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Perfluorocyclobutyl (PFCB) aromatic polyethers: Synthesis and characterization of new sulfonimide containing monomers and fluoropolymers

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Dedicated to Professor R.D. Chambers on the occasion of his 70th birthday.

Abstract

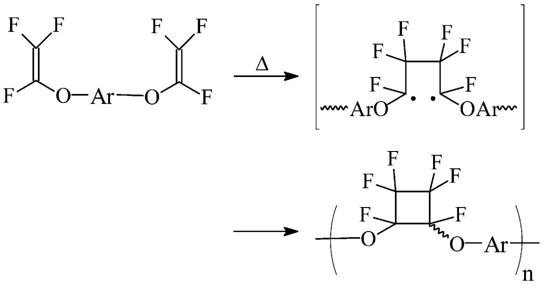
The synthesis and thermal cyclopolymerization of aryl trifluorovinyl ether monomers containing novel sulfonimide acid functionalities are described. The monomers are prepared starting from commercially available 4-bromophenol in five steps. These novel polymers explore a new versatile class of partially fluorinated polymers for potential use in fuel cells and other electrochemical applications.

Keywords: Perfluorocyclobutyl aryl ethers; Trifluorovinyl aryl ethers; Cyclopolymerization; Sulfonimides; Membranes; Fuel cells

1. Introduction

Perfluoropolymers are the leading candidates for use as proton exchange membranes (PEMs) in hydrogen–oxygen fuel cells due to their high thermal stability, oxidative stability, chemical resistance, and electrical insulating properties [1]. While sulfonic acid functionalized perfluorinated polyethers (e.g., DuPont's Nafion®) remain the most widely used material for membrane electrode assemblies (MEA), perfluorinated analogues containing the sulfonimide functional group have shown excellent potential as alternatives in PEM MEAs [2–6].

Recently, trifluorovinyl aromatic ether monomers have been developed which undergo thermal cyclopolymerization to afford thermally stable perfluorocyclobutane (PFCB) aromatic polyethers (Scheme 1) [7–9]. This cyclopolymerization does not require catalysts or initiators, but proceeds thermally due to a lower C═C π bond energy, and the strength of the resulting C–C single bond adducts formed [10–14]. Perfluorocyclobutyl (PFCB) aromatic polyethers represent a class of partially fluorinated polymers which combine the processability of engineering thermoplastics and the electrical, thermal, and chemical resistant properties of traditional fluoroplastics [15,16].



Aryl trifluorovinyl ether monomers are traditionally prepared in three steps from commercially available phenolic precursors, such as tris(hydroxyphenyl)ethane [8] and bisphenol [11]. Formation of the phenoxide followed by fluoroalkylation with 1,2-dibromotetrafluoroethane affords bromotetrafluoroethyl ether intermediates. Dehalogenation with zinc metal in refluxing anhydrous acetonitrile, provides aryl trifluorovinyl ether monomers in good overall yield. Recently a reactive aromatic trifluorviny ether

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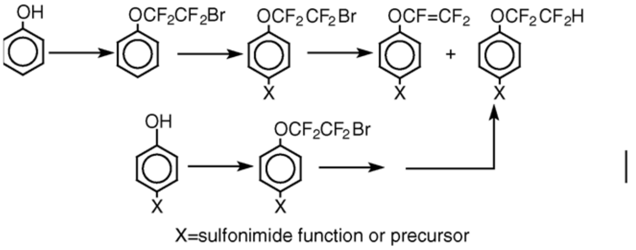
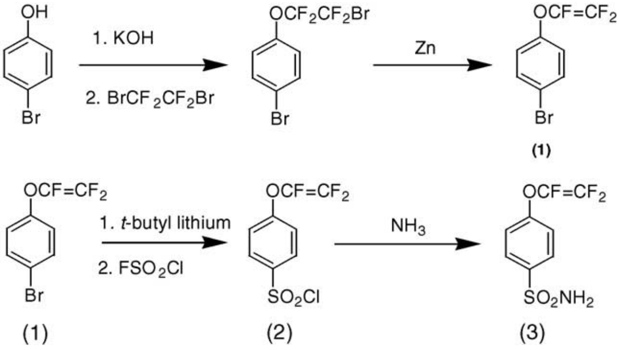


Scheme 1. Unsuccessful efforts to prepare functionalized aryl trifluorovinyl ether monomers.



Scheme 2. Synthesis of amide intermediate **3** via lithium chemistry.

intermediate was found to be susceptible to Grignard and lithium chemistry, providing a way to deliver the aromatic trifluorovinyl ether intact to a variety of substrates including phosphine oxides [12], thiophenes [13], and siloxanes [7,9,14].

We have used this methodology to introduce the $-SO_2F$ group into the 4-position of trifluorovinyl aryl ethers. This provided a route to polymerizable monomers containing the highly acidic sulfonimide function. This new class of monomers is capable of producing a variety of ionomeric polymers for possible use as PEMs in fuel cells and for other electrochemical applications.

