

Synthesis and characterisation of *p*-perfluoro{-1-[2-(2-fluorosulfonylethoxy)propoxy]}ethylated polystyrene

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A new kind of fluorinated polystyrene bearing a *p*-perfluoro{-1-[2-(2-fluorosulfonyl)propoxy]}ethyl group has been synthesised by one-electron oxidation of polystyrene by perfluoro{2-[2-(2-fluorosulfonyl)propoxy]}propionyl peroxide at different peroxide to polystyrene molar ratios. The yield of ω -fluorosulfonyl perfluoroalkylation decreases with increase in the reactant molar ratio. The modified polymer was characterised by various techniques: the ring perfluoro{-1-[2-(2-fluorosulfonyl)propoxy]}ethylation was proved by FT-IR, ¹⁹F NMR and DSC; desulfonylation of the fluorinated polystyrene appearing at 126° has been found by thermogravimetric analysis (TGA). The contact angles of water on the surface of ω -fluorosulfonyl perfluoroalkylated polystyrene were determined.

Keywords: polystyrene, perfluoro{2-[2-(2-fluorosulfonyl)propoxy]} propionyl peroxide, *p*-perfluoro{-1-[2-(2-fluorosulfonyl)propoxy]}ethylated polystyrene

Fluoropolymers have been widely used because of their unique excellent chemical resistance, low surface energy, low dielectric constant and low coefficient of friction, *etc.* However, perfluoropolymers (*e.g.* polytetrafluoroethylene, PTFE) are often intractable and their modification is crucial for practical applications. The modification by partial fluorination of commodity polymers has attracted considerable interest: fluorofunctionalisation by plasma¹ and glow discharge² has been employed to modify some vinyl polymers. Generally, these reactions are carried out under severe conditions and are not economically favourable. In 1983, Zhao and Walling established aromatic per(poly)fluoroalkylation by using per(poly)fluorodiacyl peroxides (R₂COO)₂ (FAP)³ and succeeded in the synthesis of per(poly)-fluoroalkylated polymers.⁴⁻⁵ FAPs are versatile per(poly)fluoroalkylating agents for arenes,⁶⁻⁸ aromatic heterocycles,⁹⁻¹⁰ olefins¹¹ and fullerenes.¹²⁻¹⁴ The modification of polymers reported previously is essentially an introduction of chemically “dead” per(poly)fluoroalkyl groups such as C₃F₇, *n*-C₆F₁₃, *n*-C₇F₁₅, ClCF₂CF₂, Cl(CF₂CF₂)₂, *etc.* onto aromatic nuclei. In this article, we report that the modification of polystyrene with a *p*-substituted perfluoroalkyl group which has a chemically convertible fluorosulfonyl end that can be changed to a sulfonic acid and can be widely used, for example in proton exchange membrane fuel cells (PEMFC) and catalysis.

Experimental

Materials

Perfluoro{2-[2-(2-fluorosulfonyl)propoxy]}propionyl fluoride FO₂SCF₂CF₂OCF(CF₃)CF₂O CF(CF₃)COF used for the preparation of perfluoro{2-[2-(2-fluorosulfonyl)propoxy]}propionyl peroxide (PPP) was purchased from 3F Co.Ltd, Shanghai, China.

Polystyrene (143E) was a product of BASF, Germany.

Instruments

FT-IR spectra were taken on a 983-Perkin Elmer spectrometer. ¹⁹F NMR spectra were recorded on a Varian Mercury plus-400 spectrometer. TGA analysis was carried out by using a Perkin Elmer TGA 7 Thermogravimetric Analyzer and its temperature was calibrated by courier point. Glass transition temperatures were determined on a Perkin Elmer PYRIS Differential Scanning Calorimeter. Molecular weights were measured by using a Wyatt Down EOS Instrument (Waters Styragel Column, DMF as eluent, at 70°C). Contact angle (θ_{H₂O}) measurement was conducted on a JC2000A Contact Angle Instrument (Shanghai Zhongcheng Numeric Technology & Equipment Co. Ltd) by depositing the polymer sample on a glass slide to form a thick film and deriving the contact angle from the maximum height of the water drop.

Preparation of perfluoro{2-[2-(2-fluorosulfonyl)propoxy]}propionyl peroxide (PPP)

The F113 (CCl₂FCClF₂) solution of the peroxide (PPP) was prepared from the corresponding acid fluoride according to the reported procedure,¹⁵ and kept at -50 – 70°C to avoid noticeable decomposition. Though PPP decomposes much faster at room temperature, the main decomposition products — the radical coupling product and CO₂, are fire extinguishers. And the solvent (CCl₂FCClF₂) is non-flammable. So, to handle PPP at room temperature and under freezing conditions is relatively safe. The concentration was determined by standard iodimetry.

