Macroreticular *p*-(ω-sulfonic-perfluoroalkylated) polystyrene ion-exchange resins: a new type of selective solid acid catalyst

Zhenghuan Lin and Chengxue Zhao*

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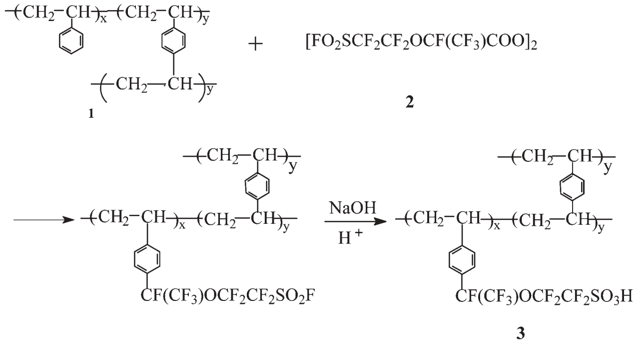
Macroreticular *p*-(ω-sulfonic-perfluoroalkylated) polystyrene (FPS) cation-exchange resins 3 have been synthesized by sequential *p*-perfluoroalkylation of macroreticular polystyrene (PS) 1 with ω-fluorosulfonylperfluorodiacyl peroxide 2, hydrolysis and acidification; the fluorinated mesoporous resins exhibited higher activity and selectivity than commercial Amberlyst 36 and Nafion NR50 in the cyclization of pseudoionone.

Since macroreticular polystyrene (PS) **1** resin was invented in the 1960s, cationic ion-exchange resins as solid acid catalysts have been widely employed in organic synthesis for several decades.[1–8] The ion-exchange resins used in organic catalysis can be divided into two categories: macroporous PS sulfonic resin (such as Amberlyst-15) and perfluorinated sulfonic resin (such as Nafion NR50). Although the exchange capacity of the former resins is above 4.2 mmol/g, the temperature of the catalytic process cannot be higher than 120 °C. In sharp contrast, the latter resins are superacid (H_0 = ∼ −12), and have extremely good chemical resistance and thermostability, but the surface area is too low, down to 0.02 m^2/g. Although the Nafion nanocomposite with SiO_2 has a greatly increased surface area, exchange capacity is rather small (0.12 mmol/g). The disadvantages of both types of resins greatly limit their applications.

Recently, Zhao *et al.*[9] have synthesized a new perfluorodiacyl peroxide **2** bearing a further convertible ω-fluorosulfonyl group. By using the peroxides, a wide variety of materials with the ω-sulfonic-perfluoroalkyl group, functionally similar to Nafion, have been synthesized.[10,11] In this communication, we wish to report the preparation of macroreticular *p*-(ω-sulfonic-perfluoroalkylated) polystyrene (FPS) resin **3** (Scheme 1) and its application as a solid acid catalyst in the cyclization of pseudoionone.

Macroreticular FPS resin **3** was prepared by the following procedure: 5 g PS beads **1** (PS26) were swelled in methylene dichloride (20 ml) overnight in a glass reactor fitted with a magnetic stirrer. At 0 °C, 120 ml F113 solution of **2** (0.5 M) were added to the beads suspension under stirring. After 40 h, the beads were filtered and washed in turn with 5% aq. $NaHCO_3$, water and ethanol. Then the beads were hydrolyzed in an excess of 30% aq. NaOH at 80 °C for 4 h. After washing with water to neutral, the beads were acidified with an excess of 3 M aq. HCl at room temperature for 24 h, then washed with water to neutral and dried at 50 °C under vacuum to constant weight.



Scheme 1

Using as our starting materials two PS resins with different degrees of crosslinking (PS26, 26%; PS40, 40%), we have synthesized two macroreticular FPS resins (FPS26 and FPS40). Their porosity was analyzed by a nitrogen sorption technique (ASAP Micromeritics 2000). The exchange capacities of FPS26 and FPS40 were determined by acidimetry. As shown in Table 1, the perfluoroalkylation brought about in the resins significant changes in specific surface area, pore volume and pore diameter distribution. The BJH pore diameter data clearly show that the fluorinated resins are mesoporous in nature. The exchange capacity of FPS26 is higher than that of FPS40. The high degree of crosslinking in FPS40 resulted in poor accessibility of **2** to the benzene ring of polymer substrate **1**.

The TGA (Perkin Elmer TGA 7) of porous PS beads shows a less than 5% weight loss below 400 °C. This low weight loss was due to residual moisture. At higher temperature, the polymer chain began to collapse. In sharp contrast, the macroreticular FPS resin showed a significant weight loss at 190 °C, mainly due to desulfonation.