2. Results and discussion

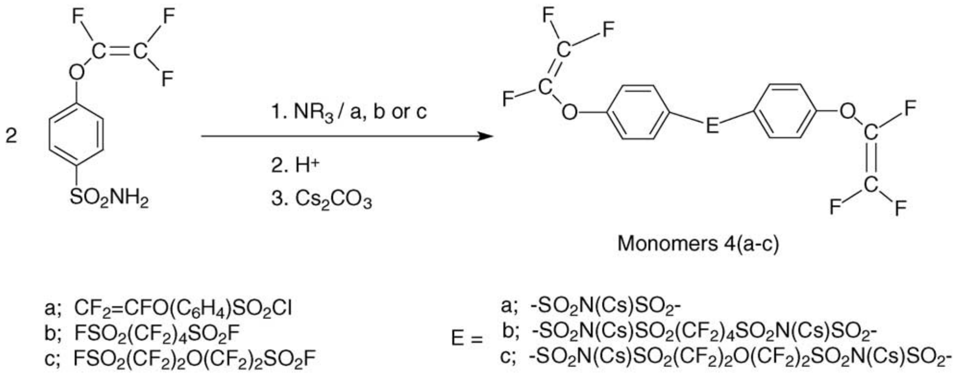
2.1. Monomer synthesis

The synthesis of sulfonimide containing aryl trifluorovinyl ether monomers initially focused on traditional methods of preparation (Scheme 1). Starting with commercially available phenolic precursors, deprotonation and fluoroalkylation with $BrCF_2CF_2Br$, and subsequent elimination of BrF with zinc would give the desired monomer intermediates. However, using phenolic starting materials such as 4-hydroxybenzenesulfonic acid sodium salt and other phenolics containing electron withdrawing substituents, the desired monomers could not be isolated pure during the elimination step. Various metal mediated eliminations (zinc, copper, Zn/CuCl, cadmium) using coordinating solvents always produced an unwanted side reaction leading to 2–7% of tetrafluoroethyl ether ($XAr–OCF_2CF_2H$). This impurity, could not be removed by any common separation methods and would act as a chain terminating agent in the cyclopolymerization of aryl ether monomers.

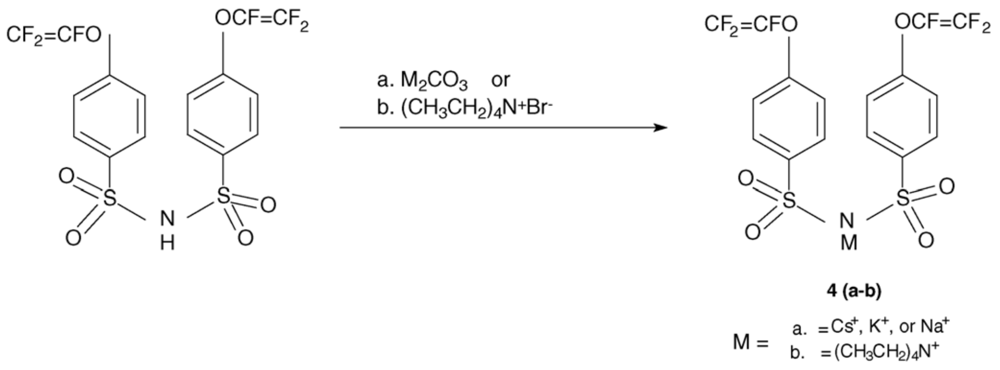
Monomer synthesis was then shifted to an intermediate based on readily available 4-bromophenol. The trifluorovinyl aryl ether **1** could then be functionalized via an aryl lithium intermediate as shown in Scheme 2.

Fluoroalkylation of bromophenol followed by elimination gave **1** in excellent yield. Treatment of **1** with *t*-butyl lithium, followed by nucleophilic attack on FSO_2Cl allowed the addition of the highly electron withdrawing sulfonyl chloride substituent forming **2** in good yield. Ammonating to the amide intermediate **3** and subsequent coupling with various sulfonyl halides ($X = Cl$ or F) using diisopropyl ethylamine gave the corresponding sulfonimide containing monomers shown in Scheme 3.

There are two noteworthy aspects to the reactions in Schemes 2 and 3: There was surprisingly no apparent attack on the vinyl group in converting **2–3** and **3–4** and the reactions with $ClSO_2F$ occurred exclusively at the S–F bond. The monomers produced from this base-assisted coupling reaction can be isolated pure in high yield. The proton of the sulfonimide functionality was easily exchanged using metal carbonates and tetraalkyl ammonium bromide as shown in Scheme 4.



Scheme 3. Coupling reactions to form sulfonimide monomers.



Scheme 4. Counterion exchange of the sulfonimide functionality.

