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Synthesis of sulfonate ester and sulfonic acid-containing poly(arylene perfluorocyclobutane)s (PFCB) by direct copolymerization of a sulfonate ester-containing precursor

Catherine Marestin*, Xavier Thiry, Sergio Rojo, Edouard Chauveau, Regis Mercier

Université de Lyon, Univ Lyon 1, CNRS, Ingénierie des Matériaux Polymères (IMP-UMR 5223), 15 Boulevard Latarjet, 69622, Villeurbanne, France

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ABSTRACT

This paper reports the first synthesis of sulfonated poly(arylene perfluorocyclobutane)s by direct polycondensation of a new sulfonate ester-containing bis(trifluorovinylether) precursor and subsequent hydrolysis of the resulting polymers. The multi-step synthesis of a bis(trifluorovinylether) monomer bearing sulfonic acid groups protected as sulfonate esters (SE-TFVE) is described. Based on this precursor and 4,4′-bis(trifluorovinyloxy)biphenyl (4,4′-TFVE), sulfonate ester-containing poly(arylene perfluorocyclobutane) copolymers (SE-PFCB) were synthesized by $2\pi + 2\pi$ step-growth cyclopolymerization. Their thermal and physico-chemical properties were characterized. Free acid polymers (SA-PFCB) were subsequently obtained by hydrolysis of sulfonate ester groups. A preliminary evaluation of the proton conductive properties of these polymers is reported.

1. Introduction

Due to their specific thermal and chemical properties, poly(arylene perfluorocyclobutane)s (PFCB) are considered as high performance engineering materials for many applications [1–3]. The incorporation of proton conducting groups in such macromolecular structures has recently been investigated for the development of fuel cell membranes [4–6]. Proton conducting PFCB are typically obtained by post-modification reactions of readily available PFCB structures. The incorporation of sulfonic acids as proton conducting groups is most often achieved by direct sulfonation [7–9], but other reactions have been used such as bromation and subsequent Ullman coupling reactions [10,11], acylation and nucleophile substitution, or metallation and reaction with 1,3-propanesultone [12]. In order to control the final polymer microstructure (the polymer ionic exchange capacity (IEC, meq H^+g^{-1}) as well as the incorporation of the sulfonic groups along the macromolecular backbone), most reported post-modification reactions are performed on block PFCB precursor polymers bearing specific sequences prone to post-modification [9,13,14].

The direct polycondensation of a sulfonic acid-containing bistrifluorovinyl precursor appears as a particularly attractive alternative as it permits a better control of the sulfonic acid groups incorporated in the polymer chains and gives access to a wide range of sulfonated poly(arylene perfluorocyclobutane)s structures. Very few examples have however been reported yet [15,16]. One probable reason is associated to synthetic difficulties. The classical sulfonation reactions of bistrifluorovinyl ether monomers are known to be unsuccessful [6], because of the significant formation of undesirable by-products. An alternative approach which consists in the sulfonation of fluoroalkylated precursors and the subsequent formation of trifluorovinyl groups has been addressed. In this case, sulfonated fluoroalkylated compounds are isolated in good yields. However, their transformations into trifluorovinyl ether compounds were unfortunately hampered by the presence of sulfonic acid groups and the excessive formation of hydrogenated compounds was observed. When the elimination reaction is performed on substrates bearing different sulfonic acid salts (in their sodium, potassium or ammonium form), the elimination reaction was ineffective, probably because of the fair solubility of the reactants in the reaction medium. Such synthetic difficulties have also been reported by other authors [6]. To the best of our knowledge, only 3 patents from LG [16], General Motor [15] and 3 M [17] claim the synthesis of functionalized bistrifluorovinyl ether monomers, either in their sulfonic acid potassium salt form or as fluorosulfonyl analogues. However, no high molecular weight polymers

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* Corresponding author.
E-mail address: Catherine.marestin@univ-lyon1.fr (C. Marestin).

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synthesized by direct $2\pi + 2\pi$ cyclodimerisation of such monomers are reported.

Therefore, the strategy described in this article for the synthesis of sulfonic acid-containing PFCB is different: we describe the multistep synthesis of a bis(trifluorovinyl ether) precursor containing sulfonic acids groups protected as sulfonate esters (SE-TFVE). A series of sulfonate ester-containing poly(arylene perfluorocyclobutane)s (SE-PFCB) are synthesized by direct polycondensation of this monomer with 4,4′-bis(trifluorovinyloxy) biphenyl (4,4′-TFVE). Subsequent hydrolysis of the resulting polymers affords sulfonic acid containing PFCB (SA-PFCB).

2. Experimental part

2.1. Materials

Dimethyl sulfoxide (DMSO) was distilled under reduced pressure. Acetonitrile was dried over NaH and distilled. Zinc was activated before use. (Zinc dust was rapidly washed with 0.1 M hydrochloric acid, filtered, and successively washed with demineralised water, acetone and diethyl ether). It was then dried under vacuum, at 140 °C for 12 h. All other chemicals were used as received unless otherwise stated. Dibromotetrafluoroethane was kindly provided by ERAS Labo.

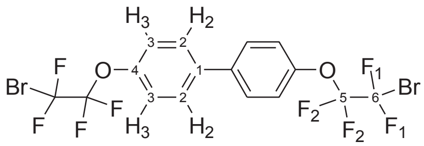
2.2. Characterization methods

^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on a Brucker Avance 200 operating at the following resonance frequencies: 200 MHz for ^{1}H, 50 MHz for ^{13}C and 188 MHz for ^{19}F, and on a Brucker Avance 400 spectrometer operating at the following resonance frequencies: 400.16 MHz for ^{1}H, 100.63 MHz for ^{13}C and 376.48 MHz for ^{19}F. Tetramethylsilane (TMS) and $CFCl_3$ were used as chemical shift references. Thermogravimetric analyses (TGA) were performed with a TA Q50 Instrument, under nitrogen and at 10 °C.min^{-1}. The polymer glass transition temperature of polymers was determined by Differential Scanning Calorimetry (DSC), with a DSC 822e Mettler Toledo equipment under argon, at 5 °C.min^{-1}. The reported values were determined after a second heat scan, by the midpoint method. Molecular weights were determined by Size Exclusion chromatography (SEC) on a system equipped with a Shimadzu LC-20AD pump and a differential refractive index detector. THF was used as eluent. SEC analyses were achieved with Waters Styragel columns (HR2+HR1+HR0.5). Reported values ($M_{n(PS)}$ and $M_{w(PS)}$) are determined from a polystyrene calibration curve.

2.3. Monomer synthesis

2.3.1. Synthesis of 4,4′-bis(2-bromo-tetrafluoroethoxy)biphenyl (FABP)

12 g (64 mmol) of 4,4’-dihydroxybiphenyl were suspended in 94.8 mL of 1.48 mol l^{-1} potassium methoxide solution in methanol, in a 250 mL round-bottom flask equipped with a condenser and a magnetic stirrer. The mixture was refluxed for 4 h. The solvent was evaporated to dryness and the crude powder was dried under vacuum at 120 °C for 12 h. The resulting dried bisphenate was suspended in 30 mL of dried DMSO in a three-necked reactor equipped with a mechanical stirrer and a nitrogen inlet. A solution of 19 mL (140.8 mmol) of 1,2-dibromotetrafluoroethane (DBFE) dissolved in 20 mL of dried DMSO was added dropwise over 3 h to the bisphenate. During the addition, the reaction mixture was slightly cooled by a water bath, so that temperature did not exceed 20 °C. The mixture was then heated at 50 °C for a night. After cooling, the mixture was poured into 100 mL of brine and extracted with dichloromethane. The organic solvent was concentrated and the residue was dissolved in 100 mL of n-hexane. Insoluble impurities were filtered off and the solvent was evaporated to dryness. The crude powder was purified by column chromatography with petroleum ether as eluent, affording 27 g (70% yield) of a white crystalline powder.