The FTIR spectrum (930-Perkin Elmer Spectrometer) of the FPS resin (Fig. 1) shows strong bands characteristic of the

Table 1 Porosity characteristics of PS beads (PS26 and PS40) and FPS resins (FPS26 and FPS40)

Resin	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Pore size (Å)	Exchange capacity (mmol/g)
PS26	128	0.64	187	10–300	—
FPS26	59	0.31	188	10–220	1.5
PS40	361	0.83	151	10–400	—
FPS40	107	0.44	146	10–300	1.3

Department of Chemistry, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai, 200240, China.
E-mail: cxzhao@sjtu.edu.cn; Fax: 86-21-54741297; Tel: 86-21-54742824
*cxzhao@sjtu.edu.cn

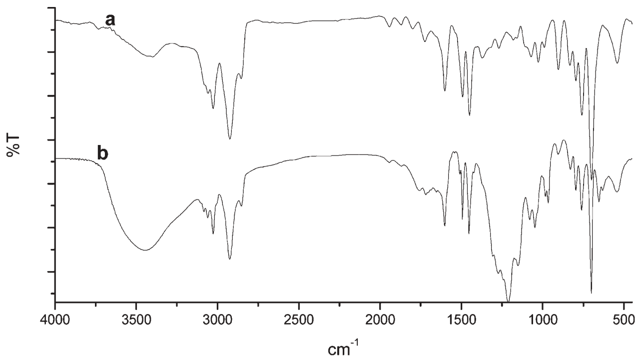


Fig. 1 FTIR spectra of macroreticular PS bead (a) and FPS resin (b).

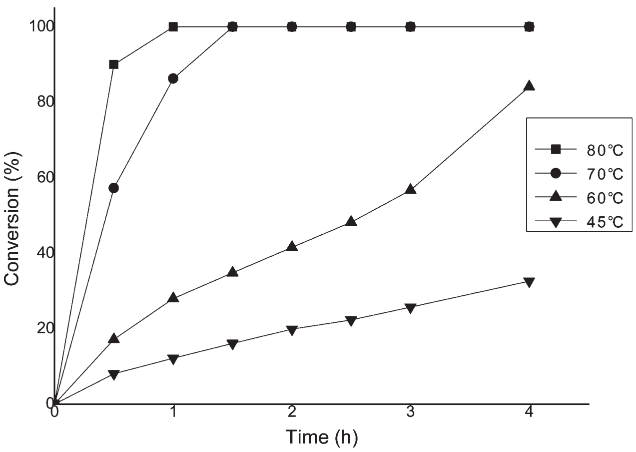
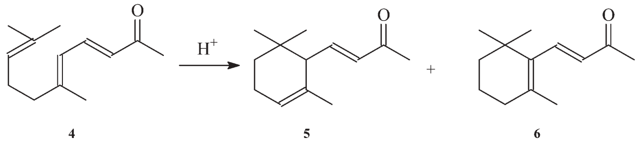


Fig. 2 The conversion of pseudoionone under catalysis of FPS40 at different temperatures.



Scheme 2

fluorinated groups: $\nu(CF_3)$ at 1312 cm^{-1}, $\nu(CF_2)$ at 1271 cm^{-1} and 1213 cm^{-1}. The peak at 820 cm^{-1}, characteristic of a *para*-disubstituted phenyl ring, provides strong evidence for *para*-ω-fluorosulfonylperfluoroalkylation. The lack of carbonyl absorption discloses the absence of ring-ω-fluorosulfonylperfluoroacyloxylation.

The novel fluorinated resin **3** was applied to the cyclization of pseudoionone **4** (Scheme 2) to produce ionone.† Ionone is one of the most important perfumes. Ionone has two familiar isomers (**5** and **6**). The isomer α-ionone **5** has an odor of violets and is widely applied in the synthesis of perfumes and cosmetics; β-ionone **6** is the main precursor of vitamin A and β-carotene.

The conversion of pseudoionone and yield of ionone under the catalysis of FPS26 and FPS40 are given in Table 2 with a comparison with the results obtained by using Amberlyst 36 and Nafion NR50 (Aldrich). The yield of ionone obtained by using Amberlyst 36 (49.17%, 3 hours) was higher than for other catalysts, because there are more acid sites on its surface. The FPS resins showed the best activity among those catalysts, a quantitative conversion being reached in only 1 hour. Moreover, the selectivity of α-ionone **5** was obviously higher than in the case of Amberlyst 36 (about 75%). The reason for such high efficiency is under investigation. Nafion NR50 was found to be no good in the reaction because of its low surface area.

In addition, we have tested the activity of FPS40 resin at different temperatures and its reusability. As shown in Fig. 2, the conversion of pseudoionone **4** is 84.16% at 60 °C. So FPS resin showed some reactive activity at low temperature. In the repeated experiment the used FPS40 resin, after being 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 **5** were 10.12% and 100% respectively. Obviously, there was slight deactivation in the catalytic reaction.

In summary, we have developed a novel method of preparing ω-sulfonic-perfluoroalkylated cation-exchange resin with a terminal perfluorosulfonic acid group similar to that of Nafion. Due to the perfluoroalkyl environment and especially high electron-withdrawing character of the α-CF_2 group, we expect the macroreticular *p*-(ω-sulfonic-perfluoroalkylated) polystyrene (FPS) resin to be a type of superacid like Nafion, however this needs to be proved by solid state NMR[12] or other methods. FPS resins showed high activity and good selectivity in favour of α-ionone in the cyclization of pseudoionone. It is expected that other catalytic reactions with high selectivity could be carried out by employing our new cation-exchange resins, and further studies are underway.

Table 2 The yield of ionone (**5** and **6**) and conversion of pseudoionone (**4**) catalyzed by cationic ion-exchange resins

					Yield of ionone (%)	
Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion of **4** (%)	α-ionone **5**	β-ionone **6**
FPS26	cyclohexane	80	0.5	75.51	5.53	0
			1	100	21.84	0
FPS40	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

Notes and references

† 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 capillary GC.

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