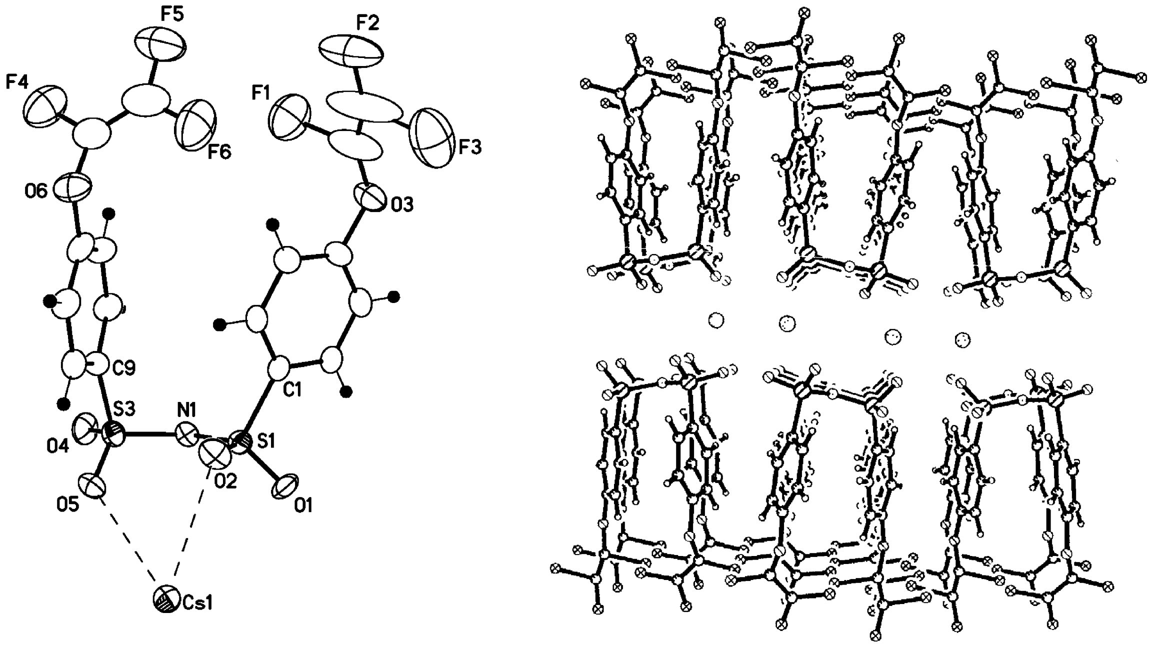
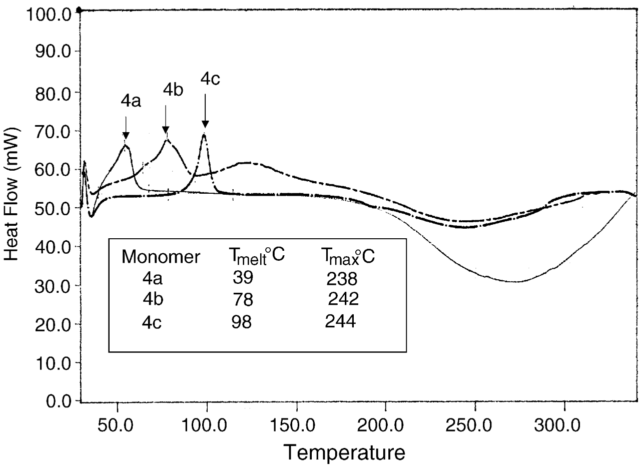


Fig. 1. Thermal ellipsoid plot (50% probability) of 1,1-bis[4-(trifluorovinyl)oxyphenylsulfonyl]imide (**4a**).

The crystal structure of monomer **4a** (Fig. 1), in the cesium form, shows many similarities to structures of bis((perfluoroalkyl)sulfonyl)imides and the isoelectronic carbon acids [17,18]. The resonance stabilization of the conjugate base anions along the O–S–N backbone leads to extended solid-state structures, where the anions behave as multidentate ligands. This links the monomers into a two dimensional polymeric layer forming a lamellar structure, resulting in domains consisting of the perfluorinated hydrophobic and ionic hydrophilic regions.

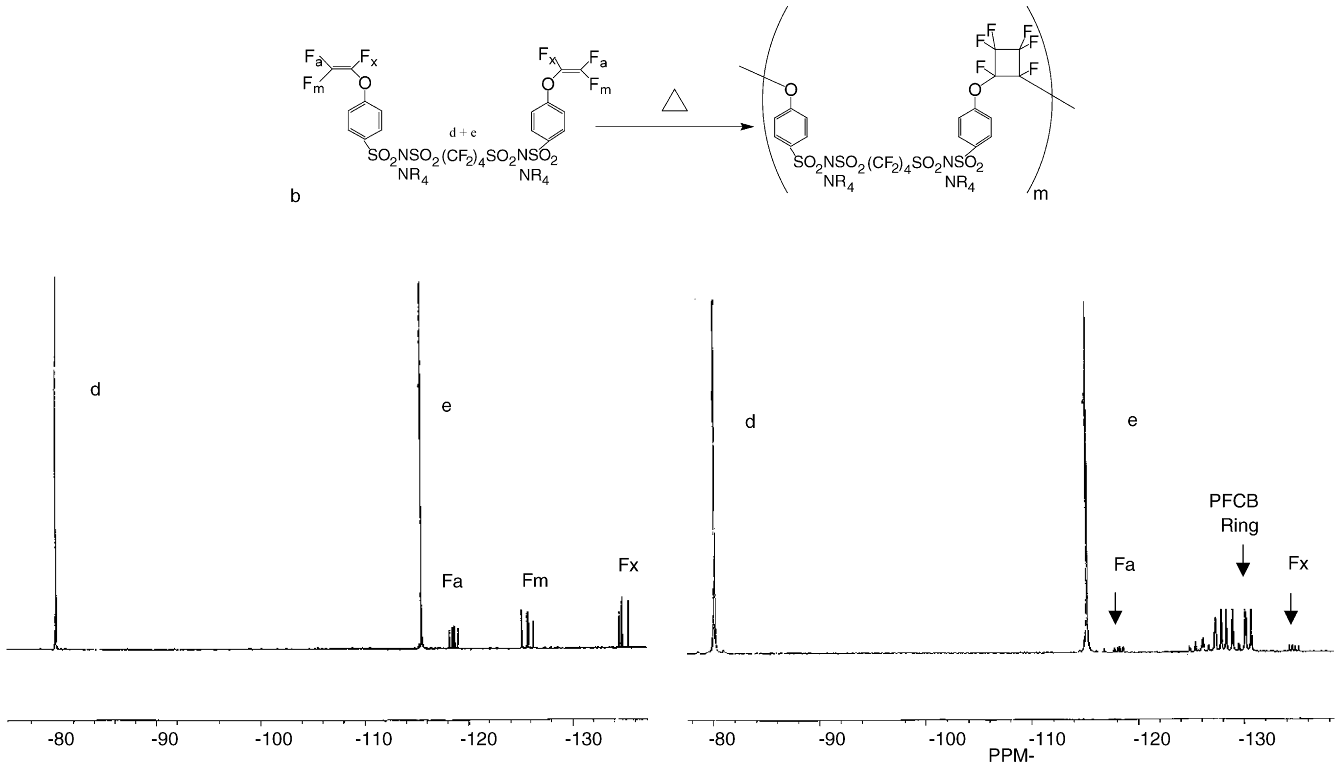
2.2. Homo- and copolymerizations of monomers

