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# Synthesis and Characterization of *p*-[ Perfluoro-1-(2-fluorosulfonylethoxy) ] ethylated Polystyrene

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A new fluorinated polystyrene bearing a *p*-substituted perfluoro[1-(2-fluorosulfonylethoxy)] ethyl group was synthesized via one-electron oxidation of polystyrene by perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide at different peroxide to polystyrene molar ratios. The yield of perfluoroalkylation decreases with the increase of the reactant molar ratio. The modified polymer has been characterized by various techniques: the ring perfluoro[1-(2-fluorosulfonylethoxy)] ethylation has been proved by FT-IR and  $^{19}\text{F}$  NMR; the X-ray photoelectron spectra (XPS) show the maximum binding energy of  $\text{F}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{C}_{1s}$  (two kinds of carbon atoms, namely C-H and C-F) and  $\text{S}_{2p}$ , respectively; desulfonation of the fluorinated polystyrene appearing at 217 °C has been found by its thermogravimetric analysis (TGA). The determinations of contact angle, refractive index and glass transition temperature of the modified polymer have disclosed that when the contact angle increases with the increase of the molar ratio, the refractive index and glass transition temperature decrease. The polydispersity values indicate that the degradation of the polymer chains did not occur during the reaction.

**Keywords** polystyrene, perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide, *p*-[perfluoro-1-(2-fluorosulfonylethoxy)]ethylated polystyrene

## Introduction

Fluoropolymers are a class of important polymers, which have been widely used owing to their unique properties such as 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 thus modifications are crucial to practical application. The modification via partial fluorination of commodity polymers has attracted considerable interest: fluorofunctionalizations by plasma<sup>1</sup> and glow discharge<sup>2</sup> have been employed to modify some vinyl polymers. Generally, these reactions are hard to carry out under mild conditions and are not economically favorable. Zhao *et al.* have firstly established an effective aromatic per(poly)fluoroalkylation by using per(poly)fluorodiacyl peroxide [(R<sub>f</sub>COO)<sub>2</sub>, FAP]<sup>3</sup> and succeeded in the synthesis of per(poly)fluoroalkylated polymers.<sup>4,5</sup> FAPs are versatile per(poly)fluoroalkylating agents

for arenes,<sup>6</sup> aromatic heterocycles,<sup>7</sup> olefins<sup>8</sup> and fullerenes.<sup>9</sup> The modification of polymers reported previously is just by introducing chemically “dead” per(poly)fluoroalkyl groups such as  $\text{C}_3\text{F}_7$ , *n*- $\text{C}_6\text{F}_{13}$ , *n*- $\text{C}_7\text{F}_{15}$ ,  $\text{ClCF}_2\text{CF}_2$ ,  $\text{Cl}(\text{CF}_2\text{CF}_2)_2$ , *etc.* In this article, we report the modification of polystyrene with *p*-substituted perfluoroalkyl group bearing a chemically convertible fluorosulfonyl end by using a new perfluoroalkylated agent perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide under very mild condition.

## Experimental

### Material

Perfluoro[2-(2-fluorosulfonylethoxy)]propionyl fluoride  $\text{FO}_2\text{SCF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$  used for the preparation of perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide (PPP) was received as a gift from 3M Co. Ltd, Shanghai, China.

### Instruments

FT-IR spectra were taken on a 930-Perkin Elmer spectrometer.  $^{19}\text{F}$  NMR spectrum was recorded on a Varian Mercury 400 spectrometer. Refractive indices were measured on a WVASE 32 ellipsometer (J. A. Woollam Company, Inc.) equipped with Xenon light ( $\lambda = 575 \text{ nm}$ ). TGA analysis was carried out by using a Perkin Elmer TGA 7 Thermogravimetric Analyzer. Glass transition temperatures were determined on a Perkin Elmer PYRIS 1 Differential Scanning Calorimeter. Molecular weights were measured on a Wyatt DOWN EOS by using THF as the eluent.

Contact angles ( $\theta_{\text{H}_2\text{O}}$ ) were tested on a JC 2000A Contact Angle Instrument (Shanghai Zhongcheng Numeric Technology & Equipment Co., Ltd) by depositing polymer sample on glass slide to give thick film and measuring the maximum height of a water drop and deriving the contact angle by simple calculation.

XPS analysis was performed on a Shenyang Scientific Instruments Works NP-1 X-ray Photoelectron Spectrometer, with a base pressure of  $1.3 \times 10^{-9} \text{ Pa}$ , using Mg K $\alpha$  anode at

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30 W. Sample was prepared by depositing sample polymer on aluminum slide. The binding energy of  $C_{1s}$  (combined with hydrogen, 284.6 eV) was taken as a reference for other peaks.

