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Aromatic monomers with pendant fluoroalkylsulfonate and sulfonimide groups

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Abstract

Novel styrene and dimethylisophthalate monomers with pendant lithium fluoroalkylsulfonate or sulfonimide functional groups have been prepared from the corresponding phenolic intermediates. One route involves several steps and uses 1,2-dibromotetrafluoroethane as the key fluorinated intermediate. A second route with fewer steps utilizes a perfluoroalkylsulfonyl-substituted vinyl ether as the source of the fluorinated substituents but affords a product with significantly higher equivalent weight.

Keywords: Fluorinated ionomers; Lithium fluoroalkylsulfonates; Lithium fluoroalkylsulfonimides; Synthesis

1. Introduction

Polymers with pendant fluoroalkylsulfonate groups have been of significant scientific and commercial interest for many years [1,2]. The best known examples are perfluorinated polymers prepared by the radical copolymerization of tetrafluoroethylene with sulfonyl fluoride-substituted perfluorovinyl ethers, such as monomer **1**. The perfluorinated backbone provides high chemical and thermal stability while the side chain functions as an exceptionally strong acid in its sulfonic acid form or as a weakly coordinating anion in its conjugate base form. Current and potential applications include membranes for chloroalkali cells, batteries and fuel cell and strong solid acid catalysts [3,4].

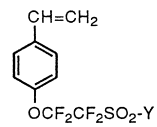
$CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$

1

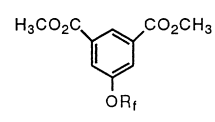
Perfluorinated polymers have special value in harsh environments, such as chloralkali cells, due to their high stability. However, highly fluorinated polymers can be difficult to process. In addition, perfluorinated vinyl ethers, such as **1**, are costly, relatively unreactive during polymerization [2] and can be polymerized only by a conventional free radical mechanism with a limited range of comonomers. Modern controlled polymerization techniques, such as living radical or anionic polymerizations, cannot be applied to the fluorinated vinyl ethers so polymer architecture cannot be finely controlled.

Several partially fluorinated polymers with pendant fluoroalkylsulfonate groups have been reported. The polymer backbones include silicone [5] and epoxy [6,7] which provide materials with improved processability and the potential for different polymer architectures. However, in these examples the linkages between the fluoroalkylsulfonate groups and the polymer backbones are generally via relative sensitive alkyl ether or amide [8,9] groups. We considered that monomers in which the fluoroalkylsulfonate group is attached via an ether linkage to an aromatic ring should have improved chemical and thermal stability. Styrene derivatives seemed of special interest because styrenes can be polymerized with a wide variety of comonomers by anionic, cationic, coordination and free radical processes opening up the potential to generate many polymers with novel architectures.

We now describe synthesis of the novel styrene monomer **2** with a pendant fluoroalkoxysulfonate group and its analog **3** with the even more weakly coordinated bis-fluoroalkylsulfonimide group [10,11]. In addition, we have prepared the isophthalate derivatives, **4** and **5**, as precursors to condensation polymers, such as polyesters. The syntheses and properties of a variety of polymers from these monomers will be reported separately.