The thermal polymerization of Monomers **4a–c** in the acid form were attempted neat and in solution. It was found that all monomers in the acid form underwent an unexpected and unknown side reactions, which led to the decomposition of



Monomer	T_{melt}°C	T_{max}°C
4a	39	238
4b	78	242
4c	98	244

Fig. 2. DSC of monomer **4** (10 °C min^{-1}).



(a) ^{19}F NMR of Monomer **4b** (b) ^{19}F NMR of Monomer **4b** at 80% conversion to **7b**

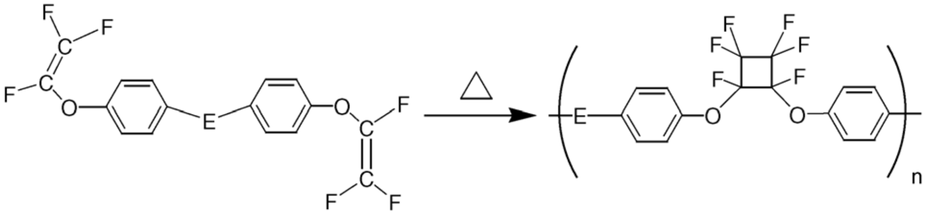
Fig. 3. (a) ^{19}F NMR of monomer **4b**. (b) ^{19}F NMR of monomer **4b** at 80% conversion to **7b**.

the monomers upon heating above 100 °C. The monomers were then polymerized in solution as the Cs^+, K^+, or Na^+ salts. Although stable at polymerization temperatures of 150–210 °C, low solubility of the monomers and the formed polymers resulted in very modest molecular weights unsuitable for membrane fabrication. Exchange of the counterion from a metal salt to a tetralkyl ammonium salt gave (Scheme 4) monomers that melted below the polymerization temperatures, allowing polymerizations to be run neat (Scheme 5). This led to higher molecular weight polymers that could be formed into clear, flexible, freestanding films.

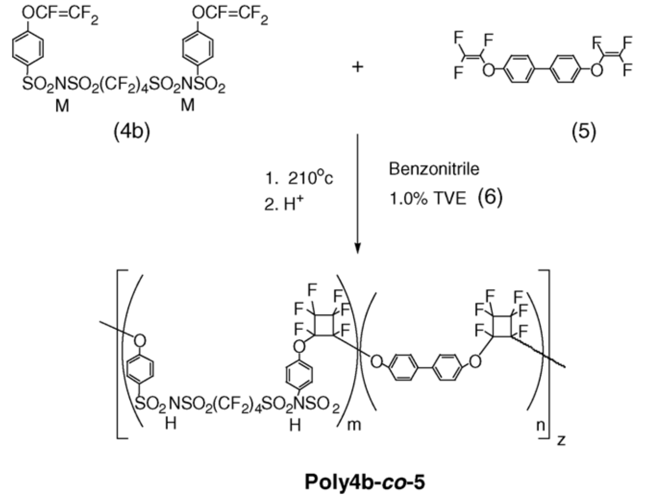
The molecular weight of the polymers obtained in this research could not be readily determined by GPC. In other unpublished work, a polymerization of **4a** as the N-methyl derivative was carried out [19]. Under similar conditions, the resultant polymer had $M_w = 50{,}000$ and $M_n = 20{,}000$ by GPC. We believe it is fair to assume that polymers **7a–c** are in this range and that **8a–c** have higher values.

Differential scanning calorimetry (DSC) of monomers (Fig. 2) as the tetraalkyl ammonium salts show the expected thermal transitions. Monomer melts are typically observed between room temperature and 100 °C which is well below the exothermic transition for the cyclopolymerization which begins at about 150 °C with a T_{max} near 244 °C. This is consistent with the literature of other aryl trifluorovinyl ether monomers [9]. These polymerizations can also be monitored by ^{19}F NMR. Following the conversion from monomer to polymer allows one to monitor the degree of polymerization to obtain suitable molecular weights for film formation (Fig. 3; Scheme 5).

The copolymerization of sulfonimide polymers were also carried out with nonfunctionalized PFCB monomers (Scheme 6), such as 1,1,1-tris(4-trifluorovinyloxyphenyl)-ethane **6** and 4,4′-(trifluorovinyloxy)biphenyl **5** to obtain polymers of various equivalent weights. These copolymers were prepared with equivalent weights from 1100 to 1260,



Scheme 5. Polymerization of sulfonimide containing monomers **4a–c**.



