Macroreticular Polystyrene Hybridized Resins with Both Perfluoroalkanesulfonic and Carboxylic Functional Groups

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ABSTRACT: Macroreticular polystyrene hybridized resins (FPSA) with both perfluoroalkanesulfonic and carboxylic functional groups have been synthesized at mild conditions by following suspension polymerization, perfluoroalkylation by \( \omega \)-fluorosulfonylperfluorodiacyl peroxides (SFAP), alkali hydrolysis and acidification. The hybridized resins were characterized by FTIR, TGA, acidimetry and nitrogen sorption technique. The influences of the crosslink degree, the chain length and amount of SFAP on the resin’s properties were also investigated. FPSA exhibited higher exchange capacity and surface area than Nafion NR 50 and better thermostability than Amberlyst 15.

1 INTRODUCTION

Cation-exchange resins are employed in organic synthesis as a kind of solid acid catalysts which exhibit obvious superiority on liquid acids in catalytic process with environmental and economic benefits for corrosiveness, safety, less waste, and ease of separation and recovery\(^{[1-9]}\). There are mainly two types of cation-exchange resins for a range of industrially important transformations: nonfluorinated sulfonic resins represented as Amberlyst-15 and perfluorosulfonic resins represented as Nafion NR 50\(^{[4]}\). The former resins are macroporous, low cost and of high exchange capacity up to 4.8 mmol/g, but low acidity and not tolerant of reactions above 120 °C. In contrast, the latter are non-porous, expensive, inaccessible for the active sites with low surface area down to 0.02 m\(^2\)/g, however, their extremely high thermal stability and chemical resistance with super acidity (\(H_0\) = ~ -12) enable them to be used in catalytic process of high temperature or low activity. The drawbacks of both the types of resins have limited their further applications in organic synthesis.

Recently, our group has synthesized a new type fluorinated cation-exchange resin, mactoreticular \(p-(\omega\)-sulfonic-perfluoroalkylated)polystyrene resins (FPS)\(^{[10-12]}\) comprised of porous polystyrene backbone and terminal perfluorosulfonic acid group similar to that of Nafion. For the dis-
Distinctive structure, FPS exhibited some of advantages of both nonfluorinated and perfluorinated resins with high exchange capacity of 2.0 mmol/g, surface area of 107 m²/g and thermostability (stable up to 190 °C). To further improve the exchange capacity of FPS, sulfonic acid was introduced into FPS through chlorosulfonation to obtain a type of hybridized macroreticular resin FPSS (Figure 1) bearing both perfluoroalkanesulfonic and sulfonic functional groups with 3.3 mmol/g exchange capacity [13]. Both FPS and FPSS showed higher activity and better selectivity and reusability than other commercial solid acids in synthesis of α-ionone and diindolylmethanes.

![Figure 1. Structure of various resins.](image)

Compared with Nafion resin, another important advantage of the fluorinated cation-exchange resins is that the backbone of FPS can be changed with the different composing of monomer in polymerization, which makes it possible that FPS is further functionalized to meet different application. In this work, we have synthesized a kind of backbone of macroreticular poly(styrene-acrylonitrile) (PSA) through free radical suspension polymerization. Following by perfluoroalkylation, hydrolysis and acidification of PSA, Macroreticular polystyrene hybridized resins (FPSA) with both perfluoroalkanesulfonic and carboxylic functional groups were obtained. The structure and properties of FPSA were characterized by FTIR, TGA and nitrogen sorption technique. The effect of reaction conditions on the properties of FPSA was also studied.

2 Experimental

2.1 The synthesis of PSA

The stabilizer PVA (1 g) was dissolved in water (200 ml) in a 500 ml flask immersed in a water bath maintained at 80 °C. After cooled to room temperature, the organic phase composed by monomers mixture (n_{styrene} : n_{acrylonitrile}=2:1), porogen and BPO was then added rapidly to the
aqueous solution at stirring speed of 400 rpm. The temperature was then raised at 80 ºC. 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 ºC under vacuum and sieved.

2.2 The synthesis of FPSA

PSA beads (5 g) were swelled in methylene dichloride (20 ml) overnight in a glass reactor fitted with a magnetic stirrer. At 0 ºC, 0.4 M F113 solution of SFAP was added to the beads suspension under stirring. After 40 h, the beads were filtered and washed three times with NaHCO₃, water and ethanol. Then beads were hydrolyzed in excess 30% aq. NaOH at 80 ºC 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 ºC under vacuum to obtained the resulted FPSA resins.