*Preparation of perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide (PPP)*

The F113 solution of the peroxide was prepared from the corresponding acid fluorine according to the reported procedure<sup>10</sup> and kept under freezing condition before use. The concentration was determined by standard iodimetry.

*Reaction of polystyrene with perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide*

4.16 g (40 mmol) of polystyrene was dissolved in 75 mL of dichloromethane in a three-neck flask with magnetic stirring. After flushing with nitrogen, 2.0 mmol of the peroxide (the molar ratio of PPP:PS = 1:20) in F113 was dropped slowly (within 2 h) into the polystyrene solution at room temperature, and then the reaction mixture was stirred for additional 7–8 h. The polymeric product was precipitated by methanol, collected and purified by reprecipitation from dichloromethane/methanol binary solvent. After filtration, the product was dried under vacuum at 65 °C overnight.

The reactions at different molar ratios of 1:10, 1:5 and 1:2 were conducted by the same procedure.

## Results and discussion

The *p*-substituted perfluoro[1-(2-fluorosulfonylethoxy)]ethyl polystyrene (**3**) was synthesized via ET-reaction<sup>3</sup> between polystyrene **1** and perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide (**2**) at room temperature in Freon 113 ( $CCl_2FCClF_2$ ) solution (Scheme 1).

The reaction was carried at various molar ratios of the

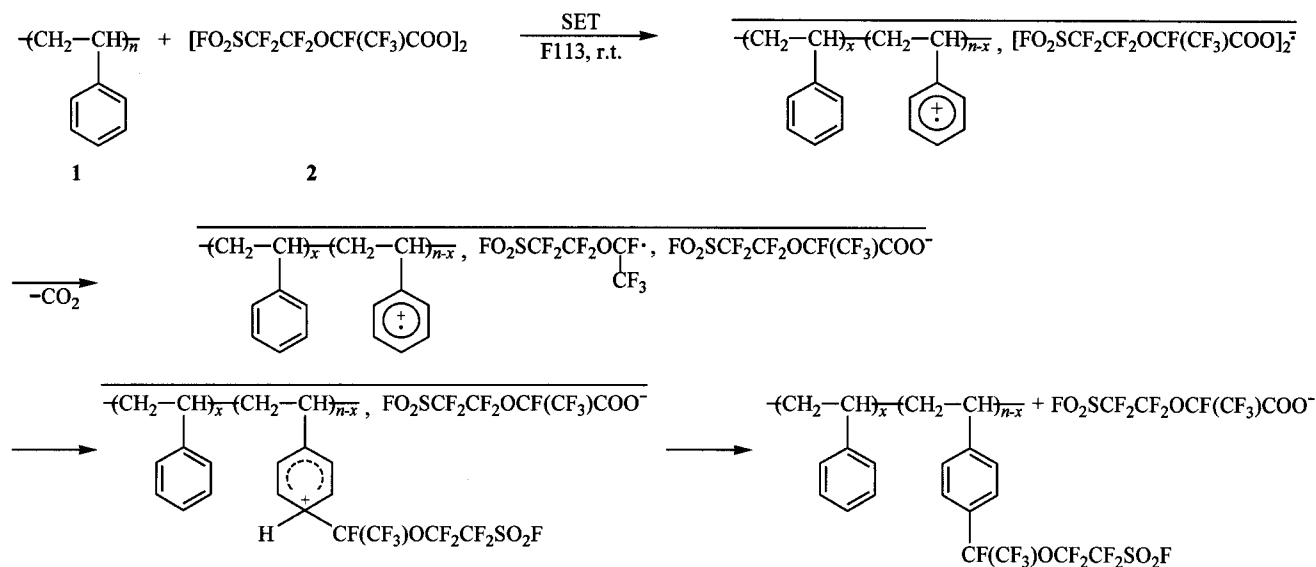
reactants (**2:1** = 1:20, 1:10, 1:5 and 1:2).

The *p*-substituted perfluoro[1-(2-fluorosulfonylethoxy)]-ethylation of the phenyl ring of polystyrene can be proved by the characteristic FT-IR (Fig. 1) and <sup>19</sup>F NMR spectra.