Scheme 6. Copolymerization of sulfonimide containing monomers.

as determined by NMR. The trifunctional monomer, 2,4,6-[(trifluorovinyl)oxy]toluene, was added as a 1% comonomer for improved branching sites in the polymer. The resulting polymers could be dissolved in tetrahydrofuran and films obtained by solution casting onto a silicon wafer. Thermal analysis of different equivalent weight copolymers (**poly4b-*co*-5**) in the acid form indicated T_g values ranging from 118 to 141 °C and thermal stabilities up to 300 °C (Fig. 4). Membrane conductivities (two point probe cell with Pt foil electrodes) were measured giving results approaching that of 1100 EW Nafion® ($\times 10^{-1}$ S cm^{-1}).

3. Experimental

3.1. General information

^{1}H NMR (200 MHz) and ^{19}F NMR (188 MHz) spectra were obtained on a Bruker AC 200 spectrometer system. Chloroform-d and acetonitrile-d_6 were used as solvents and chemical shifts were referenced to residual ^{1}H and internal $CFCl_3$. NMR was used as the primary criteria for purity of starting materials and compounds. The very characteristic ^{1}H and ^{19}F NMR signals for starting materials and products allows easy detection of impurities at the 0.5% level or less.

Infrared spectra were obtained on a Perkin-Elmer 2000 series FT-IR using Spectrum for Windows software. Solid samples were analyzed as KBr pellets. Liquids were run as film between two KCl plates and polymer samples were run as freestanding films.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were obtained on Perkin-Elmer 7 Series instruments. DSC samples were run in SS pans under a nitrogen atmosphere at a scan rate of 10 °C min^{-1}. TGA analyses were run at 10 °C min^{-1}, in nitrogen.

4-[(Trifluorovinyl)oxy]bromobenzene (**1**) was prepared by published methods [7] and tris(trifluorovinyloxyphenyl)ethane, TVE (**6**) and 4,4′-(trifluorovinyloxy)biphenyl (**5**) were generously donated by Dow Chemical Company. PFCB intermediates, monomers, and polymers, are now commercially available from Tetramer Technologies, LLC and distributed by Oakwood Chemicals, Inc., Columbia, SC (see: http://www.oakwoodchemical.com). All other starting materials, reagents and solvents were obtained from commercial sources and used as received unless otherwise noted.

3.2. 4-(Trifluorovinyloxy)benzenesulfonyl chloride (*2*)

In a 2-neck 250 mL roundbottom flask purged with nitrogen, 20 g (79.05 mmol) of **1** was added to 50 mL of dry ether. The solution was cooled to −80 °C. Over 30 min, 52 mL (86.96 mmol) of 1.7 M *t*-butyl lithium was slowly added by syringe. The solution was allowed to stir for 2 h at −80 °C. This solution was then added dropwise, using vacuum/nitrogen flow techniques, through a double ended needle into a separate 2-neck 250 mL roundbottom flask containing 25 mL of ether and 25 g (212 mmol) of FSO_2Cl

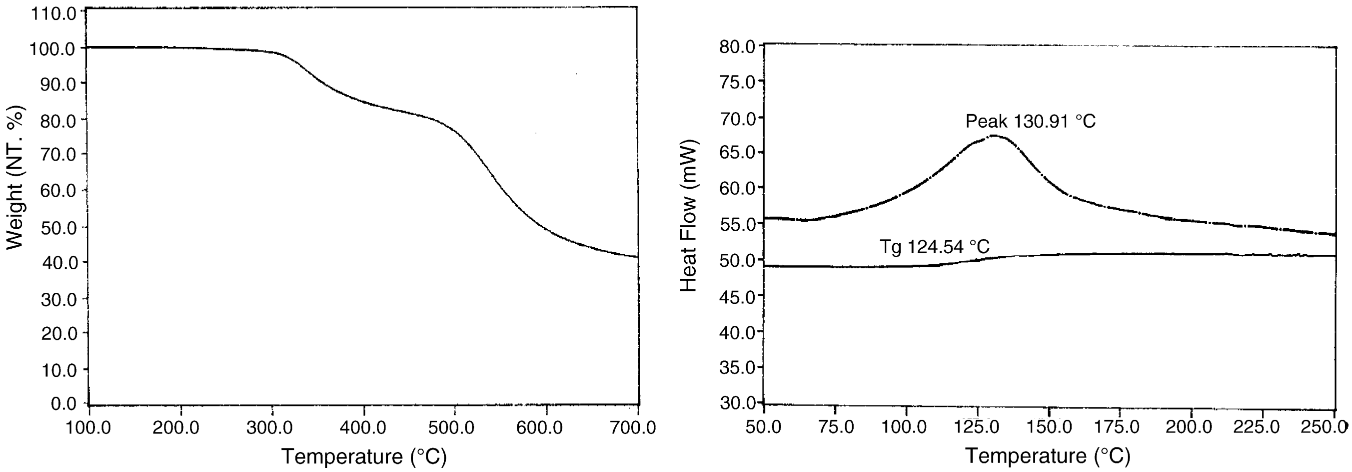
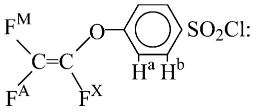


Fig. 4. (a) TGA of copolymer **8b** (1100 equiv. weight) in nitrogen (10 °C min^{-1}). (b) DSC of Copolymer **8b** (1100 equiv. wt.) at 10 °C min^{-1} showing first and second heating curves.

cooled to −80 °C. The mixture was allowed to stir at −80 °C for 10 min. Then, as the mixture was flash warmed in air, 50 mL of deionized water was added to the flask to neutralize any remaining lithium intermediate. The mixture was then allowed to warm to 22 °C. The organic and aqueous layers were separated using a separatory funnel. The product was vacuum distilled (10^{-2} Torr) at 100 °C giving 14 g of clear liquid **2** in 65% yield.