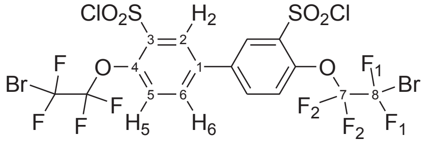
(FABP)

^{19}F NMR (DMSO-d_6, 188 MHz): δ −70.15 (t, F_1, J_{F1-F2} = 5.6 Hz), −85.29 (t, F_2, J_{F2-F1} = 5.6 Hz). ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.82 (d, $4H_2$, J_{H-H} = 8.0 Hz), 7.43 (d, $4H_3$, J_{H-H} = 8.0 Hz). ^{13}C RMN (DMSO-d_6, 50 MHz): δ 147.66 (C_4), 137.92 (C_1), 128.73 (C_2), 121.92 (C_3).

2.3.2. Synthesis of 4,4′-bis(2-bromo-tetrafluoroethoxy)-3,3′-bis(chlorosulfonyl)-biphenyl (CSFABP)

A 250 mL reactor equipped with a condenser and a magnetic stirrer was charged with 10 g (13.5 mmol) of 4,4′-bis(2-bromo-tetrafluoroethoxy) biphenyl dissolved in 30 mL of 1,2-dichloroethane. 40 mL (600 mmol) of chlorosulfonic acid were added dropwise.

The mixture was stirred at 90 °C for 20 min. The evolution of the reaction was monitored by ^{19}F NMR. After completion of the reaction, the mixture was added dropwise to 200 mL of ice-water and the product was extracted with dichloromethane. The organic phases were collected and concentrated. After crystallization in chloroform/ethanol (50/50), 8.75 g (60% yield) of pure compound were isolated.

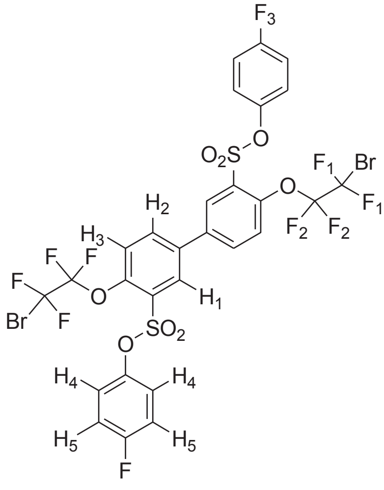


(CSFABP)

^{19}F NMR (DMSO-d_6, 188 MHz): δ −68.09 (t, F_1), −82.55 (t, F_2). ^{1}H NMR (DMSO-d_6, 200 MHz): δ 8.06 (d, $2H_2$, J_{H2-H6} = 2.2 Hz), 7.69 (dd, $2H_6$, J_{H6-H5} = 8.6 Hz, J_{H6-H2} = 2.2 Hz), 7.43 (d, $2H_5$, J_{H-H} = 8.6 Hz). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 144.72 (C_4), 140.54 (C_1), 136.09 (C_3), 128.17 (C_2), 127.28 (C_6), 121.27 (C_5).

2.3.3. Synthesis of 4,4′-bis(2-bromo-tetrafluoroethoxy)-3,3′-bis(4-fluorobenzenesulfonate)-biphenyl (SE-FABP)

In a 100 mL round-bottom flask equipped with a magnetic stirrer and an addition funnel, were placed 3.49 g (30.8 mmol, 2.2 equivalents) of 4-fluorophenol, 0.32 g (2.8 mmol, 0.2 equivalents) of diazabicyclooctane (DABCO) and 12 mL of dichloromethane. The mixture was cooled at 0 °C in an ice water bath and 3.8 mL (22 mmol, 2 equivalents) of triethylamine were added. 10.39 g (14 mmol, 1 equivalent) of 4,4'-bis(2-bromo-tetrafluoroethoxy)-3,3'-bis(chlorosulfonyl)-biphenyl dissolved in 25 mL of dichloromethane were added dropwise. The evolution of the reaction was monitored by ^{19}F NMR. After completion of the reaction the organic phase was washed with demineralised water, dried over sodium sulfate, filtered and the solvent was evaporated. The yellow crude solid was refluxed in petroleum ether. The product was collected by filtration, rinsed with petroleum ether and dried under vacuum at 130 °C giving 11.46 g of a white powder (92% yield).

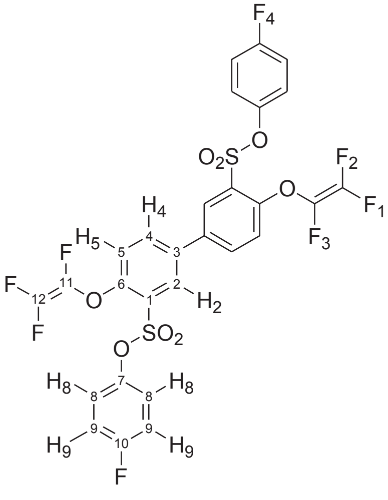


(SE-FABP)

^{19}F NMR (DMSO-d_6, 188 MHz): δ −70.13 (t, F_1), −84.48 (t, F_2), −113.97 (s, F_3). ^{1}H NMR (DMSO-d_6, 200 MHz): δ 8.25 (dd, 2H_2, $J_{H2\text{-}H3}$ = 8.8 Hz), 8.105 (d, 2H_1), 7.90 (d, 2H_3, $J_{H3\text{-}H2}$ = 8.8 Hz), 7.31–7.11 (m, 8 H, H_4 and H_5).

2.3.4. Synthesis of 4,4′-bis(trifluorovinyloxy)-3,3′-bis(4-fluorobenzensulfonate)-biphenyl (SE-TFVE)

11.46 g (12.84 mmol) of 4,4'-bis(2-bromo-tetrafluoroethoxy)-3,3'-bis(4-fluorobenzenesulfonate)-biphenyl, 3 g (44.96 mmol) of actived zinc and 60 mL of dry acetonitrile were placed in a high-pressure reactor equipped with a magnetic stirrer, a temperature sensor and a pressure sensor. The reaction mixture was heated at 110 °C. After completion of the reaction (monitored by ^{19}F NMR), the excess of zinc and salts formed were filtered and washed with diethyl ether. 100 mL of demineralised water were added to the filtrate and the mixture was extracted several times with diethyl ether. The organic phase was dried over sodium sulfate, filtered and the solvent was evaporated. The crude yellow oil was purified by chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (90:10). Several successive crystallizations in a hexane/ethyl acetate (78:22) were necessary to obtain a polymer grade monomer as a white solid (5.45 g - 61% yield).