The FT-IR spectra show strong absorption bands between 1100 and 1350  $cm^{-1}$  which are characteristic for the fluorinated groups<sup>4,5</sup>:  $\nu_{(CF_3)}$  at 1312  $cm^{-1}$ ,  $\nu_{(CF_2)}$  at 1242  $cm^{-1}$  and 1218  $cm^{-1}$ ,  $\nu_{(SO_2F)}$  at 1492  $cm^{-1}$  overlapped with  $\nu_{C-C}$  of phenyl ring. The peak at 820  $cm^{-1}$ , which is characteristic of a para-disubstituted phenyl ring (860–800  $cm^{-1}$ )<sup>11</sup>, provides a strong evidence for para-substitution. There is no appearance of characteristic peaks for meta-disubstituted phenyl ring (810–750  $cm^{-1}$ )<sup>11</sup> and ortho-disubstituted phenyl ring (770–735  $cm^{-1}$ )<sup>11</sup>. The lack of carbonyl absorption discloses the absence of ring- $\omega$ -fluorosulfonyl-perfluoroacyloxylation. The <sup>19</sup>F NMR spectrum ( $CDCl_3$ , using trifluoroacetic acid in a capillary as the internal standard) shows the [1-(2-fluorosulfonylethoxy)]ethyl group [ $-CF(CF_3)OCF_2CF_2SO_2F$ ] of the fluorinated polystyrene (at the ratio **2:1** = 1:5) appearing at  $\delta$  -50.9 (1F),  $\delta$  -33.0 (2F),  $\delta$  -5.3–0.5 (5F) and  $\delta$  124.2 (1F).

With the increase in reactant molar ratio, the fluorine content and the  $n_r/n_p$  value (the proportion of reacted phenyl ring) of the perfluoroalkylated polystyrene increase as usual, while the yield of perfluoroalkylation decreases (shown in Table 1). A reasonable explanation is: at the reactant ratio of 1:20, the polystyrene was in large excess over PPP, all the peroxide completely reacted with phenyl rings via single electron transfer and so that the  $n_r/n_p$  value (1:20) reached up to the reactant molar ratio; at higher reactant molar ratios (1:10, 1:5 and 1:2) or higher PPP concentrations, PPP was increasingly consumed by forming radical coupling product [ $FO_2SCF_2CF_2OCF(CF_3)$ ]<sub>2</sub> in its unimolecular thermal decomposition and radical-induced decomposition.

**Scheme 1** Synthesis of the *p*-substituted polystyrene **3** via SET reaction between PS **1** and the peroxide **2**



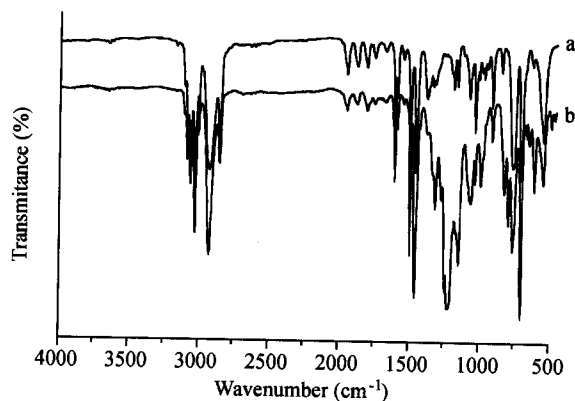


Fig. 1 FT-IR spectra of PS (a) and the modified polystyrene 3 (b) (at 2:1 = 1:5).

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

Reactant molar ratio	Fluorine content (%)	$n_r/n_p^a$	Yield (%)
1:20	7.2	1:20	100
1:10	11.5	1:11	91
1:5	15.4	1:8	62
1:2	24.2	1:4	50

<sup>a</sup> The ratio of the number of perfluoroalkylated phenyl ring to the number of all participated phenyl ring in the reaction.

As shown in Table 2, the molecular weight of the perfluoroalkylated polystyrene increases with the increase of the reactant molar ratio, and the molecular weights are higher than that of polystyrene. The narrower polydispersity ( $M_n/M_w$ ) of the perfluoroalkylated polystyrene than those of polystyrene indicates that the degradation of the polymer chains did not occur under the reaction condition. The similar result has been reported previously by Sawada.<sup>7d</sup>

Table 2 The molecular weights and polydispersities of the perfluoroalkylated polystyrene at different reactant ratios

Reactant molar ratio	1:20	1:10	1:5	1:2	PS
$M_n (\times 10^5)$	1.2	1.4	1.5	1.8	1.1
$M_n/M_w$	1.54	1.24	1.40	1.31	1.99

The phenyl ring-substitution of perfluoro[1-(2-fluorosulfonylethoxy)] ethyl group can be further proved by XPS (Fig. 2) and TGA (Fig. 3). There are four peaks corresponding to the maximum binding energy of the elements of the fluorine, oxygen, carbon and sulfur in the X-ray photoelectron spectrum of the modified polymer (at the ratio 2:1 = 1:2): the maximum binding energy of  $F_{1s}$  is at 688.4 eV (very strong), that of  $O_{1s}$  at 533.3 eV, two peaks of  $C_{1s}$  at 292.1 eV (peak A) and 284.6 eV (peak B) because there are two kinds of carbon atoms in the sample: fluorinated carbon atoms (peak A) corresponding to those of the perfluoro[1-(2-fluorosulfonylethoxy)] ethyl group and the hydrogenated carbon atoms (peak B), and that of  $S_{2p}$  at 170.6 eV, respectively.

