

Synthesis and Characterization of *p*-Perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylated poly(α -methyl styrene)

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Received 27 May 2005; accepted 1 September 2005

DOI 10.1002/app.23138

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *p*-Perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **3** was synthesized via electron transfer of perfluoro-di{2-[2-(2-fluorosulfonyl-ethoxy)propoxy]}propionyl peroxide **2** and poly(α -methyl styrene) **1** at different reactant molar ratios (2 : 1). The modified polymer **3** was characterized by various techniques. The ring *p*-substitution was proved by FTIR and ¹⁹FNMR. The desulfonation appeared at above 124°C was found by TGA. The molecular weight determined by GPC increased with the increase of reactant molar ratio, and the polydispersity val-

ues indicated there was no degradation of the parent polymer chain in the reaction. Followed by hydrolysis and acidification, the modified polymer **3** could be further quantitatively converted into its sulfonic form **4**. Ion exchange capacity of novel polyelectrolyte **4** can be controlled by changing reactant molar ratio (2 : 1). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3615–3618, 2006

Key words: poly(α -methyl styrene); modification; fluoropolymer; polyelectrolytes

INTRODUCTION

Owing to their unique properties, such as excellent chemical resistance, low surface energy, low dielectric constant, low coefficient of friction, etc., fluoropolymers are used widely. However, the perfluoropolymers are often intractable, and so the fluorofunctionalization of polymers is of great practical importance, such as elementary fluorination,¹ plasma fluorination,² and glow discharge.³ But none of them could be carried out under mild conditions and are not economically favorable.

In 1983, Zhao et al.⁴ discovered a new aromatic perfluoroalkylation reaction using perfluorodiacyl peroxides [(R_fCOO)₂]. Since then, this kind of reaction has been widely used in the synthesis of fluorinated materials, such as arenes,⁵ aromatic heterocycles,⁶ olefins,⁷ fullerenes,^{8–10} and per(poly)fluoroalkylated polymers, for various purposes.^{11,12}

However, the modification of polymers reported previously is only by introducing so-called dead per(poly)fluoroalkyl groups such as *n*-C₃F₇, *n*-C₆F₁₃, *n*-C₇F₁₅, ClCF₂CF₂, H(CF₂CF₂)_{1,2,3}, Cl(CF₂CF₂)_{1,2,3}, etc. In this article, we report that the modified poly(α -methyl styrene) **3** bearing fluorinated functional group similar to Nafion was synthesized via single electron transfer reaction of poly(α -methyl styrene) **1** and perfluoro-di{2-[2-

(2-fluorosulfonyl-ethoxy)propoxy]}propionyl peroxide **2** under mild condition.¹³

EXPERIMENTAL

Materials

Perfluoro{2-[2-(2-fluorosulfonyl-ethoxy)propoxy]}propionyl fluoride FO₂SCF₂CF₂O—CF(CF₃)CF₂OCF(CF₃)COF used for the preparation of perfluoro-di{2-[(2-fluorosulfonyl-ethoxy)ethoxy]}propionyl peroxide was purchased from 3F Co. Ltd., Shanghai, China. Poly(α -methyl styrene) (Aldrich) was purified by precipitation before use.