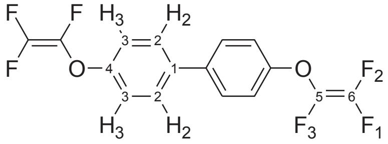


(SE-TFVE)

^{19}F NMR (DMSO-d_6, 376 MHz): δ −116.65 (s, F_4), −118.16 (dd, F_1, $J_{F1\text{-}F2}$ = 93.1 Hz, $J_{F1\text{-}F3}$ = 58.7 Hz), −126.10 (dd, F_2, $J_{F2\text{-}F1}$ = 93.1 Hz, $J_{F2\text{-}F3}$ = 109.2 Hz), −138.47 (dd, F_3, $J_{F3\text{-}F1}$ = 58.7 Hz, $J_{F3\text{-}F2}$ = 109.2 Hz). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.17 (dd, 2H_4, $J_{H4\text{-}H5}$ = 8.8 Hz, $J_{H4\text{-}H2}$ = 2.4 Hz), 8.03 (d, 2H_2, $J_{H2\text{-}H4}$ = 2.4 Hz), 7.86 (dd, 2H_5, $J_{H5\text{-}H4}$ = 8.4 Hz, $J_{H5\text{-}H2}$ = 1.2 Hz), 7.27–7.16 (m, 8 H, H_8 and H_9). ^{13}C NMR (DMSO-d_6, 200 MHz): δ 160.84 (d, C_{10}, $^1J_{C\text{-}F}$ = 506 Hz), 151.44 (C_6), 145.12 (C_7), 136.50 (C_4), 135.08 (C_3), 130.26 (C_2), 124.54 (C_1), 123.89 (d, C_8, $^3J_{C\text{-}F}$ = 18 Hz), 117.22 (d, C_9, $^2J_{C\text{-}F}$ = 48 Hz), 117.22 (C_5).

2.3.5. Synthesis of 4,4′-bis(trifluorovinyloxy)biphenyl (4,4′-TFVE)

To a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer were added 8.24 g (15.15 mmol) of 4,4'-bis(2-bromo-tetrafluoroethoxy) biphenyl, 3 g (45 mmol) of actived zinc and 50 mL of acetonitrile. The mixture was refluxed and the reaction was monitored by ^{19}F NMR. After completion of the reaction, the excess of zinc and salts formed were filtered over celite and washed with diethyl ether. 200 mL of water were added to the filtrate which was extracted several times with diethyl ether. The organic phase was dried over sodium sulfate, filtered and the solvent was removed. The crude product was purified by chromatography on silica gel using petroleum ether as eluent to give 3.15 g of a white solid (60% yield).



4,4’-TFVE

^{19}F NMR (DMSO-d_6, 188 MHz): δ −118.48 (dd, F_1, $J_{F1\text{-}F2}$ = 97.8 Hz, $J_{F1\text{-}F3}$ = 56.4 Hz), −126.36 (dd, F_2, $J_{F2\text{-}F1}$ = 97.8 Hz, $J_{F2\text{-}F3}$ = 109.0 Hz), −134.20 (dd, F_3, $J_{F3\text{-}F2}$ = 109.0 Hz, $J_{F3\text{-}F1}$ = 56.4 Hz). ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.72 (d, 2H_2, $J_{H\text{-}H}$ = 8.0 Hz), 7.36 (d, 2H_3, $J_{H\text{-}H}$ = 8.0 Hz). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 153.74 (C_4), 136.11 (C_1), 128.61 (C_2), 116.12 (C_3).

2.4. Synthesis of polymers

2.4.1. Synthesis of sulfonate ester containing poly(arylene perfluorocyclobutane)s (SE-PFCB)

900 mg (1.296 mmol) of sulfonate ester precursor, 953.3 mg (2.754 mmol) of 4,4′-TFVE and 1.85 g of diphenyl ether were introduced in a Schlenk tube equipped with a mechanical stirrer and a nitrogen inlet. The reaction mixture was heated at 250 °C for 5 h, under nitrogen, in a tubular oven. After cooling, the viscous solution was poured in petroleum ether. The polymer was isolated by filtration, thoroughly rinsed with petroleum ether and dried under vacuum at 100 °C.

2.4.2. Synthesis of sulfonic acid containing PFCB (SA-PFCB)

0.5 g of the SE-PFCB precursor were dissolved in 2 mL of NMP. 2 mL of a potassium methoxide solution in MeOH (1.5 mol L^{-1}) were then added to the polymer solution. The basic hydrolysis of the sulfonate esters (in sulfonic acids, potassium salt form) was monitored by ^{19}F NMR, by direct analysis of the medium. After completion of the reaction, the polymer was precipitated in methanol, isolated by filtration, thoroughly rinsed with methanol and dried under vacuum.

2.5. Membrane preparation

Thin SA-PFCBK films were obtained by conventional solution casting method, from a 20 wt% polymer solution in DMAC. The solutions were cast onto clean glass plates and successively dried overnight at 50 °C, 1 h at 80 °C, 1 h at 120 °C, 1 h at 150 °C and 1 h at 180 °C. The resulting films were peeled off by immersion in water. The membranes were re-acidified by immersion in a 2 M sulphuric acid solution for 12 h and thoroughly rinsed with demineralised water.

2.6. Conductivity measurements

Proton conductivities of the membranes were measured in-plane using the four point probe method, with a Fumatech MK3 conductivity measuring cell equipped with a Gamry 600 potentiostat. A 4 cm by 1 cm membrane of SA-PFCBH was placed in a thermostated cell equipped with a humidity controller and a temperature sensor. Measurements were performed at 95% relative humidity (RH), at 90 °C and over a frequency range of 0.1–10^6 Hz. A first analysis was done after 5 min equilibration and six other measurements were recorded every 10 min.

3. Results and discussion

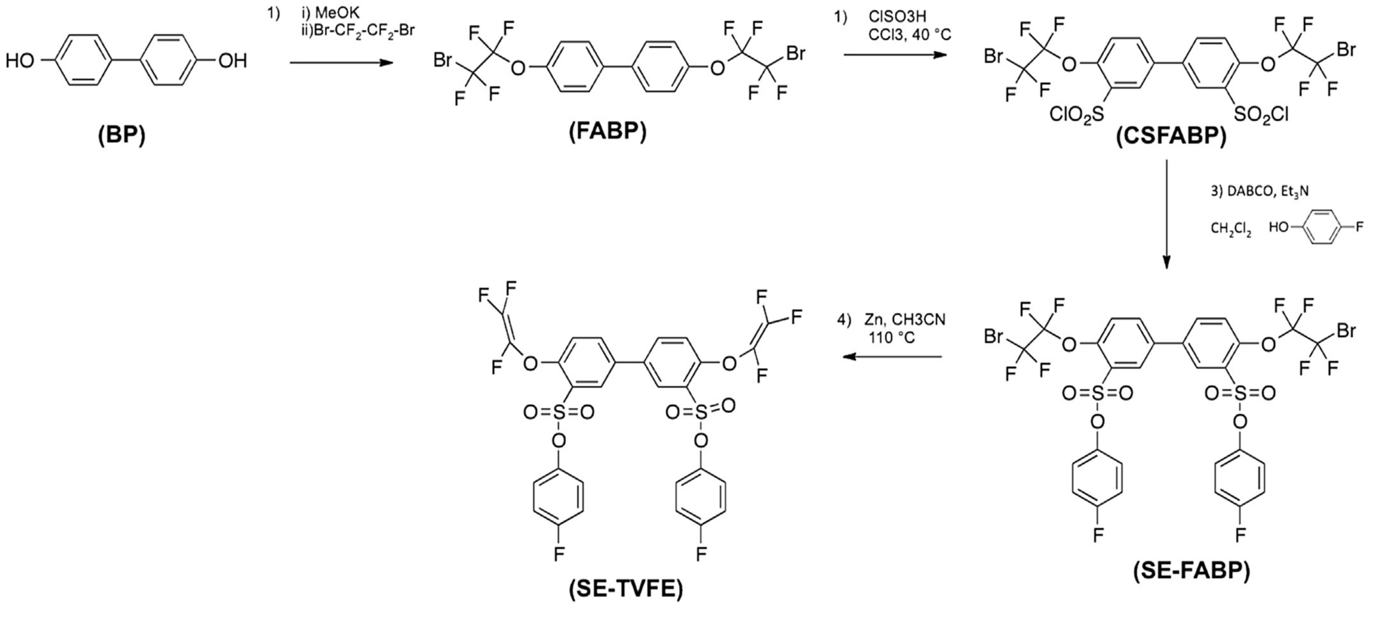
The work described in this article reports the synthesis of a functionalized monomer from a multi-step synthesis, its polymerization affording sulfonate ester-containing PFCB (SE-PFCB), the elaboration of thin membranes from these polymers and a last treatment leading to sulfonic acid-containing PFCB (SA-PFCB). The physico-properties of the resulting polymers are presented.