Reaction of polystyrene with perfluoro{2-[2-(2-fluorosulfonylethoxy)}propionyl peroxide (PPP)

Polystyrene 4.16 g (40 mmol) was dissolved in dichloromethane (75 ml) in a three-neck flask with magnetic stirring. After flushing with nitrogen, peroxide (2.0 mmol, the molar ratio of PPP: PS = 1:20) in F113 was dropped slowly (within 2 h) into the solution maintained at 0°C. The reaction mixture was stirred for an additional 24 h. The polymeric product was precipitated by dropping methanol into the reaction mixture. The polymer was collected and reprecipitated from a dichloromethane / methanol binary solvent. After filtration, the product was dried for 24 h under vacuum at 60°C.

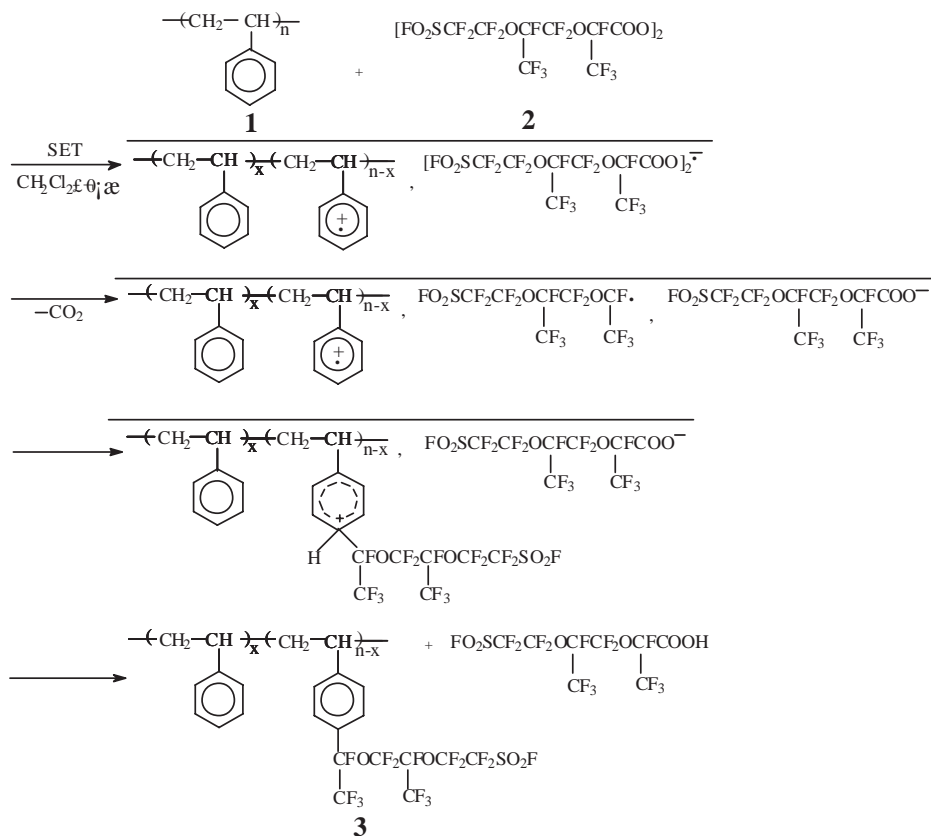
The reaction at different molar ratios (PPP:PS) of 1:10, 1:5, 1:4, 1:3, 1:2 and 1:1 as conducted in the same way.

Table 1 Fluorine content, *n_r/n_p* ratio and yield of the perfluoroalkylated polystyrene at different reactant ratios

Reactant molar ratio (PPP : PS)	Fluorine content/%	<i>n_r/n_p</i> ^a	Yield/%
1:20	10.57	1:21.4	93.3
1:10	16.07	1:12.6	79.5
1:5	23.36	1:7.3	68.4
1:4	25.17	1:6.4	62.3
1:3	26.42	1:5.9	50.8
1:2	30.94	1:4.4	45.6
1:1	40.85	1:2.2	44.6

^aThe ratio *n_r/n_p* stands for the number of perfluoroalkylated phenyl ring to the number of all participated phenyl ring in the reaction.

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Scheme 1 Mechanism of the reaction of PPP with PS.