Procedures

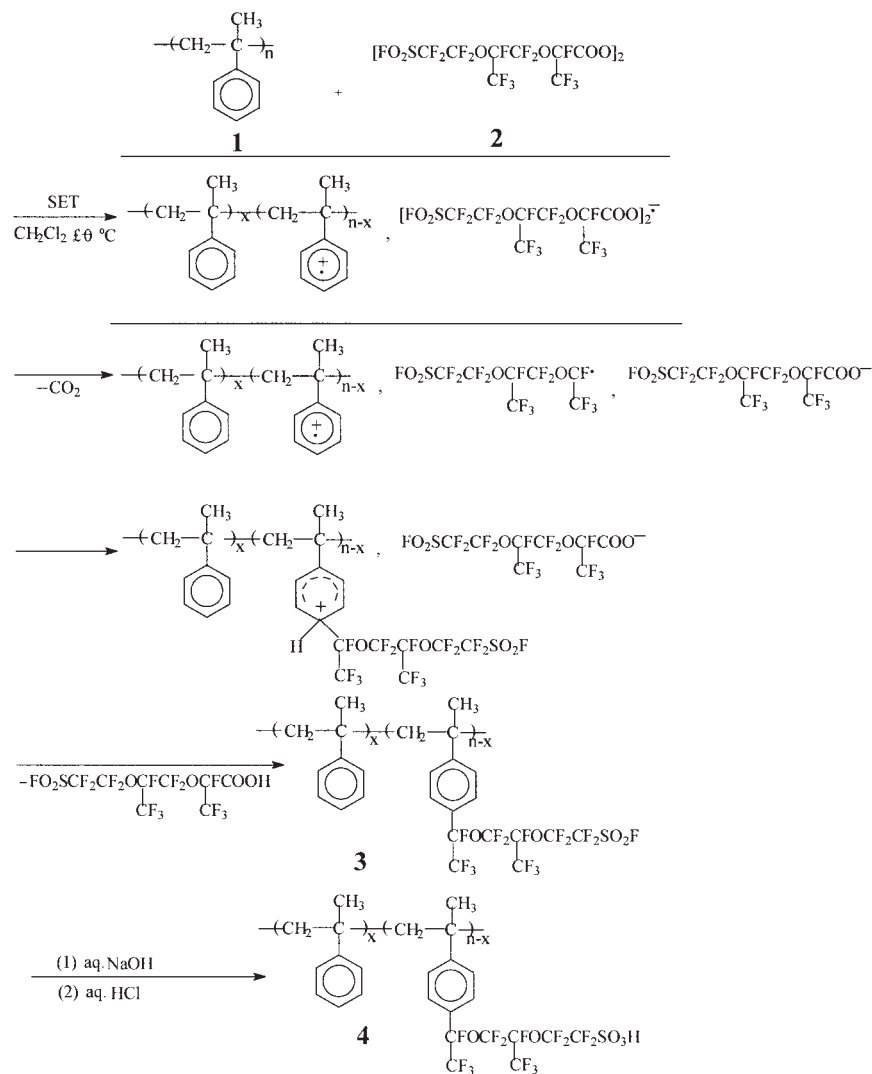
Preparation of perfluoro-di{2-[2-(2-fluorosulfonyl-ethoxy)propoxy]}propionyl peroxide **2**^{14,15}

The F113(CCl₂FCClF₂) solution of the peroxide **2** was prepared according to the reported procedure and kept under freezing condition before use. The concentration of the peroxide **2** in F113 was determined by standard iodimetry.

Synthesis of *p*-perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **3**

Poly(α -methyl styrene) **1** (4.72 g; 40 mmol) was dissolved in 75 mL of dichloromethane in 250 mL single neck flask with magnetic stirring. After flush-

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Scheme 1

ing with nitrogen, appropriate peroxide **2** in F113 was quickly added into the flask at 0°C, and then the reaction mixture was stirred for additional 24 h. The polymeric product was precipitated by methanol, collected, and purified by reprecipitation from dichloromethane/methanol binary solvent. After filtration, the product was dried for 24 h under vacuum at 50°C.

Preparation of *p*-perfluoro{1-[2-(2-sulfonic-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **4**

p-Perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **3** (3.2 g) was dissolved in 50 mL of dichloromethane in a flask with magnetic stirring. Then the polymeric solution was hydrolyzed in excess 3 mol/L aq. NaOH at 80°C for 4 h. After washing with water to neutral pH, the polymeric solution was acidified in excess 1 mol/L aq. HCl at room temperature for 24 h, then washed with water to neutral and dumped

into hot water to vaporize solvent, and finally, the polymeric product **4** was precipitated. After filtration, the polymeric product was dried for 24 h under vacuum at 50°C.

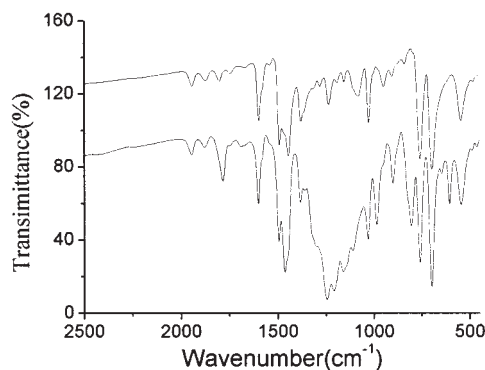


Figure 1 FTIR spectrum of poly(α -methyl styrene) **1** (a) and the modified poly(α -methyl styrene) **3** (b) prepared at molar ratio 1 : 2 (2 : 1).