2,

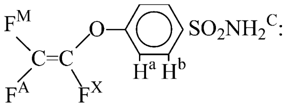


^{19}F NMR ($CDCl_3$) AMX δ −116.69 (A, 1F, d-d), $J_{am} = 94$ Hz, $J_{ax} = 60$ Hz; δ −123.35 (M, 1F, d-d), $J_{am} = 94$ Hz, $J_{mx} = 111$ Hz; δ −135.54 (X, 1F, d-d), $J_{ax} = 60$ Hz, $J_{mx} = 111$ Hz. ^{1}H NMR δ 8.05 (H^b, 2H, d), δ 7.28 (H^a, 2H, d) $J_{ab} = 9$ Hz.

3.3. *4-(Trifluorovinyloxy)benzenesulfonyl amide (**3**)*

In a 100 mL roundbottom flask, 10 g (36.8 mmol) of **2** was placed under vacuum (10^{-2} Torr) and cooled to −196 °C. Liquid ammonia (40 mL) was then condensed into the flask. The mixture was allowed to warm to room temperature under a nitrogen purge, allowing the excess ammonia to boil off. To the remaining solids, 25 mL of acetone was added and the mixture was filtered to remove ammonium chloride. The acetone was then removed from the filtrate by rotoevaporation and the solid was dried under dynamic vacuum giving 8.5 g of **3** in 91% yield.

3,

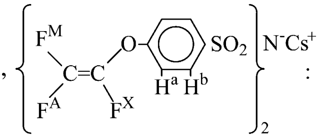


^{19}F NMR (CD_3CN) AMX δ −118.13 (A, 1F, d-d), $J_{am} = 98$ Hz, $J_{ax} = 58$ Hz; δ −125.38 (M, 1F, d-d), $J_{am} = 98$ Hz, $J_{mx} = 109$ Hz; δ −135.49 (X, 1F, d-d), $J_{ax} = 58$ Hz, $J_{mx} = 109$ Hz. ^{1}H NMR δ 7.92 (H_b, 2H, d), δ 7.34 (H^a, 2H, d) $J_{ab} = 9$ Hz, δ 5.69 (H^c, 2H, s).

3.4. *1,1-Bis[4-(trifluorovinyl)oxyphenyl sulfonyl]imide Cesium salt (**4a**)*

In a 50 mL roundbottom flask, 5 g (19.8 mmol) of **3** and 20 mL of dry acetonitrile were added and allowed to stir at room temperature. To the solution, 5 g (38.75 mmol) of diisopropylethylamine was added and allowed to stir for 20 min followed by the dropwise addition of 5 g (19.8 mmol) of **2**. After 24 h stirring at room temperature, 20 mL of 35% HCl was added followed by 20 mL of ether. Using a seperatory funnel, the aqueous and organic layer were separated. To the ether layer 50 mL of an aqueous solution of cesium carbonate was added producing a white precipitate. The precipitate was filtered and washed several times with water and methylene chloride. The solid was then dried under dynamic vacuum at 80 °C for 14 h, giving 8.5 g of pure **4a** in 85% yield.

4a,



^{19}F NMR (CD_3OD) δ −118.41 (A, 1F, d-d), $J_{am} = 95$ Hz, $J_{ax} = 59$ Hz; δ −125.34 (M, 1F, d-d), $J_{am} = 95$ Hz, $J_{mx} = 109$ Hz; δ −135.04 (X, 1F, d-d), $J_{ax} = 59$ Hz, $J_{mx} = 109$ Hz. ^{1}H NMR δ 7.65 (H_b, 2H, d), δ 7.05 (H_a, 2H, d) $J_{ab} = 8.75$ Hz. IR (cm^{-1}) (KBr pellet) 3520–3250 (br); 1836 (m); 1667 (m); 1593 (m); 1491 (m); 1405 (sh); 1319 (s); 1277 (s); 1082 (s); 1036 (s); 829 (s); 802 (s).

Crystals of **4a** (Cs^+) for X-ray were obtained from CH_3CN. The crystallographic data is given in Table 1. The structure is shown in Fig. 1 (see Section 2).

Table 1
Crystallographic data

Crystal data	
Empirical formula	$C_{16}H_8NO_6F_6S_2Cs$
Formula weight (g mol^{-1})	621.26
Color; habit	Colorless, plate
Size (mm)	0.20 × 0.20 × 0.10
Space group	Monoclinic, $P2_1/c$ (#14)
Unit cell dimensions	
a (Å)	22.903(2)
b (Å)	13.7310(13)
c (Å)	6.3690(6)
β (°)	95.772(3)
V (Å^3)	1992.7(3)
Formula units/cell	4
D_{calc} (g cm^{-3})	2.071
$F(0\,0\,0)$	1200
Data collection[a]	
Unit cell reflections	14624 ($I \geq 5\sigma(I)$)
2θ range	5.4–52.7°
Scan type	ω/0.5° frames
Scan speed	30 s/frame (two scans)
Reflections collected	19232
Reflections unique (R_{int})	4043 (0.107)
Indices	(±28,±17,±7)
Crystal decomposition	Negligible (±1%)
Absorption coefficient	2.159 mm^{-1}
Min./max. transmission	0.40/1.00
Refinement[a]	
Final residuals ($I > 2\sigma(I)$)	$R_1 = 0.0617$; $wR_2 = 0.1425$
Final residuals (all data)	$R_1 = 0.1266$; $wR_2 = 0.748$
Goodness-of-fit	$S = 1.022$
Largest Δ/σ	0.004
Reflections used (observed)	4043 (2504)
Parameters refined	307
Data-to-parameter ratio	13.2:1
Max./min. difference peaks	1.09/−1.13 e$^-$/Å^3

