susceptibility of the imino functionality towards hydrolysis in the presence of strong protic acids. Table 7 shows the all catalysts behaved high activities. It is worthy to point out the FPS1 resin used very short time (4 h) to reaching high yield (93%) of DIM **5**, yet it took Amberlyst-35 24 h to reach 94%

Scheme 3.
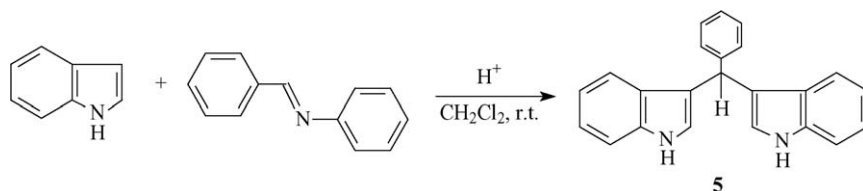
Scheme 4.

Table 7
The yield of DIM **5** catalyzed by various solid acids

Catalyst	Reaction time (h)	Yield [a] of DIM **5** (%)
FPS1	4	93
Amberlyst-15	24	89
Amberlyst-35	24	94
KSF[b]	12	86

[a] Isolated yield.
[b] Catalyst loading 20 mol%.

yield. So the activity of FPS resin was higher than other catalyst in the reaction.

4. Conclusions

Via suspension copolymerization of styrene and divinylbenzene followed by perfluoroalkylation with ω-fluorosulfonylperfluorodiacyl peroxides, hydrolysis and acidification, we have developed a novel ω-sulfonic-perfluoroalkylated polystyrene cation-exchange resin with terminal perfluorosulfonic acid group similar to that of Nafion. The synthetic conditions of the resins were much milder than that of Nafion. With high exchange capacity (2.0 mmol/g), surface area (107 m^2/g) and thermostability (stable up to 190 °C), the fluorinated macroreticular resins exhibit some of the advantages of both nonfluorinated resin and perfluorinated resin. The resins showed higher activity and better selectivity and reusability than other commercial solid acids in synthesis of α-ionone and diindolylmethanes. The macroreticular FPS resins can be anticipated to be widely useful in organic catalysis.

Acknowledgements

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