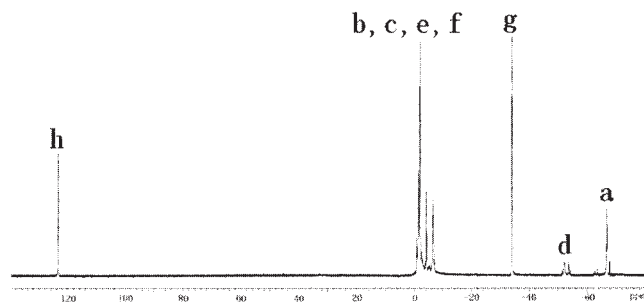


Figure 2 ^{19}F -NMR spectra of the modified poly(α -methyl styrene) **3** prepared at molar ratio 1 : 2 (2 : 1).

Instrumentation

FTIR spectra were taken on a 983-Perkin-Elmer spectrometer. ^{19}F -NMR spectrum was recorded on a Varian Mercury plus-400 spectrometer. Fluorine elementary analysis was measured by ELEMER ELMER 2400-II machine. Molecular weights were measured on a Wyatt DOWN EOS by using DMF as the eluent. TGA analysis was carried out by using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. Ion exchange capacity was calculated by Fluorine element analysis.

RESULTS AND DISCUSSION

The *p*-perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}-ethylated poly(α -methyl styrene) **3** was synthesized via ET-reaction⁴ between poly(α -methyl styrene) **1** and *p*-perfluoro{2-[2-(2-fluorosulfonyl-ethoxy)propoxy]}-propionyl peroxide **2**, and subsequently, the product **3** was converted into new ion exchange resin **4**, as depicted in Scheme 1. The polymer substrate **1** is an alkylated benzene in character and therefore a good electron donor. It might transfer an electron to the one-electron oxidant, peroxide **2**. Then the radical anion $2\cdot$ collapsed in the original cage to $\text{R}_f\text{COO}\cdot$, which underwent very fast decarboxylation generating $\text{R}_f\cdot$. The $\text{R}_f\cdot$ radical attacked the radical cation 1^+ to give the perfluoroalkylation product **3**, which is converted easily into the final product **4** by further hydrolysis and acidification.

TABLE I
Fluorine Content, n_f/n_p Ratio, and Yield of the Modified Poly(α -methyl Styrene) **3** at Different Reactant Ratios

Molar ratio 2:1	Fluorine content (%) in 3	n_f/n_p in 3	Yield (%) of 3
1 : 20	9.65	1 : 20.1	94.8
1 : 10	14.67	1 : 11.5	79.8
1 : 5	21.31	1 : 6.4	67.6
1 : 2	32.63	1 : 2.5	57.6
1 : 1	38.63	1 : 1.32	43.1

TABLE II
The Molecular Weights and Polydispersities of the Modified Poly(α -methyl Styrene) **3** Obtained at Different Reactant Ratios

Molar ratio 2:1	1:20	1:10	1:5	1:2	1:1	PMS
M_n (10^3)	4.85	5.26	6.85	9.84	14.79	3.92
M_w/M_n	1.08	1.24	1.21	1.47	1.52	1.78

FTIR spectrum (Fig. 1) indicates clearly the presence of the *p*-perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylation of the phenyl ring of poly(α -methyl styrene) **1**. FTIR spectrum shows strong characteristic absorption bands for the fluorinated groups between 1100 and 1350 cm^{-1} : $\nu(\text{CF}_3)$ at 1312 cm^{-1} , $\nu(\text{CF}_2)$ at 1242 and 1218 cm^{-1} , and $\nu(\text{SO}_2\text{F})$ at 1492 cm^{-1} overlapped with $\nu(\text{C}-\text{C})$ of phenyl ring. The characteristic peak of para-disubstituted phenyl ring (860–800 cm^{-1})^{11,16} appears at 820 cm^{-1} . There is no appearance of characteristic peaks for meta-disubstituted phenyl ring (810–750 cm^{-1}) and ortho-disubstituted phenyl ring (770–735 cm^{-1}).^{11,16}

The lack of carbonyl absorption confirmed the ring perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}propionyl oxylation did not occur. This is because the perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]} perfluoro{2-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethyl propionyl oxylation radical in the cage underwent extremely fast decarboxylation before attacking the open para-phenyl carbon of the polymeric radical cation under the reaction condition (at 0°C in CH_2Cl_2).

^{19}F -NMR spectrum (Fig. 2) shows {2-[2-(2-fluorosulfonyl-ethoxy)}]ethylgroup- $\text{CF}^a(\text{CF}_3^b)\text{OCF}_2^c\text{CF}^d(\text{CF}_3^e)\text{OCF}_2^f\text{CF}_2^g\text{SO}_2\text{F}^h$ of the modified poly(α -methyl styrene) **3** (at the ratio 2 : 1 = 1 : 2) appears at δ -67.7 (a,1F), δ -53.8 (d,1F), -34.2 (g,2F), δ -6.5–0.1(b,c,e,f,7F), and δ 123.4(h,1F).