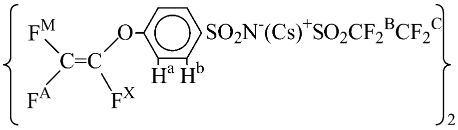
[a] Rigaku AFC8/Mercury CCD; graphite monochromated Mo Kα radiation (λ = 0.71073 Å); temperature = 20 ± 1 °C; solved by direct methods, refined using full-matrix least-squares on F^2(SHELXTL PLUS).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center: CCDC 262537 (**4a**). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (http://www.ccdc.cam.ac.uk/conts/retrieving).

*3.5. 1,1′-Bis[4-(trifluorovinyl)oxyphenylsulfonyl]-1,4-(disulfonyl octafluorobutyl) diimide Dicesium salt (**4b**)*

In a 50 mL roundbottom flask, 5 g (19.8 mmol) of **3** and 20 mL of dry acetonitrile were added and allowed to stir at room temperature. To this solution, 10 g (77.31 mmol) of diisopropylethylamine was added and allowed to stir for 20 min, followed by the dropwise addition of 2.9 g (8.0 mmol) of 1,4-di(sulfonyl-fluoride)octafluorobutane. After 24 h of stirring at room temperature, 20 mL of 35% HCl was added followed by 20 mL of ether. Using a seperatory funnel, the aqueous and organic layer were separated, and 50 mL of an aqueous solution of cesium carbonate was added to the ether layer producing a white precipitate. The precipitate was filtered and washed several times with water and methylene chloride. The solid was then dried under dynamic vacuum at 80 °C for 14 h, giving 6.8 g of **4b** in 80% yield.

4b,

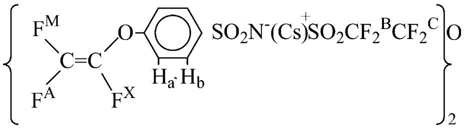


^{19}F NMR (CD$_3$CN) δ −119.25 (C, 4F, s); δ −112.21 (B, 4F, s); AMX δ −118.70 (A, 1F, d-d), J_{am} = 98 Hz, J_{ax} = 58 Hz; δ −125.77 (M, 1F, d-d), J_{am} = 98 Hz, J_{mx} = 110 Hz; δ −135.05 AMX (X, 1F, d-d), J_{ax} = 58 Hz, J_{mx} = 110 Hz. ^{1}H NMR δ 7.91 (H$_b$, 2H, d), δ 7.25 (H$_a$, 2H, d) J_{ab} = 8.9 Hz. IR (cm^{-1}) (KBr pellet) 3098 (s); 2997 (s); 1836 (m); 1591 (m); 1486 (m); 1395 (sh); 1326 (s); 1276 (s); 1196 (s); 1144 (s); 1092 (sh); 1053 (sh); 842 (m); 793 (m) cm^{-1}.

*3.6. 1,1′-Bis[4-(trifluorovinyl)oxyphenylsulfonyl]-1,5-(disulfonyl octafluoro-3-oxopentyl) diimide Dicesium salt (**4c**)*

In a 50 mL roundbottom flask, 5 g (19.8 mmol) of **3** and 20 mL of dry acetonitrile were added and allowed to stir at room temperature. Ten grams (77.3 mmol) of diisopropylethylamine was added to the solution and it was stirred for 20 min, followed by the dropwise addition of 2.9 g (8.0 mmol) of 1,5-di(sulfonylfluoride)-3-oxo-octafluoropentane. After 24 h of stirring at room temperature, 20 mL of 35% HCl was then added, followed by 20 mL of ether. Using a seperatory funnel, the aqueous and organic layers were separated. Fifty microliters of an aqueous solution of cesium carbonate was added to the ether layer producing a white precipitate. The precipitate was filtered and washed several times with water and methylene chloride. The solid was then dried under dynamic vacuum at 80 °C overnight, giving 6.8 g of pure **4c** in 80% yield.

4c, **4c**



^{19}F NMR (CD$_3$CN) δ −80.35 (C, 2F, s); δ −115.58 (B, 2F, s); AMX δ −118.74 (A, 1F, d-d), J_{am} = 98 Hz, J_{ax} = 58 Hz; δ −125.72 (M, 1F, d-d), J_{am} = 98 Hz, J_{mx} = 109 Hz; δ −134.98 (X, 1F, d-d), J_{ax} = 58 Hz, J_{mx} = 109 Hz; δ 66.59 (1F, s) ^{1}H NMR δ 7.93 (H$_b$, 2H, d), δ 7.25 (H$_a$, 2H, d) J_{ab} = 8.9 Hz. IR (cm^{-1}) (KBr pellet) 3103 (s); 2997 (s); 1839 (s); 1594 (m); 1489 (m); 1324 (sh); 1280 (s); 1197 (s); 1147 (s); 1091 (sh); 1008 (m); 845 (m); 788 (s) 684 (m) cm^{-1}.