3.1. Monomer synthesis and characterization

Aromatic sulfonyl chlorides (such as tosyl chloride) are commonly used in organic chemistry as convenient protecting agents for alcohols and phenols [18]. It is well known that cyclohexylarene sulfonate can be thermally cleaved, affording the formation of sulfonic acids containing compounds and cyclohexene in high yields [19]. The thermal decomposition temperature of sulfonate esters depends on the nature of the alcohol involved (sulfonate esters of primary alcohols are more stable than those of secondary or tertiary alcohols [20]. In addition, many sulfonate esters are easily hydrolysed with various chemical agents (NaI, piperidine, NaN_3, HBr, BBr_3, NaOH) [21]. In this case, the deprotection reaction allows the regeneration of the protecting alcohol/phenol and releases a sulfonic acid-containing product. This reaction has therefore recently been considered as an elegant way to protect sulfonic acids as sulfonate esters groups [22]. Different advantages can be expected from this strategy. The use of sulfonate esters-containing monomers can be required if the presence of sulfonic acids is incompatible with the polymerization reaction. It can also facilitate the synthesis and characterization of well-defined sulfonate ester-containing polymer architectures, which are finally hydrolysed in their sulfonic acid-containing analogues. In this way, the synthesis of poly(vinylsulfonate)s has been successfully performed by polymerizing sulfonate ester-containing precursors and by a final hydrolysis of the polymer obtained (LiBr, 2-butanone, 24 h @reflux) [23]. Other authors used a similar method for the synthesis of poly(styrene-bloc styrene sulfonic acid [24,25].

In this work, such a strategy has been considered, with the synthesis of sulfonate ester containing trifluorovinyl ether monomers. Highly pure sulfonate ester-containing bisTFVE monomer (SE-TFVE) was prepared by a four steps procedure, according to the synthetic pathway described in Scheme 1:

The fluoroalkylated biphenol (FABP) was prepared from commercially available 4,4′-biphenol (BP), by formation of a phenoxide and subsequent fluoroalkylation with dibromotetrafluoroethane according to a well-known procedure [3]. FABP was purified by flash chromatography in order to remove any undesirable tetrafluoroethyl ether (Ar-O-CF_2CF_2H) containing by-product formed in this step. Sulfonyl chloride groups were incorporated on this substate in the presence of a large excess of chlorosulfonic acid, affording chlorosulfonated fluoroalkylated biphenol (CSFABP). Because of the electrophilic character of the chlorosulfonation reaction, the sulfonyl chloride groups were easily grafted in ortho position to the ether groups. The expected structure was confirmed



Scheme 1. Multi-step synthesis of sulfonate ester-containing bistrifluorovinyl ether monomer. 1) Fluoroalkylation 2) Chlorosulfonation 3) Protection step 4) Elimination.

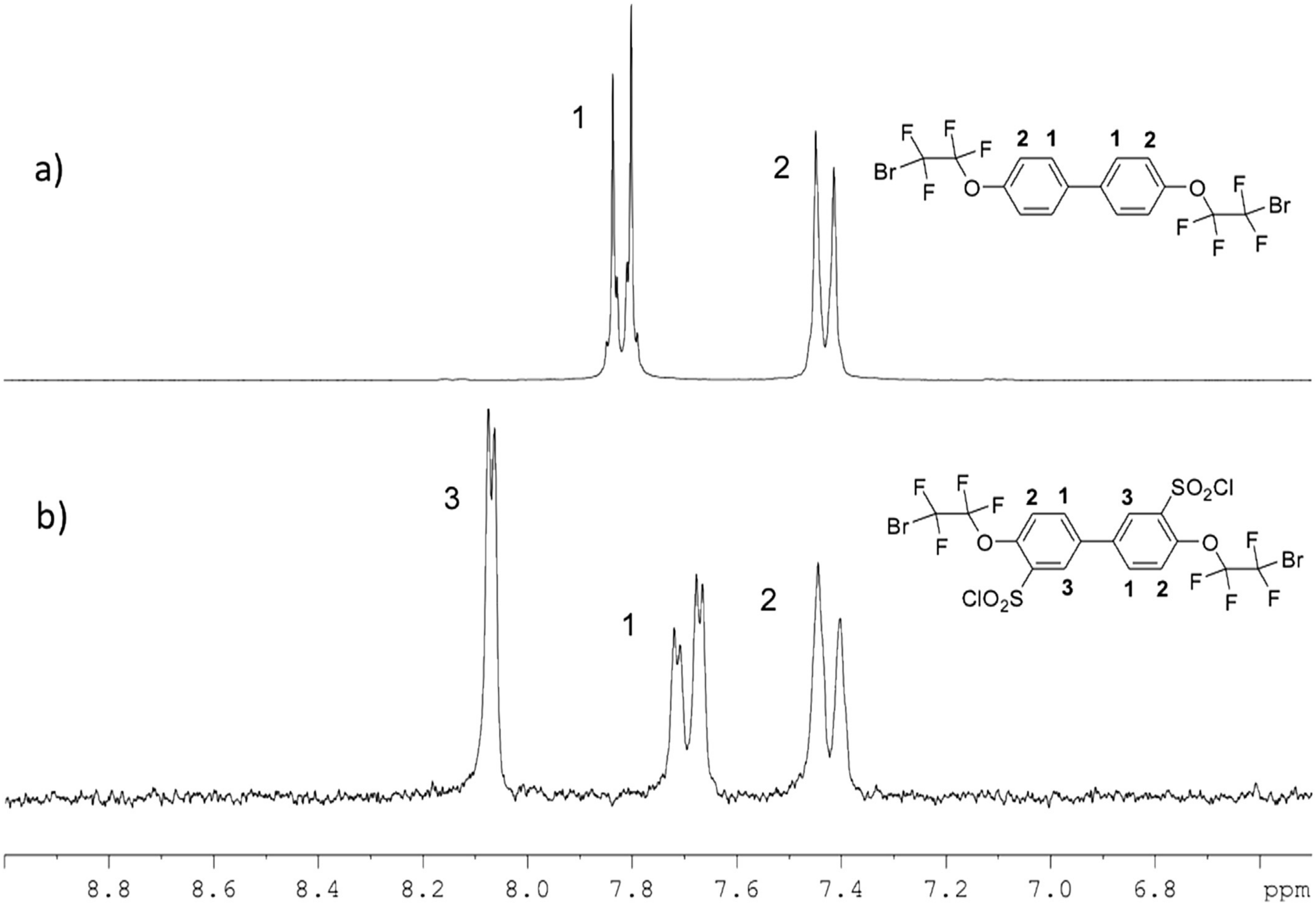


Fig. 1. ^{1}H NMR (DMSO-d_6) of a) FABP, b) CSFABP.