2. Y = OLi
3. Y = N(Li)SO_2CF_3



4. R_f = $CF_2CF_2SO_3Li$
5. R_f = $CF_2CFHOCF_2CF(CF_3)OCF_2CF_2SO_3Li$

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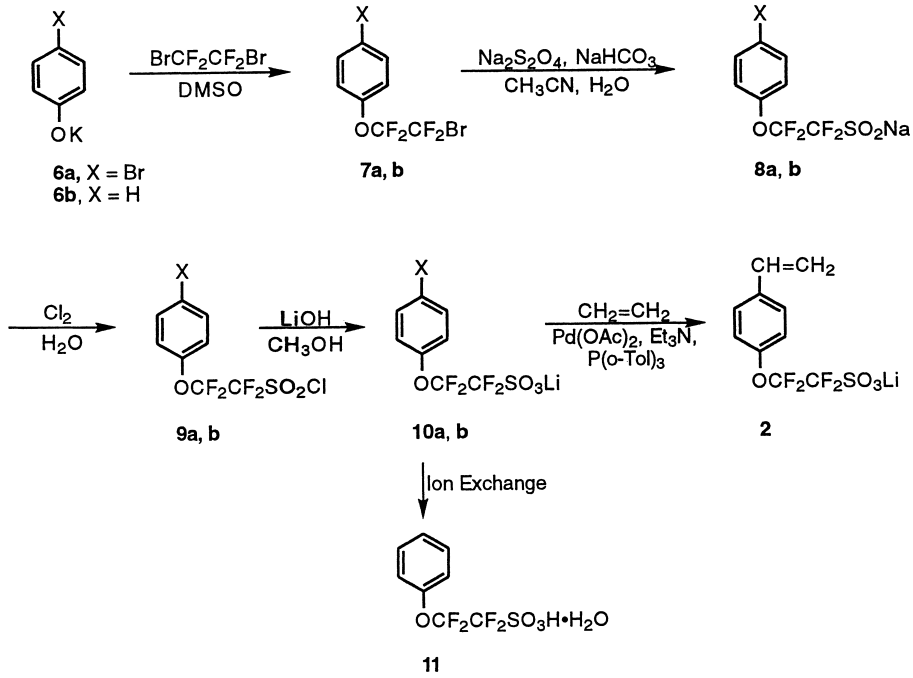


Scheme 1. Synthesis of lithium sulfonate monomer **2**.

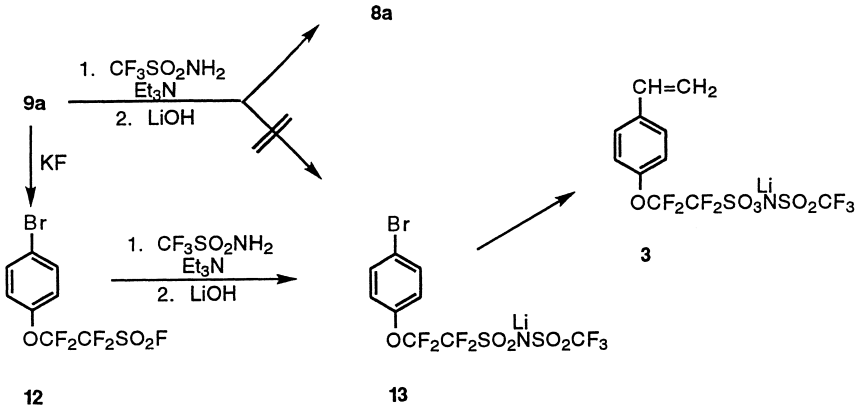
2. Results and discussion

Synthesis of the styrene fluorosulfonate monomer **2** is outlined in Scheme 1. Reaction [12,13] of potassium salt of 4-bromophenol with 1,2-dibromotetrafluoro-ethylene affords ether **7a** which is transformed in high yield to the sulfinate **8a** on reaction with sodium dithionite and sodium bicarbonate in aqueous DMF [14]. The sulfinate reacts with elemental chlorine in water to provide the sulfonyl chloride **9a** [15]. The sulfonyl chloride is converted to the corresponding lithium sulfonates **10a** on reaction with lithium hydroxide in aqueous THF. The lithium salt is soluble in polar organic solvents which facilitate its purification by recrystallization to analytical purity. The styrene **2** is obtained from **10a** and ethylene under typical Heck reaction conditions using ethylene in the presence of a Pd catalyst. Monomer **2** is a crystalline solid, readily soluble in polar organic solvents such as THF, ether and DMF.

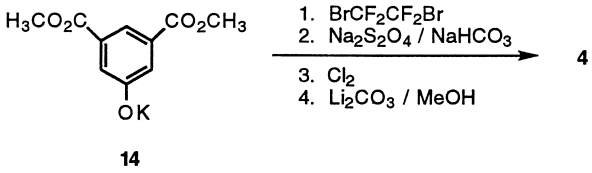
The synthesis of **2** involves several steps but all go in good yield using readily available and relatively inexpensive reagents. Most of the reactions in Scheme 1 were known [12–15] but had not been previously combined in this fashion.