3 RESULTS AND DISCUSSION

Through free radical suspension copolymerization, a series of macroreticular poly(styrene-acrylonitrile) resins PSA with different crosslink degree were synthesized. Via single electron-transfer (SET) induced perfluoroalkylation of macroreticular PSA with SFAP, followed by hydrolysis and acidification, the target resins FPSA were synthesized (Scheme 1). The SET reaction mechanism was proposed by Zhao et al.

![Scheme 1. Synthesis route of FPSA resins.](image)

The FTIR spectra of FPSA resin shows strong characteristic bands of the fluorinated groups in the range from 1000 cm⁻¹ to 1350 cm⁻¹: ν(CF₃) at 1317 cm⁻¹, ν(C-O-C) at 1042 cm⁻¹, ν(CF₂) at 1249 and 1212 cm⁻¹ with ν(OH) at 3455 cm⁻¹. In addition, the peak at 820 cm⁻¹, characteristic of a para-disubstituted phenyl ring, provides strong evidence for para-ω-fluorosulfonylperfluoroalkylation. The TGA of macroreticular PSA 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 FPSA resin appeared a significant weight loss at 197 °C, mainly due to desulfonation (Figure 2 left).

Figure 2. (left) TGA of resin PSA and FPSA; (right) the adsorption and desorption isotherm of FPSA.

The porosity of macroreticular PSA and the fluorinated resins (FPSA-0, FPSA-1) 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 data clearly show that the fluorinated resins are mesoporous in nature. The adsorption and desorption isotherm of FPSA-0 is shown in Figure 2 (right). From the plot, it is clear that there are very little micropores in the interior of FPSA resin.

<table>
<thead>
<tr>
<th>Resins</th>
<th>Crosslink degree (wt %)</th>
<th>BET surface area (m²/g)</th>
<th>BJH pore volume (cm³/g)</th>
<th>BJH pore diameter (nm)</th>
<th>Exchange capacity (mmol/g)</th>
<th>T_d(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA</td>
<td>27.00</td>
<td>105.00</td>
<td>0.55</td>
<td>19.30</td>
<td>/</td>
<td>&gt; 400.00</td>
</tr>
<tr>
<td>FPSA-0</td>
<td>27.00</td>
<td>66.00</td>
<td>0.42</td>
<td>24.60</td>
<td>1.45</td>
<td>197.00</td>
</tr>
<tr>
<td>FPSA-1</td>
<td>27.00</td>
<td>81.00</td>
<td>0.43</td>
<td>21.30</td>
<td>1.07</td>
<td>185.00</td>
</tr>
</tbody>
</table>

The porous structure and the properties of FPSA can be varied by changing synthetic conditions mainly including the crosslink degree, the chain length and amount of the perfluoroalkylating agent. By changing these factors, a series of FPSA resins were prepared. As shown in Figure 3 (left), proton exchange capacity and fluoroalkylation ratio of the FPSA resins decrease with the increase in crosslink degree. This is because that the bigger crosslink degree results in PSA
beads' smaller pore diameter, greater steric hindrance or less accessibility of SFAP to the benzene rings. However, if crosslink degree is too low, the rigidity of the PSA beads is poor. Irregularly shaped and weak beads are vulnerable to mechanical attrition and easy to collapse. Therefore, crosslink degree should be moderate in order to balance the mechanical strength and exchange capacity.

Figure 3 (left) also shows the effect of the chain length of perfluoroalkylating agent on the property of macroreticular FPSA resins. The exchange capacity and fluoroalkylation ratio of FPSA-1 using peroxide SFAP-1 (n =1) as fluoroalkylated reagent is significantly lower than that of FPSA-0 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.

As shown in Figure 3 (right), to add more SFAP-0 certainly increased the exchange capacity and fluoroalkylation ratio of the resulted resins. At lower molar ratio between SFAP-0 and PSA, the addition of exchange capacity and fluoroalkylation 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 FPSA was not high.

**Figure 3.** Exchange capacity (EC) and perfluoroalkylation ratio of FPSA at different crosslink degree (left) and amount of SFAP (right).

## 4 SUMMARY

Via suspension copolymerization, perfluoroalkylation, hydrolysis and acidification, we have developed a novel method of preparing macroreticular hybridized cation-exchange resin FPSA bearing two different acid functional groups: carboxylic and perfluoroalkanesulfonic groups. With moderate exchange capacity (1.8 mmol/g), surface area (81 m$^2$/g) and thermostability (stable up to 197 ºC), the fluorinated resin FPSA exhibits some of the advantages of both nonfluorinated resin and perfluorinated resin. FPSA resin is promising in organic catalysis as hybridized solid acid, and further studies are underway.
REFERENCES