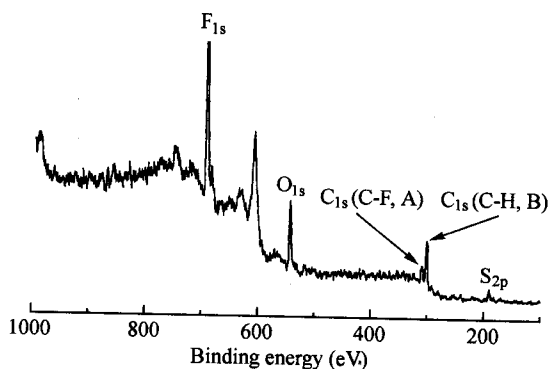


Fig. 2 X-Ray photoelectron spectroscopy of the modified polystyrene 3 (at 2:1 = 1:2).

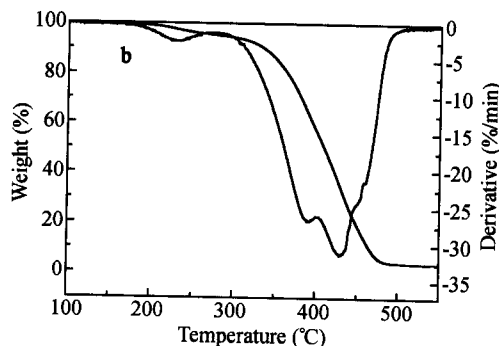
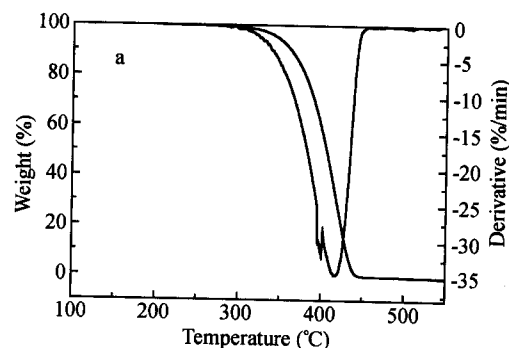


Fig. 3 TGA curves of polystyrene (a) and the modified polystyrene 3 (b) (at 2:1 = 1:2).

The TGA curve a (Fig. 3) indicates that the degradation of PS into its monomer started at 368 °C. The modified PS (at the ratio 2:1 = 1:2) shows the similar degradation starting at 359 °C (curve b), only 9 degrees lower than that of its parent polymer. An important feature of curve b is that the small loss of weight occurred at 217 °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 the modified PS starts at much higher temperature (217 °C) than that for most aromatic sulfonic acids (180 °C)<sup>12</sup> and even for perfluorinated polymeric sulfonic acid Nafion (long term use at  $\leq 170$  °C).<sup>13</sup>

The introduction of perfluoro[1-(2-fluorosulfonylethoxy)] ethyl groups into PS also causes significant changes in contact angle, refractive index and glass transition temperature. The results are shown in Table 3.

**Table 3** Contact angle, refractive index and glass transition temperature of polystyrene **1** and the fluorinated polystyrene **3**

	PS	Reactant ratio (2:1)			
		1:20	1:10	1:5	1:2
$\theta_{\text{H}_2\text{O}}$ (°)	95	100	104	107	109
$n_{\text{D}}$	1.5991	1.5861	1.5665	1.5470	—
$T_{\text{g}}$ (°C)	103	94	89	85	80

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, and get bigger with the increase of the reactant ratio. In contrast, the refractive indices of the samples of **3** obtained at larger molar ratios get smaller. It is believed that those changes are brought about by the segregation of the perfluoroalkyl groups on the polymer surface.<sup>14</sup>

Owing to possible incompatibility of the perfluoro[1-(2-fluorosulfonylethoxy)]ethyl groups with the main chains and a disordering of the molecular arrangement caused by the phenyl ring-substitution, the glass transition temperature of the fluorinated polystyrene **3** is much lowered than that of the parent polymer PS, and decreases with the increase of the molar ratio.

## Conclusion

The perfluoro[1-(2-fluorosulfonylethoxy)]ethylated polystyrene (**3**) was synthesized by aromatic perfluoro[1-(2-fluorosulfonylethoxy)]ethylation of polystyrene (**1**) using perfluoro[2-(2-fluorosulfonylethoxy)]propionyl peroxide (**2**) and characterized by FT-IR, <sup>19</sup>F NMR, XPS, TGA, DSC, contact angle and refractive index determinations. The yield of perfluoroalkylation decreases with the increase of the reactant molar ratio. The polydispersity values indicate that the degradation of the polymer chains did not occur in the reaction.

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