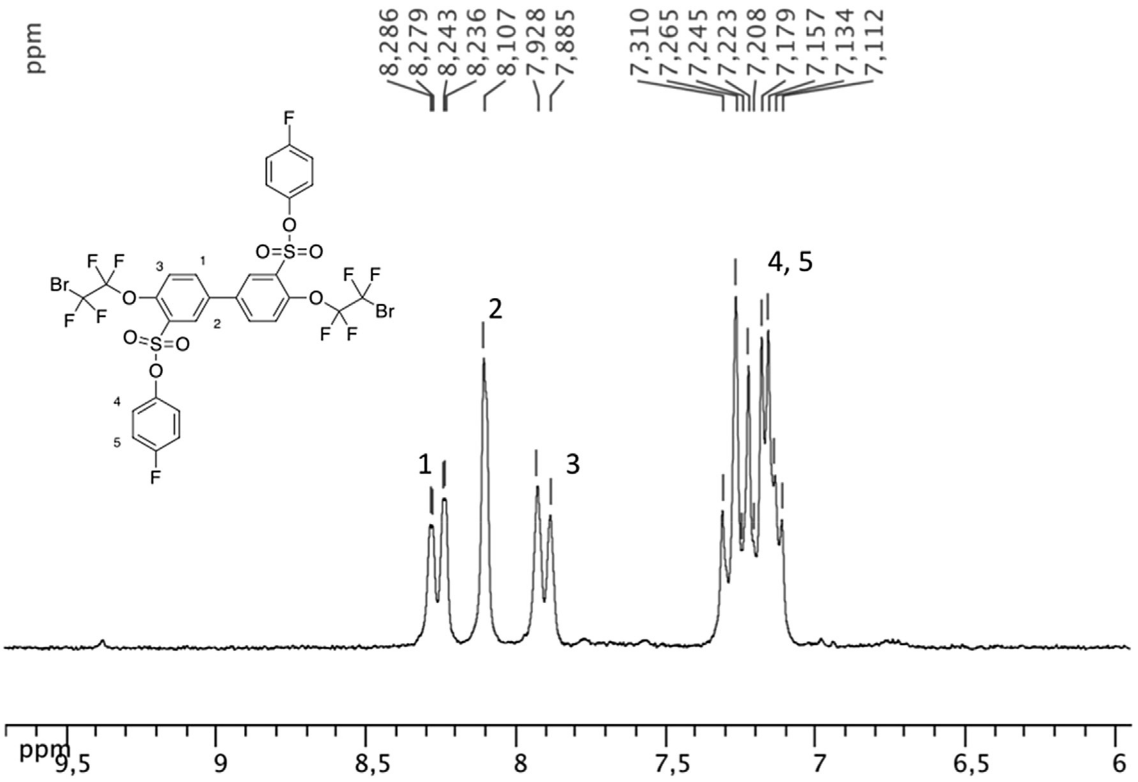


Fig. 2. ^{1}H NMR (DMSO-d_6) of SE-FABP.

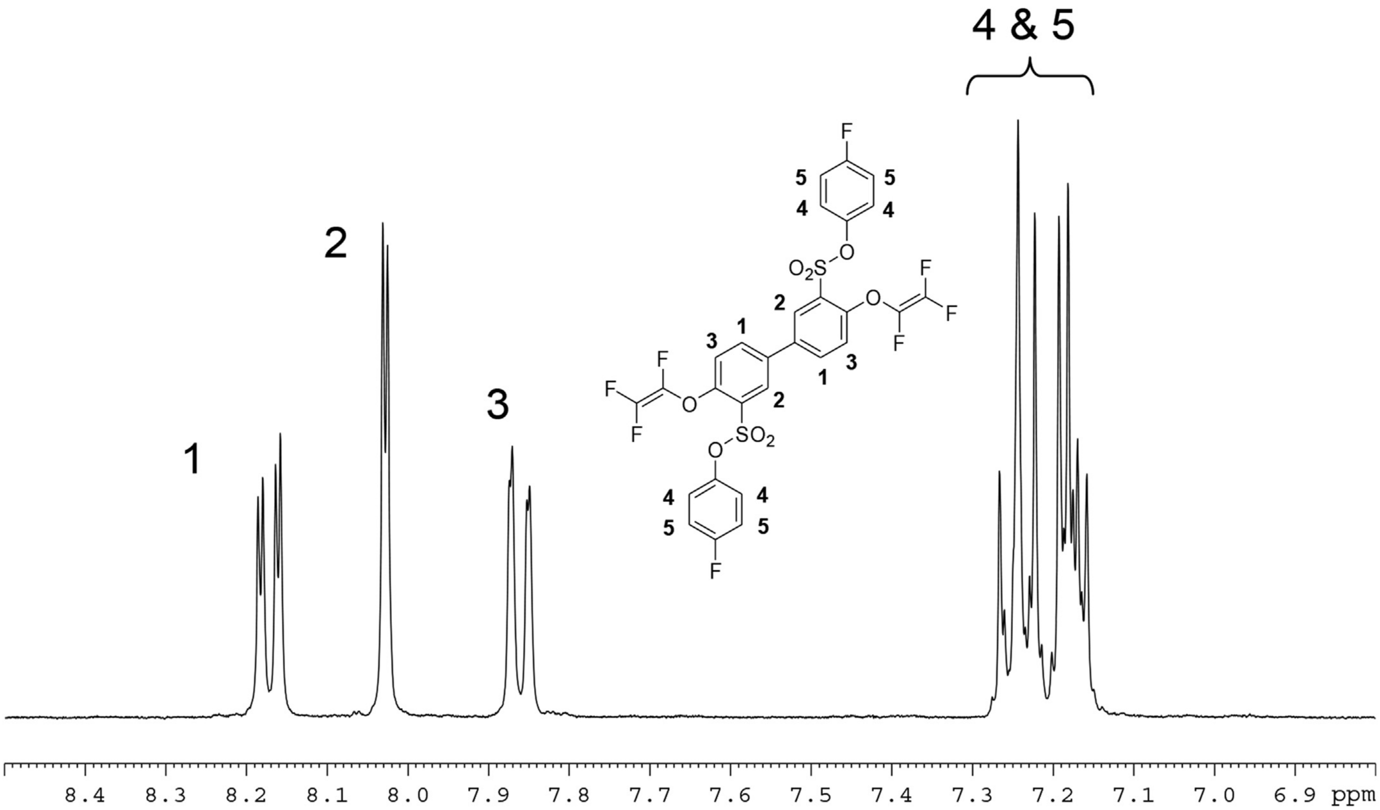


Fig. 3. ^{1}H NMR spectrum (DMSO-d_6) of SE-TFVE.