As shown in Table I, both the fluorine content and

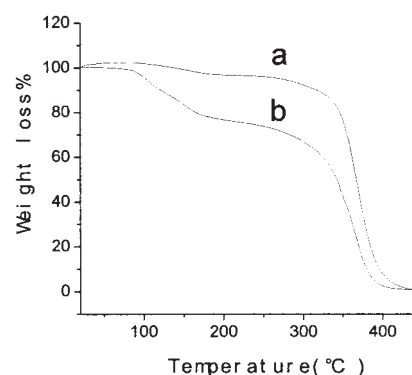


Figure 3 TGA curves of poly(α -methyl styrene) **1** (a) and the modified poly(α -methyl styrene) **3** (b) prepared at molar ratio 1 : 1 (2 : 1).

TABLE III
IEC Values of the Novel Polyelectrolyte **4** at Different Reactant Molar Ratios

Molar ratio(2 : 1)	IEC (mmol/g)
1 : 20	0.34
1 : 10	0.52
1 : 5	0.75
1 : 2	1.15
1 : 1	1.36

the n_r/n_p value (the proportion of reacted phenyl ring) of the modified poly(α -methyl styrene) **3** were increasing with the increase of reactant molar ratio, but the yield of perfluoroalkylation was decreasing slightly. At the lower reactant molar ratio, the substrate polymer **1** (electron donor) was in large excess over the peroxide **2**; thus, the perfluoroalkyl radicals $\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}(\text{CF}_3)\text{CF}$ that were from decomposition of the peroxide could completely react with phenyl rings via single-electron transfer. However, at the higher molar ratios (higher concentrations of peroxide **2**), the perfluoroalkyl radicals was increasingly consumed by forming radical coupling product $[\text{FO}_2\text{SCF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)]_2$. Consequently, the yield of the *p*-perfluoroalkylation of polymer was reduced.

In Table II, the molecular weight of the modified poly(α -methyl styrene) **3** increased with the reactant molar ratio. The molecular polydispersity (M_w/M_n) of the modified poly(α -methyl styrene) **3** compared with poly(α -methyl styrene) **1** indicated that there was no degradation of the polymer main chains in reaction.

The TGA curves indicate that the weight loss of the substrate polymer **1** started at 347°C [Fig. 3(a)], and the modified polymer **3** (at the ratio 2 : 1 = 1 : 2) shows the similar weight loss temperature starting at 341°C [Fig. 3(b)], which is only 6°C lower than that of its parent polymer. An important feature of curve b is that the small weight loss occurred at 124°C. Apparently, the weight loss is caused by the desulfonation of $-\text{SO}_2\text{F}$ and not by the main-chain degradation.

The modified poly(α -methyl styrene) **3** could be converted into the corresponding sulfonic form **4** via further hydrolysis and acidification. As shown in Table III, ion exchange capacity (IEC) of new polyelectrolyte **4** increased continually with the increase of reactant molar ratio. The IEC of **4** can be well controlled in the range of 0.34 and 1.36 mmol/g by increasing the molar ratio. For example, at higher molar ratio 1 : 1, the IEC reached up to 1.36 mmol/g.

This value is high enough for **4** to be used as polyelectrolyte material. This kind of novel polyelectrolyte of *p*-perfluoro{1-[2-(2-sulfonic-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **4** possesses both good ion exchange capacity and perfluoroalkyl side chain similar to Nafion, and will be employed possibly in proton exchange membrane for fuel cell and cation exchange resin for catalysts.

CONCLUSIONS

The *p*-perfluoro{1-[2-(2-fluorosulfonyl-ethoxy)propoxy]}ethylated poly(α -methyl styrene) **3** was synthesized by aromatic perfluoro{1-[2-(2-fluorosulfonyl)ethoxy]} ethylation of poly(α -methyl styrene) **1** using perfluoro{1-[2-(2-fluorosulfonyl)propoxy]} {2-[2-(2-fluorosulfonyl-ethoxy)propoxy]} propionyl peroxides **2** at 0°C in CH_2Cl_2 . The yield of perfluoroalkylation decreases with the increase of the reactant molar ratio. The polydispersity values indicate that there is no degradation of the polymer chains in the reaction. The modified poly(α -methyl styrene) **3** could be converted into the corresponding sulfonic resin **4** by alkali hydrolysis and acidification. Ion exchange capacity of novel polyelectrolyte **4** increases with the increase of the reactant molar ratio.

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