Although the various fluorinated lithium sulfonate salts have generally shown good thermal stability (>200°C), it was of interest to determine stability of the free acid, which might be useful for other applications. The unsubstituted sulfonate **10b** was prepared by the same route beginning with phenol. A solution of **10b** in water was passed slowly through a column containing a large excess of Dowex® ion exchange resin in the acid form. The aqueous solution was concentrated and the resulting solid was dried for several days at 45°C and 0.05 mm. Recrystallization from boiling benzene afforded white crystals in excellent yield. Elemental analysis and proton and fluorine NMR spectra agreed well with the structure $PhOCF_2CF_2SO_3H{\cdot}H_2O$ (**11**). On heating, it remained a white solid up to its melting point of 83–84°C, at which point it turned dark and evolved a gas. Thus, the very strong free acid can be isolated as a monohydrate which is stable at room temperature, but decomposes rapidly at about 80°C. Polymeric versions of this acid will presumably show similar thermal stability.

In an initial effort to prepare a lithium fluoroalkylsulfonylimide salt (Scheme 2), the sulfonyl chloride **9a** was reacted with trifluoromethanesulfonamide and triethylamine according to a procedure for synthesis of imide salts from perfluoroalkylsulfonyl fluorides [16]. However, the expected salt **13** is not formed; the major product from **9a** is the sulfinate **8a**. A control experiment demonstrates that triethylamine alone rapidly reduces **9a** to **8a**, indicating a major difference in the chemistry of perfluoroalkylsulfonyl chlorides and fluorides. A sulfonamide could be prepared by reacting **9a** with ammonia. It seems likely that reaction of this sulfonamide with trifluoromethanesulfonyl fluoride will provide a fluoroalkylsulfonylimide salt but this process has not yet been tried. The sulfonyl chloride **9a** is readily converted to the sulfonyl fluoride **12** using potassium fluoride. Reaction of **12** with trifluoromethanesulfonamide and triethylamine, followed by cation exchange, affords the lithium sulfonimide **13** in good yield. Compound **13** is converted to the styrene monomer **3** using the Heck reaction as described above.



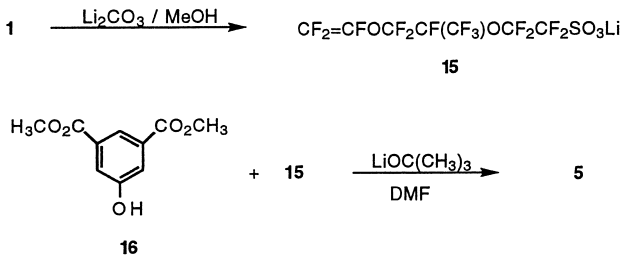
Scheme 2. Synthesis of lithium sulfonimide monomer **3**.



Scheme 3. Synthesis of lithium sulfonate monomer **4**.

The isophthalate monomer **4** is prepared by a similar route (Scheme 3) starting with the potassium salt of dimethyl 5-hydroxyisophthalate. Hydrolysis of the sulfonyl chloride intermediate to the lithium sulfonate was accomplished without affecting the ester groups using lithium carbonate in methanol.

A related fluoroalkylsulfonate substituted isophthalate monomer **5** was prepared as shown in Scheme 4. The perfluorovinyl ether monomer **1** can be converted to its lithium sulfonate form **15** without affecting the sensitive vinyl ether group by reaction with lithium carbonate in methanol [17]. Reaction of **15** with dimethyl 5-hydroxyisophthalate in the presence of a catalytic amount of lithium *tert*-butoxide affords the diester **5** in excellent yield. Additions of phenols to vinyl ethers are well known and have previously been accomplished on functionalized vinyl ethers [18]. Attempted reaction of the phenol with **1**, however, results in a complex mixture presumably resulting from reaction of the nucleophile with both the vinyl ether and



Scheme 4. Synthesis of lithium sulfonate monomer **5**.

the sulfonyl fluoride group. After conversion of the sulfonyl fluoride to its lithium sulfonate form, only the vinyl ether reacts with the nucleophile.

Although the synthesis in Scheme 4 appears more attractive than that described in Scheme 3 due to the number of steps, choice of the preferred monomer is less obvious. Intermediate **1** in Scheme 4 is far more costly than any of the materials in Scheme 3 and requires several steps for its preparation. Furthermore, the monomer **5** contains far more fluorine which is probably wasted and potentially troublesome for some applications. The molecular weights of **4** and **5** are 396 and 660, respectively, with much of the difference being additional fluorocarbon groups which do not provide value.