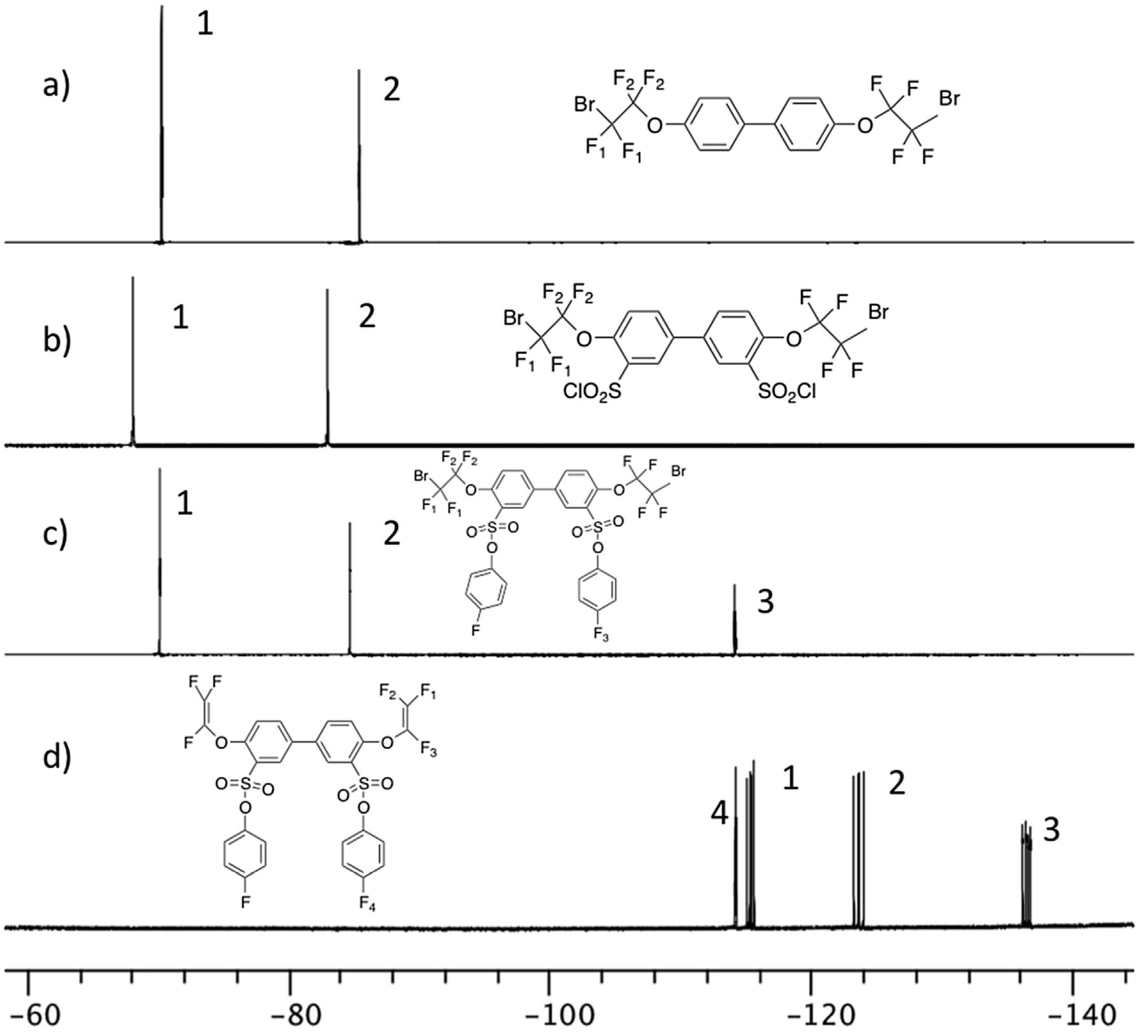


Fig. 4. ^{19}F NMR spectra (DMSO-d_6) a) FABP, b) CSFABP, c) SE-FABP, d) SE-TFVE.

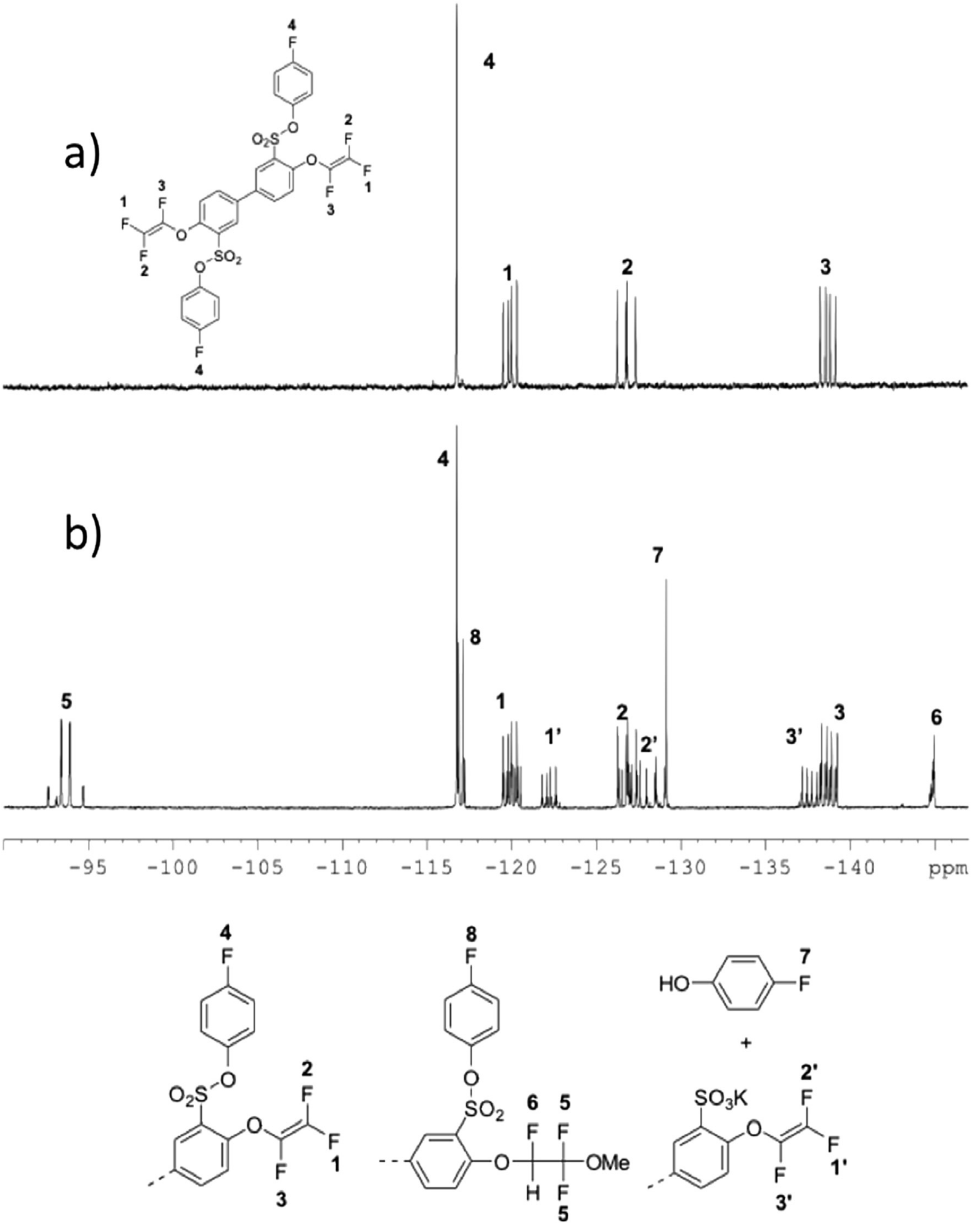


Fig. 5. ^{19}F NMR of a) SE-TVFE and b) SE-TVFE in MeOK.

by ^1H NMR (Fig. 1). This precursor was found to be readily prone to hydrolysis. Therefore, it was freshly prepared before use as reactant for the synthesis of sulfonate ester.