*3.7. Conversion of **4a–c** (Cs) to **4a–c** (Et$_4$N)*

Each of the monomers was exchanged from the Cs salt to the Et$_4$N salt by reaction with aqueous Et$_4$NBr. In a typical procedure **4c** (Cs) (5.0 g, 4.5 mmol) was added to 30 mL of 0.96 M Et$_4$NBr in 100 mL beaker. This mixture was stirred at 80 °C for 6 h and the liquid decanted at 22 °C. An additional 30 mL of 0.96 M Et$_4$NBr was then added and stirred for 6 h at 80 °C. The mixture was filtered and the white solid was washed with a small portion of distilled water. Drying under dynamic vacuum for 12 h at 50 °C gave **4c** (Et$_4$N) in essentially quantitative yield. The ^{19}F NMR for **4a–c** (Et$_4$N) was identical to **4a–c** (Cs). The ^{1}H NMR was identical except for characteristic Et$_4$N peaks: δH 1.19 (12 H, t), δ 3.16 (8H,q), $^3J_{HH}$ = 7.3 Hz.

*3.8. Homopolymerization of monomers **4a–c** (Et$_4$N) to polymers **7a–c***

Bulk polymerization of monomers **4a–c** (1.0 g) as the Et$_4$N salts (see Scheme 4), were carried out neat in a flask under nitrogen for 8 h at 175 °C and then heating at 210 °C for an additional 16 h. Upon cooling, the polymers were recovered and boiled two times in 50% nitric acid for 30 min. The polymers were washed with deionized water until neutral with subsequent boiling for 1 h in deionized water. The resulting polymers were then dried under vacuum (10^{-2} Torr) at 100 °C giving essentially a quantitative yield of polymers **7a–c** (see Scheme 5).

- **7a** (H$^+$) ^{19}F NMR (CD$_3$CN/DMSO) cyclobutyl-F$_6$ at δ −125.71, −126.30, −126.91, −127.48, −128.24, −128.86, −129.11, −129.43, −130.60, −131.16, −132.04, −132.5 ^{1}H NMR δ 7.91 (H$_b$, b), δ 7. 36 (H$_a$, b).
- **7b** (H$^+$) ^{19}F NMR (CD$_3$CN) δ −112.50 (4F, s), δ −119.84 (4F, s), cyclobutyl-F$_6$ at δ −127.73, −128.13, −128.93, −129.46, −130.12, −130.72, −130.97, −131.30, −131.48 ^{1}H NMR δ 7.88 (H$_b$, b), δ 7. 38 (H$_a$, b).
- **7c** (H$^+$) ^{19}F NMR (CD$_3$CN) δ −80.35 (4F, s), δ −115.60 (4F, s), cyclobutyl-F$_6$ at δ −127.73, −128.13, −128.93,

$-129.46, -130.12, -130.72, -130.97, -131.30, -131.48$ ^{1}H NMR δ 7.90 (H_b, b), δ 7. 36 (H_a, b).

*3.9. Copolymerization of Monomers **4a–c** (Et_4N) to polymers **8a–c***

A typical copolymerization was carried out in a 100 mL roundbottom flask equipped with a mechanical stirrer and a nitrogen purge. The functionalized monomer **4a–c** (Et_4N) was added with unfunctionalized monomer **5** and 1% of trifunctional monomer **6** in appropriate amounts to obtain the desired equivalent weights. In a typical run, 1.0 g of **4b** (0.92 mmol), 1.4 g of **5** (4.05 mmol) and 1% of **6** (0.46 mmol) were allowed to react. The reaction vessel was stirred at 75 rpm and heated to 175 °C for 16 h. Fifty percent (w/w) of benzonitrile was added to the flask and the temperature was increased to 210 °C for an additional 24 h. The benzonitrile was then removed under vacuum (10^{-2} Torr). Upon cooling, the polymer was recovered and boiled two times in 50% nitric acid for 30 min. The polymer was then washed with deionized water until neutral with subsequent boiling in deionized water for 1 h. The resulting polymer was vacuum dried (10^{-2} Torr) at 100 °C giving an essentially quantitative yield of **8b** (1100 equiv. weight).

- **8a** (H^+) ^{19}F NMR (CD_3CN) δ -111.35 (4F, b), δ -118.53 cyclobutyl-F_6 at δ -126.0 through -134.0, ^{1}H NMR δ 7.21 (H_c, b), δ 7.54 (H_a, 2H, b), δ 7.90 (H_b, b).
- **8b** (H^+) ^{19}F NMR (CD_3CN) δ -111.35 (4F, b), -111.35 cyclobutyl-F_6 at δ -126.0 through -134.0, ^{1}H NMR δ 7.21 (H_c, b), δ 7.54 (H_a, 2H, b), δ 7.90 (H_b, b).
- **8c** (H^+) ^{19}F NMR (CD_3CN) δ -111.35 (4F, b), -111.35 cyclobutyl-F_6 at δ -126.0 through -134.0, ^{1}H NMR δ 7.21 (H_c, b), δ 7.54 (H_a, 2H, b), δ 7.90 (H_b, b).

4. Conclusions

An aryl lithium intermediate containing the trifluorovinyl ether group was prepared and utilized to obtain a key sulfonyl chloride starting material. The latter allowed the synthesis of polymerizable trifluorovinyl aryl ethers containing the sulfonimide function. Thermal bulk cyclopolymerization of these monomers yielded the first examples of sulfonimide containing perfluorocyclobutane polymers as clear, flexible, freestanding films. Analyses of these polymers show good thermal stability, and conductivities approaching that of other ionomeric materials, such as Nafion®. Sulfonimide-containing PFCB polymers clearly provide a versatile platform for a new ionomeric materials useful for fuel cells and other electrochemical applications.

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