3. Experimental

*3.1. Synthesis of 1-bromo-2-(4-bromophenoxy)tetrafluoroethane (***7a***)*

4-Bromophenol (Aldrich, 348.4 g, 2.01 mol) was dissolved in 1.95 l of 1.033 N potassium hydroxide in methanol. This solution was evaporated to dryness on a rotary evaporator and the resulting solid was dried at 140°C and 0.1 mm. The solid was mixed with 600 ml of DMSO under nitrogen. 1,2-Dibromotetrafluoroethane (571.6 g, 2.2 mol) was added dropwise at 30–40°C. The resulting mixture was heated to 60°C for 6 h. It was cooled to room temperature and diluted to 3 l with ice and water. The organic layer was separated and the aqueous solution was extracted with 2×75 ml of methylene chloride. The methylene chloride extracts were concentrated on a rotary evaporator and the residue combined with the original organic layer. This material was washed with 2×400 ml of water, dried over anhydrous magnesium sulfate and filtered. The filtrate was distilled giving 641.2 g (92%) of product, bp 57°C at 0.6 mm. ^{1}H NMR (δ, $CDCl_3$) 7.1 (d, 2H), 7.5 (d, 2H); ^{19}F NMR (δ, $CDCl_3$) −68.6 (2F), −86.6 (2F).

Anal. Calcd. for $C_8H_4F_4OBr_2$: C, 27.30; H, 1.15; Br, 45.41; F, 21.59. Found: C, 27.27; H, 1.16; Br, 44.85; F, 20.87.

*3.2. Synthesis of sodium 2-(4-bromophenoxy)tetrafluoroethanesulfinate (**8a**)*

Compound **7a** (366.5,1.04 mol) was added under nitrogen to a stirred mixture of 1.026 l of distilled and deoxygenated water, 186.5 g of sodium bicarbonate, 500 ml of dimethylformamide and 357.6 g of sodium dithionite. This mixture was heated to 65°C resulting in a rapid gas evolution. Gas evolution ceased after about 1 h and the mixture was heated to 70–75°C for 3 h. It was cooled to about 10°C in an ice water-bath and 1 l of ethyl acetate was added. The mixture was filtered and the solid was washed with ethyl acetate. The combined filtrates were separated into aqueous and organic layers and the organic layer was washed with 4×50 ml of saturated aqueous sodium chloride solution. The organic layer was concentrated on a rotary evaporator to about 1/4 its initial volume and filtered. The solid was washed with ethyl acetate. The combined organic solutions were concentrated to dryness on a rotary evaporator giving 362.6 g (97%) of white solid **8a** which was converted to the sulfonyl chloride without further purification. ^{1}H NMR (δ, CD_3OD) 7.2 (d, 2H), 7.6 (d, 2H); ^{19}F NMR (δ, CD_3OD) −132.8 (2F), −81.9 (2F).

*3.3. Synthesis of 2-(4-bromophenoxy)tetrafluoroethanesulfonyl chloride (**9a**)*

The sulfinate **8a** was dissolved in a mixture of 600 ml of deoxygenated water and 300 ml of 1,1,2-trichlorotrifluoroethane (CFC-113) in a round bottom flask equipped with a dry-ice condenser and cooled to 5–15°C. Chlorine gas (134 g) was bubbled into this mixture over about 1 h. The resulting yellow mixture was stirred 1 h without external cooling. It was warmed to 20°C and an additional 200 ml of CFC-113 was added. The organic layer was separated and the aqueous solution was extracted with 100 ml of 1,1,2-trichlorotrifluoroethane. The combined organic solutions were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The residue was distilled through a short Vigreux column giving 361.1 g (97%) of product, bp 71°C at 0.3 mm. ^{1}H NMR (δ, $CDCl_3$) 7.1 (d, 2H), 7.6 (d, 2H); ^{19}F NMR (δ, $CDCl_3$) −79.0 (2F), −107.9 (2F).

Anal. Calcd. for $C_8H_4F_4BrClSO_3$: C, 25.86; H, 1.08; F, 20.46; S, 8.63. Found: C, 26.07; H, 1.17; F, 18.74; S, 8.59.