Sulfonate ester fluoroalkylated biphenol (SE-FABP) was synthesized in quasi-quantitative yield (92%) by reaction of 4-fluorophenol on the disulfonylchloride precursor, in the presence of triethylamine and catalytical amounts of DABCO.

This fluoroalkylated compound (Fig. 2) was then dehalogenated by a treatment with activated zinc. In the presence of sulfonate ester protecting groups, the formation of trifluorovinyl ethers requires higher temperatures than in classical experimental conditions (reflux in acetonitrile), as described for the synthesis of 4,4′ bistrifluorovinylether biphenol. Therefore, the reaction was performed under pressure, at 110 °C. In the course of the reaction, some undesirable mono and di-CF_2H containing side-products were produced. The purification of the crude compound is of utmost importance as any tetrafluoroethyl ether containing monomer would behave as chain terminating agents in the course of a polycondensation reaction, and subsequently preclude the synthesis of high molecular weight polymers.

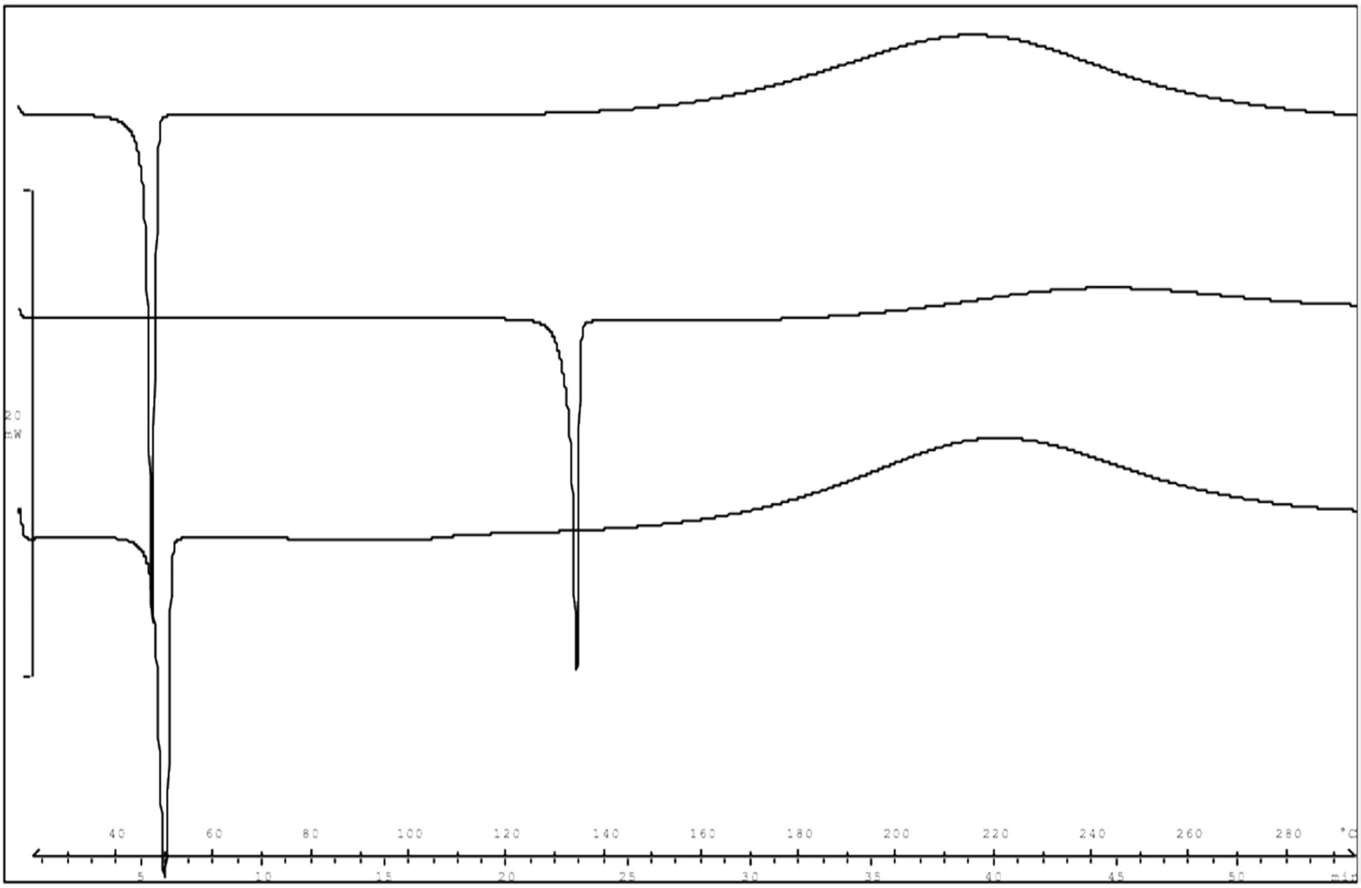


Fig. 6. DSC thermograms of 4,4′-TFVE (1), SE-TFVE (2), and of a mixture of monomers (84% of 4,4′-TFVE and 16% of SE-TFVE) (3).

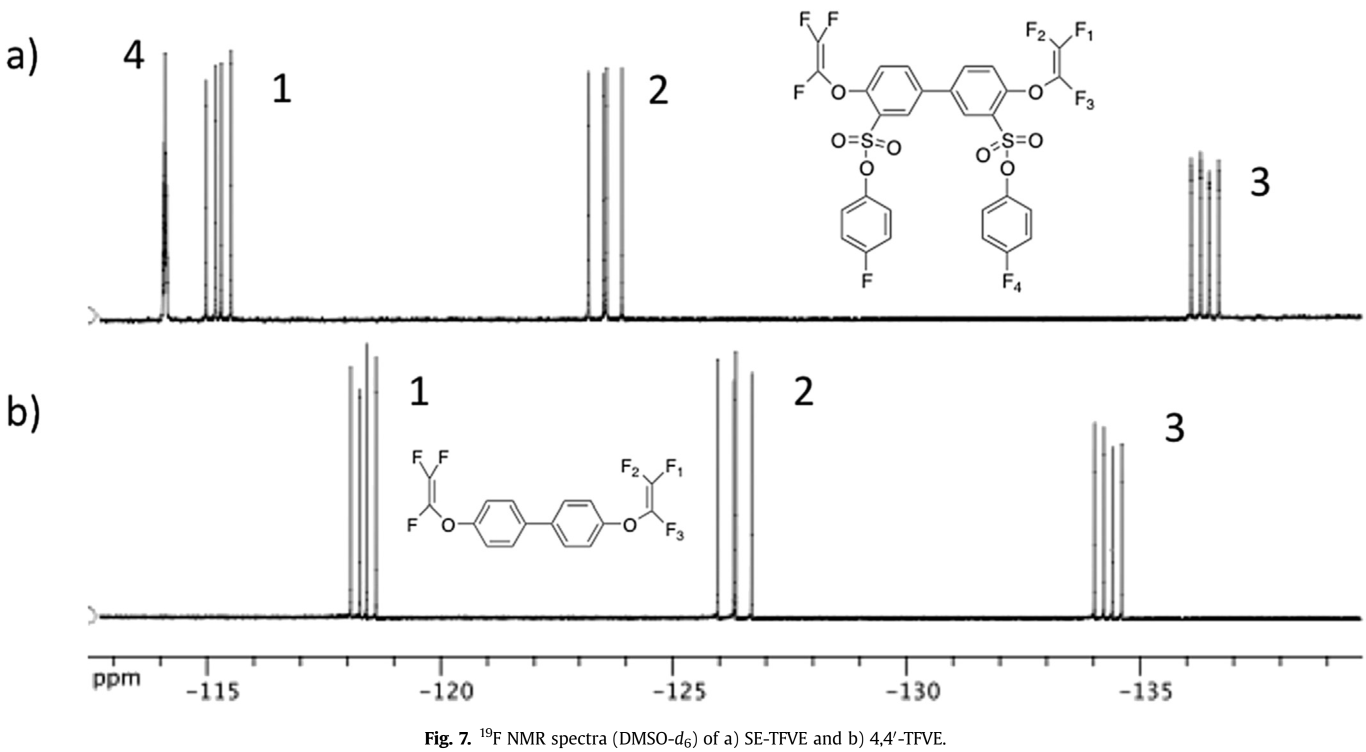


Fig. 7. ^{19}F NMR spectra (DMSO-d_6) of a) SE-TFVE and b) 4,4′-TFVE.