Results and discussion

The *p*-perfluoro{1-[2-(2-fluorosulfonyl)propoxy]}ethylated polystyrene **3** was synthesised via ET-reaction³ between polystyrene (ps) **1** and perfluoro{2-[2-(2-fluorosulfonyl)propoxy]}propionyl peroxide **2** at 0°C in F113 solution (Scheme 1).

The reaction was carried at various molar ratios of the reactants (2:1 = 1:20, 1:10, 1:5, 1:4, 1:3, 1:2 and 1:1).

With increasing in reactant molar ratio (2:1), the fluorine content and the n_r/n_p value (the proportion of reacted phenyl ring) of the perfluoroalkylated polystyrene increases, while the yield of perfluoroalkylation decreases (shown in Table 1). A reasonable explanation is: at the reactant ratio of 1:20, the PS was in large excess over PPP, the peroxide almost completely reacted with polystyrene via single electron transfer so that the n_r/n_p value (1:21.4) nearly reached the reactant molar ratio; at higher PPP concentrations, PPP was increasingly consumed by radical coupling $[\text{FO}_2\text{SCF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)]_2$ due to the accelerated bimolecular electron transfer, unimolecular thermal decomposition and radical-induced decomposition of PPP.

The *p*-substituted perfluoro{1-[2-(2-fluorosulfonyl)propoxy]} ethylation of the phenyl ring of PS can be proved by the characteristic FT-IR (Fig. 1) and ¹⁹F NMR spectra of the product **3**.

The FT-IR spectra show strong absorption bands between 1100 and 1350 cm^{-1} which are characteristic for the fluorinated groups:⁴⁻⁵ $\nu(\text{CF}_3)$ at 1312 cm^{-1} , $\nu(\text{CF}_2)$ at 1242 cm^{-1} and 1218 cm^{-1} , $\nu(\text{SO}_2\text{F})$ at 1492 cm^{-1} overlapped with $\nu(\text{C}-\text{C})$ of phenyl ring. The peak at 820 cm^{-1} is characteristic of a *para*-disubstituted phenyl ring (860–800 cm^{-1}). There is no appearance of characteristic peaks for a *meta*-disubstituted phenyl ring (810–750 cm^{-1}) or an *ortho*-disubstituted phenyl ring (770–735 cm^{-1}). The lack of carbonyl absorption indicates the absence of ring ω -fluorosulfonyl perfluoroacyloxylation.

The ¹⁹F NMR spectra (in CDCl_3 , trifluoroacetic acid in a capillary tube as the standard) shows that the 1-[2-(2-fluorosulfonyl)propoxy] ethyl group $-\text{CF}^{\text{a}}(\text{CF}_3)^{\text{b}}\text{OCF}_2^{\text{c}}\text{CF}^{\text{d}}(\text{CF}_3)^{\text{e}}\text{OCF}_2^{\text{f}}\text{CF}_2^{\text{g}}\text{SO}_2\text{F}^{\text{h}}$ polymer **3** (at the ratio 2:1=1:2) appearing at δ -67.0 (a, 1F), δ -52.3 (d, 1F), δ -34.2 (g, 2F), δ -6.8-0.03 (b, c, e, f, 7F) and δ 123.4 (h, 1F).

As shown in Table 2, the molecular weight of the perfluoroalkylated polystyrene increases with the reactant molar ratio. The narrower polydispersity (M_n/M_w) of the perfluoroalkylated polystyrene than that of polystyrene indicates that the degradation of the polymer

chains did not occur under the reaction condition. A similar result has been reported previously by Sawada.¹⁰

The TGA curve **a** (Fig. 2) indicates that the degradation of PS into its monomer started at 368°C. The modified PS (at the ratio 2:1=1:5) shows similar degradation starting at 315°C (curve b). An important feature of curve b is that a small loss of weight

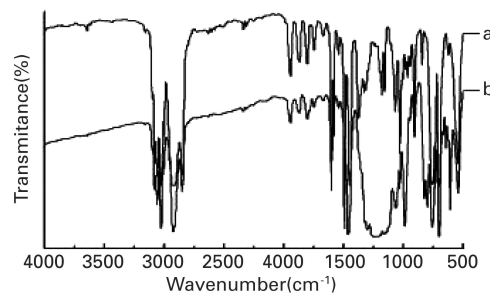


Fig. 1 FT-IR spectra of PS (a) and the perfluoroalkylated polystyrene **3** (at 2:1=1:5).