*3.4. Synthesis of lithium 2-(4-bromophenoxy)tetrafluoroethanesulfonate (**10a**)*

Lithium hydroxide monohydrate (57.3 g, 1.365 mol) was dissolved in 600 ml deoxygenated distilled water. THF (150 ml) was added and this solution was heated to 35°C. The heat source was removed and 237 g (0.64 mol) of **9a** was added dropwise over 45 min at a rate so that the exotherm maintained the solution at about 55°C. After the addition was complete, the solution was held at 55°C for an additional 1.5 h. The solution was cooled to room temperature. Its pH was adjusted to 7 by addition of about 3 ml of concentrated hydrochloric acid and the aqueous solution was evaporated to dryness on the rotary evaporator. The solid was slurried with ether and filtered. The ether solution was treated with three volumes of hexane resulting in deposition of a white solid. The solid was filtered off and washed with hexane. The filtrate was evaporated and the residue was again precipitated from ether solution by addition of hexane. The combined precipitates were recrystallized from acetonitrile with cooling in the refrigerator with the filtrate concentrated several times to collect additonal fractions. The combined recrystallized product was dissolved in ether, filtered and concentrated on a rotary evaporator. The product was dried at 100°C and 0.1 mm giving 173.9 g (76%) of the title compound as a white solid. ^{1}H NMR (δ, CD_3OD) 7.2 (d, 2H), 7.6 (d, 2H); ^{19}F NMR (δ, CD_3OD) −116.9 (2F), −81.6 (2F).

Anal. Calcd. for $C_8H_4F_4BrLiSO_3$: C, 26.76; H, 1.12; F, 17.83; S, 8.93. Found: C, 26.57; H, 1.26; F, 18.94; S, 8.77.

*3.5. Synthesis of lithium 2-(4-ethenylphenoxy)tetrafluoroethanesulfonate (**2**)*

A 1 l autoclave was charged with 69 g (0.19 mol) of **10a**, 200 ml of acetonitrile, 0.88 g $Pd(OAc)_2$, 2.48 g of tri-*o*-tolylphosphine and 200 ml of triethylamine. The autoclave was closed, cooled, evacuated and charged with ethylene to 110 psi. The mixture was heated with stirring to 85°C for 24 h, holding the gas pressure at 120–125 psi by venting or adding ethylene as needed. The mixture was cooled to room temperature and vented to atmospheric pressure. The autoclave contents were recovered using a mixture of acetonitrile and ether to rinse. The mixture was treated with 8.9 g of lithium hydroxide monohydrate in 150 ml of water with vigorous stirring and filtered through celite. The celite was washed with acetonitrile and ether. The combined filtrates were evaporated to dryness at 75–80°C and 5 mm. The residue was extracted with 0.5 l of ether and filtered. The filtrate was diluted with 0.5 l of hexane and the resulting precipitate was collected, precipitated a second time from a mixture of ether and hexane and dried at 65°C and 0.05 mm giving 20.6 g of product. An additional 12.8 g of product was obtained by concentrating the above ether and hexane filtrates and reprecipitating the residue for a total yield of 33.4 g (58%) of the title product. ^{1}H NMR (δ, CD_3CN) 5.27 (d, 1H), 5.80 (d, 1H), 6.78 (dd, 1H), 7.27 (d, 2H), 7.51 (d, 2H); ^{19}F NMR (δ, CD_3CN) −116.6 (2F), −80.8 (2F).

Anal. Calcd. for $C_{10}H_7F_4LiO_4S$: C, 39.23; H, 2.30; F, 24.82; Li, 2.27; S, 10.47. Found: C, 38.18; H, 2.78; F, 22.23; Li, 2.10; S, 9.55.

3.6. Synthesis of 2-(4-bromophenoxy)tetrafluoroethanesulfonyl fluoride (**12**)

The sulfonyl chloride **9a** (130 g, 0.35 mol) was added dropwise to a stirred mixture of 105 g (1.8 mol) oven-dried potassium fluoride and 500 ml of acetonitrile under nitrogen at room temperature. After 24 h at room temperature, a fluorine NMR spectrum showed about an 80% conversion of the sulfonyl chloride to fluoride. The mixture was warmed to 30–35°C and then allowed to stir for 3 days at room temperature. It was filtered and the solid rinsed with acetonitrile. The combined filtrates were concentrated on a rotary evaporator at 40°C and 150 mm and the residue was distilled on a Kugelrohr at 80–85°C and 5 mm into a dry-ice cooled receiver. The liquid distillate was distilled through a 12 ft Vigreux column giving 111.5 g (90%) of the title product as a colorless liquid, bp 81–82°C at 4.5 mm. ^{1}H NMR (δ, $CDCl_3$) 7.1 (d, 2H), 7.5 (d, 2H); ^{19}F NMR (δ, $CDCl_3$) −81.7(2F), −111.5 (2F), +44.2(1 F).

Anal. Calcd. for $C_5H_4F_5BrSO_3$: C, 27.06; H, 1.14; F, 26.75; S, 9.03; Br, 22.5. Found: C, 27.13; H, 1.05; F, 26.88; S, 8.94; Br, 22.35.

3.7. Synthesis of lithium N-(trifluoromethanesuIfonyl)-2-(4-bromophenoxy) tetrafluoroethanesulfonamide (**13**)

Freshly sublimed trifluoromethanesulfonamide (15.51 g, 0.104 mol) was added to 240 ml of triethylamine which was freshly distilled from lithium aluminum hydride. The mixture was warmed to 40°C to dissolve the solid, then cooled to room temperature. The sulfonyl fluoride **12** (35.7 g, 0.101 mol) was added and solution was heated at 70–75°C for 18 h. An F NMR spectrum of the solution showed a trace of sulfonyl fluoride remained so the mixture was treated with an additional 1 g of trifluoromethanesulfonamide and heated for 16 h at 70–75°C. The resulting red mixture was concentrated on the rotary evaporator. The residue was dissolved in methylene chloride, washed three times with water, dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator to 46.24 g of red oil which was the triethylammonium salt of the title product. ^{1}H NMR (δ, $CDCl_3$) 1.32 (t, 9H), 3.20 (q, 6H), 7.13 (d, 2H), 7.5 (m, 3H (aromatic+NH)); ^{19}F NMR (δ, $CDCl_3$) −79.38 (3F) −81.0 (2F), −116.9 (2F). This salt was dissolved in 100 ml of methanol under nitrogen and treated with 79.95 ml of 0.9908 M aqueous lithium hydroxide. After stirring for 15 min, the solution was evaporated to dryness at 65–75°C under vacuum. The solid was dissolved in methanol, concentrated in vacuum and dried at 0.1 mm. The resulting solid was dissolved in 175 ml of ether and hexane was added slowly until a red oil precipitated leaving a colorless upper layer. The upper layer was decanted and evaporated giving 30.9 g of crude title salt. The salt was twice recrystallized from mixtures of ether and hexane to give 29.7 g (60%) of the title product as a white powder. ^{1}H NMR (δ, CD_3OD) 7.20 (d, 2H), 7.60 (d, 2H); ^{19}F NMR (δ, CD_3OD) −79.02 (3F) −80.21 (2F), −115.5 (2F).

Anal. Calcd. for $C_9H_4BrF_7LiNO_5S_2$: C, 22.06; H, 0.82; N, 2.86; F, 27.14; S, 13.08; Br, 16.30; Li, 1.42. Found: C, 22.16; H, 0.83; N, 2.85; F, 25.66; S, 12.57; Br, 16.14; Li, 1.34.

3.8. Synthesis of lithium N-(trifluoromethanesulfonyl)-2-(4-ethenylphenoxy)-tetrafluoroethanesulfonamide (**3**)

A 1 l pressure vessel was charged under nitrogen with 73.5 g (0.15 mol) of **13**, 300 ml of acetonitrile, 1.15 g $Pd(OAc)_2$, 3.09 g of tri-*o*-tolylphosphine and 120 ml of triethylamine. The autoclave was closed, cooled, evacuated and charged with ethylene to 100 psi. The mixture was heated with stirring to 85°C for 14 h, holding the gas pressure at 125 psi by venting or adding ethylene as needed. The mixture was cooled to room temperature and vented to atmospheric pressure. The autoclave contents were recovered using a mixture of acetonitrile and water to rinse. The mixture was treated with 6.3 g of lithium hydroxide monohydrate and 100 ml of water with vigorous stirring. Ether (300 ml) was added and the mixture was filtered through celite. A trace of 4-*tert*-butylcatechol was added to the filtrate which was concentrated to a solid. The residue was dissolved in ether. A small aqueous layer was separated and the ether was dried over anhydrous sodium sulfate. This solution was filtered and concentrated to an oil on a rotary evaporator. Methylene chloride (50 ml) was added and the mixture was filtered. Hexane was added to the cloud point and the mixture was filtered. The filtrate was concentrated under vacuum resulting in separation of an oil. Trituration of the oil with hexane caused crystallization. The crystals were collected and dried giving 53.1 g (81%) of the title product. A trace of 4-*tert*-butylcatechol was added to prevent polymerization. ^{1}H NMR (δ, acetone-d6) 5.25 (d, 1H) 5.80 (d, 1H), 6.80 (dd, 1H), 7.30 (d, 2H), 7.55 (d, 2H); ^{19}F NMR (δ, acetone-d6) −78.78 (3F), −79.77 (2F), −115.52 (2F).