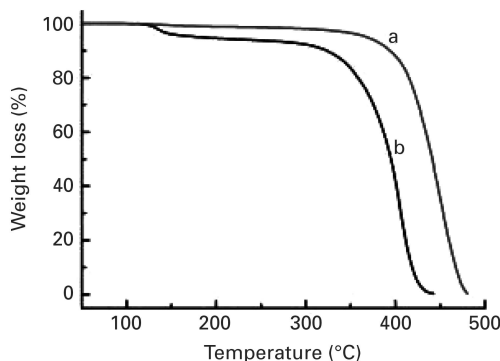
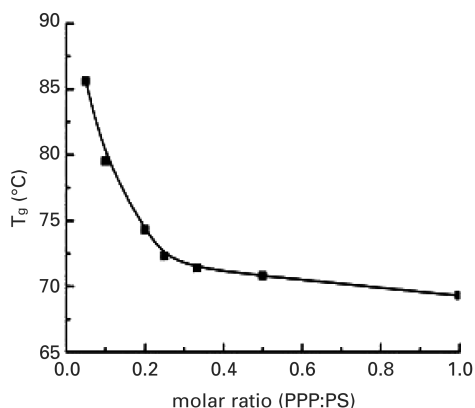


Fig. 2 TGA curve of polystyrene (a) and ω -fluorosulfonyl-perfluoroalkylated polystyrene **3** (at 2:1=1:5).

Table 2 The molecular weights and polydispersities of perfluoroalkylated polystyrene **3** obtained at different reactant ratios

Reactant molar ratio	1:20	1:10	1:5	1:4	1:3	1:2	1:1	PS
Mn($\times 10^5$)	1.18	1.30	1.45	1.59	1.65	1.84	2.62	0.9409
Mw /Mn	1.99	1.80	2.01	2.29	2.10	1.67	1.73	2.3482

**Fig. 3** Glass transition temperature of ω -fluorosulfonylperfluoroalkylated PS **3**.

occurred at 126°C. Apparently, the weight loss was not caused by the main-chain degradation, but the desulfonylation characteristic of all sulfonylated organic molecules and polymers. Notably, the desulfonylation of modified PS starts at lower temperature (126°C) than that for most aromatic sulfonic acids (180°C)¹⁶ and even for perfluorinated polymeric sulfonic acid Nafion (long term use at $\leq 170^\circ\text{C}$).¹⁷

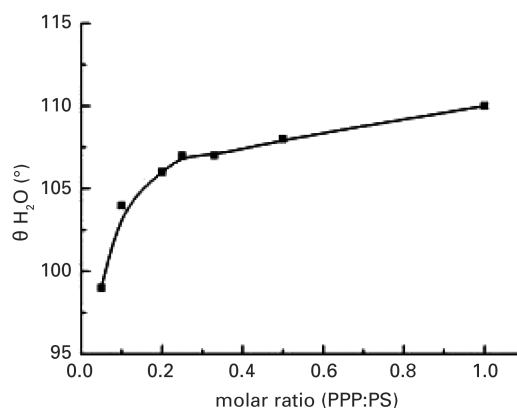
The DSC determinations disclosed that the glass transition temperatures T_g of the fluorinated polystyrene **3** obtained at different reactant ratios are all lower than that of the parent polymer PS (103°C). As shown in Fig. 3, with the increase of the molar ratio, the T_g decreases further to about 70°C. This is owing to a possible incompatibility of the perfluoro{1-[2-(2-fluorosulfonyl) propoxy]} ethyl groups with the main chains and a disordering of the molecular arrangement caused by the phenyl ring-substitution.

The fluorinated polystyrene **3** possesses much lower surface energy than PS as proved by the contact angle determination. The contact angles ($\theta_{\text{H}_2\text{O}}$) of the samples of **3** are larger than those of PS (95°), and get bigger with the increasing reactant ratio.

Conclusion

The perfluoro{1-[2-(2-fluorosulfonyl)propoxy]} ethylated polystyrene **3** was synthesised by aromatic perfluoro{1-[2-(2-fluorosulfonyl)propoxy]} ethylation of polystyrene **1** using perfluoro {2-[2-(2-fluorosulfonyl)propoxy]} propionyl peroxide (PPP) **2** and was characterised by FT-IR, TGA, ¹⁹F NMR, and DSC. The yield of perfluoroalkylation decreases with the increase of the reactant molar ratio (PPP:PS). The polydispersity values indicate that the degradation of the polymer chains did not occur in the reaction.

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**Fig. 4** Contact angle of ω -fluorosulfonylperfluoroalkylated PS **3**.

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