Anal. Calcd. for $C_{11}H_7F_7NO_5S_2Li \times 2.4H_2O$: C, 27.49; H, 2.48; N, 2.91; F, 27.67; Li, 1.44; S, 13.34. Found: C, 27.48; H, 2.24, N, 3.03; F, 28.55; Li, 1.47; S, 15.26.

3.9. Synthesis of dimethyl 5-(1,1,2,2-tetrafluoro-2-bromoethoxy)isophthalate

A solution of 70.5 g of 95% potassium methoxide (0.956 mol) in 500 ml dry methanol was added to a suspension of 200.97 g (0.956 mol) dimethyl 5-hydroxyisophthalate in 400 ml of dry methanol cooled to 0–5°C. The mixture was allowed to warm to room temperature and decanted from a small amount of white solid. The methanol solution was concentrated on a rotary evaporator and the solid was dried at 150°C and 0.1 mm to give 226.4 g. This salt was dissolved in 600 ml of dry DMSO and heated to 65°C. 1,2-Dibromotetrafluoroethane (259.8 g, 1 mol) was added dropwise resulting in an exotherm to 80°C. After addition was complete, the mixture was maintained at 75–85°C for 4 h. It

was cooled to room temperature and diluted to 2 l with ice water. The aqueous solution was decanted from a viscous gum and extracted with 200 ml methylene chloride. The methylene chloride extract was concentrated and the residue was combined with the viscous gum and washed with water. The organic material was taken up in methylene chloride, dried over anhydrous sodium sulfate and concentrated on a rotary evaporator. The residue was distilled in a Kugelrohr apparatus at 140°C and 0.2 mm giving 257.6 g of material which was 93% pure by GLPC. Chromatography on silica gel, eluting with hexane and then 1–4% ethyl acetate in hexane gave the desired product in the first fractions. The combined fractions were concentrated on the rotary evaporator and the residue was distilled in a Kugelrohr at 125°C and 0.1 mm to give 239.6 g (62%) of the title product. ^{1}H NMR (δ, $CDCl_3$) 3.98 (s, 6H), 8.05 (m, 2H), 8.60 (m, 1H); ^{19}F NMR (δ, $CDCl_3$) −68.7 (2F), −86.4 (2F).

Anal. Calcd. for $C_{12}H_9F_4BrO_5$: C, 37.04; H, 2.33; F, 19.53; Br, 20.54. Found: C, 36.95; H, 2.08; F, 19.34; Br, 20.57.

3.10. Synthesis of 3,5-di(CO_2CH_3)-Ph-$OCF_2CF_2SO_2Cl$

A 5 l round bottom flask was charged with 109.2 g sodium bicarbonate, 600 ml of deionized water, 226.4 g of sodium dithionite and 300 ml of DMF. The mixture was heated to 65°C and dimethyl 5-(1,1,2,2-tetrafluoro-2-bromoethoxy)isophthalate (316.2 g, 0.81 mol) was added over 15 min. After addition was complete, the mixture was warmed to 80–85°C for 4 h and then maintained at 50°C overnight. The mixture was cooled to room temperature and filtered. The solid was washed with ethyl acetate which was added to the filtrate. A lower aqueous layer was extracted with 2×100 ml methylene chloride and 2×100 ml ethyl acetate. All the organic layers were combined, washed with 3×50 ml brine, dried over anhydrous sodium sulfate and concentrated on a rotary evaporator. The residue was dried at 120°C and 0.1 mm to give a yellow-orange solid which was used in the next step without further purification. ^{1}H NMR (δ, DMSO-d6) 3.95 (s, 6H), 7.97 (m, 2H), 8.40 (m, 1H); ^{19}F NMR (δ, $CDCl_3$) −80.9 (2F), 131.3 (2F). This solid was dissolved in 1 l deionized water and 300 ml of CFC-113 was added. The flask was fitted with a dry-ice condenser. Chlorine gas was bubbled into the mixture until an excess was present. A precipitate formed which was not completely soluble in the CFC-113, so 500 ml of methylene chloride were added. The excess chlorine was vented into a scrubber, the organic layer was separated and the aqueous layer was extracted with 3×250 ml methylene chloride. The combined organic layers were washed with 100 ml brine, dried over anhydrous sodium sulfate, concentrated on a rotary evaporator and distilled using a Kugelrohr at 150°C and 0.2 mm to give 277.3 g of faintly yellow solid. This material was recrystallized from CFC-113 to give, in three crops, 257.4 g (78%) of white solid. ^{1}H NMR (δ, $CDCl_3$) 3.95 (s, 6H), 8.10 (m, 2H), 8.70 (m, 1H); ^{19}F NMR (δ, $CDCl_3$) −79.0 (2F), −108.0 (2F).

Anal. Calcd. for $C_{12}H_9ClF_4O_7S$: C, 35.26; H, 2.22; Cl, 8.67; F, 18.59; S, 7.84. Found: C, 35.39; H, 2.05; Cl, 8.95; F, 18.29; S, 7.66.

3.11. Synthesis of 3,5-di(CO_2CH_3)-Ph-$OCF_2CF_2SO_3Li$ (**4**)

To a suspension of 262 g (0.64 mol) 3,5-di(CO_2CH_3)-Ph-$OCF_2CF_2SO_2Cl$ in 1 l of anhydrous methanol was added 52.1 g (0.71 mol) of anhydrous lithium carbonate. This mixture was heated to 40°C, then allowed to stir at room temperature for 96 h. The solution was filtered and concentrated on the rotary evaporator. The solid was recrystallized from 6 l acetonitrile, collecting two crops. The combined solid was dried at 180°C and 0.1 mm to give 179.1 g (71%) of product. ^{1}H NMR (δ, DMSO-d6) 3.95 (s, 6H), 7.95 (m, 2H), 8.40 (m, 1H); ^{19}F NMR (δ, $CDCl_3$) −80.9 (2F), 116.5 (2F).

Anal. Calcd for $C_{12}H_9F_4SO_8Li$: C, 36.38; H, 2.29; F, 19.18; S, 8.24; Li, 1.75. Found: C, 36.29; H, 2.47; F, 19.08; S, 8.24; Li, 1.69.

3.12. Synthesis of 3,5-di(CO_2CH_3)Ph-$OCF_2CFHOCF_2CF(CF_3)OCF_2CF_2SO_3Li$ (**5**)

Dimethyl 5-hydroxyisophthalate (28.76 g, 0121 mol) was dissolved in 200 ml of anhydrous DMF under argon. Lithium *tert*-butoxide (0.749 g) was added and the mixture was warmed to 40°C, then cooled to room temperature. Solid **15** (51.3 g, 0.114 mol) was added and the solution was warmed to 40°C. A slight exotherm was noted. The solution was stirred for 2 h at 40°C, then allowed to stir for 3 days at room temperature. Hydrochloric acid (9.5 ml of 1.0 M) was added and the solution was concentrated on a rotary evaporator. The residue was dried at 145–150°C and 0.05 mm on a Kugelrohr. The dried solid was dissolved in 500 ml of ether. Hexane was added dropwise until a gummy precipitate formed. The mixture was filtered and the filtrate was concentrated and dried at 100°C and 0.1 mm giving 74.0 g of white solid. Anal. Calcd. for $C_{17}H_{10}F_{13}O_{10}SLi$: C, 30.92; H, 1.53; F, 37.41; S, 4.86; Li, 1.05. Found: C, 30.77; H, 1.77; F, 38.89; S, 4.69; Li 0.99.

4. Conclusions

Two routes using readily available starting materials have been described for the synthesis of aromatic monomers having pendant fluoroalkylsulfonate groups. Products are obtained in good yields. The pendant groups are attached to the aromatic rings by robust ether linkages. We have prepared a variety of free radical polymers and copolymers from the styrene monomers **2** and **3** and novel polyesters from monomers **4** and **5**. Details will be reported separately.

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