A polymer grade monomer was obtained by successive crystallisations in ethyl acetate/hexane. NMR (^{1}H and ^{19}F) were used to assess for the efficiency of the purification method as well as to evidence the purity of the final compound (see ^{1}H spectrum in Fig. 3).

In the frame of this multi-step synthesis, ^{19}F NMR proved to be a very sensitive tool and was considered as a method of choice to monitor the evolution of the different reactions as well as to identify the different compounds formed (Fig. 4).

The peaks respectively at − 70.15 ppm and − 85.29 ppm are assigned to the fluorine atoms F_1 and F_2 of the fluoroalkylated biphenol. The incorporation of electro-withdrawing SO_2Cl substituents induces an upfield shift from - 70.15 to - 68.09 ppm for the peak corresponding to fluorine F_1 and from - 85.29 to - 82.55 ppm for the peak corresponding to fluorine F_2. Upon the protecting step, the reaction with 4-fluorophenol leads to a slight downfield variation of chemical shifts of these two fluorine atoms, from −68.09 to −70.13 ppm for F_1 and from −82.55 to −84.48 ppm for F_2. The 4-fluorophenol addition is also characterized by the apparition of a new peak at - 126.42 ppm. A quantitative analysis confirms a quantitative conversion of SO_2Cl functions.

Upon delalogenation reaction with zinc metal, the two singlets corresponding to the fluoroalkyl fluorines (F_1 and F_2), initially present at −70.13 ppm and −84.48 ppm disappear and 3 signals characterising trifluorovinyl ether groups centered at −119, - 125 and − 134 ppm appear.

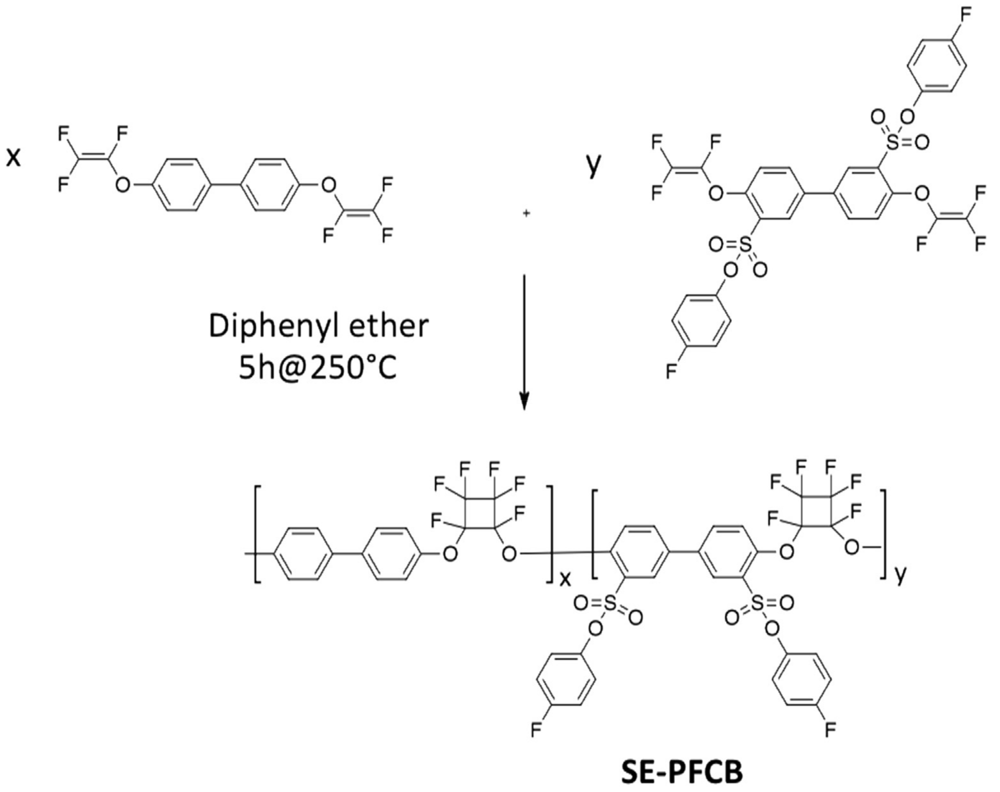
The basic hydrolysis of 4-[(α,β,β-trifluorovinyl)oxy]benzene sulfonyl chloride in the presence of KOH and methanol was reported by Améduri et al. [26] to enable the formation of sulfonic acid groups in the presence of trifluorovinyl ethers with an 88% yield. Such experimental conditions were therefore expected to enable the formation of sulfonic acid containing bistrifluorovinyl ether monomer from SE-TVFE. Unfortunately, on the substrate studied in this work, all attempts (by varying the reaction temperature, basic agent…) were unsuccessful: these experimental conditions were found to affect the integrity of the TFVE groups, even at very low temperature (MeOH, −75 °C). The fluorine NMR spectra of the reaction media (Fig. 5) suggest that the base readily reacts with the trifluorovinyl groups, by nucleophilic addition. These results are in agreement with the work described by Moody et al. [27].

The thermal properties of SE-TFVE were evaluated by TGA and DSC. No obvious decomposition is observed until the main-chain decomposition A 5% weight loss is observed above 331 °C (Supporting information, Figure S1). No significant weight loss was recorded after a 24 h isotherm at 110 °C. These results attest for the high thermal stability of this monomer. As shown in Fig. 5, both 4,4′-TFVE and SE-TFVE are crystalline and exhibit melting transitions around 46 °C and 133 °C, respectively.

At higher temperatures exothermal phenomena are attributed to the thermal cyclodimerisation of these monomers. This result is in agreement with those typically reported for various bistrifluorovinyl ether monomers as TFVE groups thermally react above 150 °C and provide the formation of hexafluorocyclobutane rings [28,29].

This cycloaddition reaction involves the formation of a biradical intermediate which is stabilised by the presence of electron-donating groups [3]. Comparing the DSC behaviour of the two monomers (Fig. 6), it clearly appears that the exotherm onset of the non-fnunctionalized monomer occurs at lower temperature than its sulfonate ester-containing analogue. This can be attributed to the deactivating effect of the electron-withdrawing sulfonate ester groups on the biphenyl. In a mixture composed of 84% of 4,4′-TFVE and 16% of SE-TFVE, it seems that 4,4′-TFVE melts rapidly, behaving as a solvent for the second monomer.

Comparing the ^{19}F NMR spectra of the two bis TFVE monomers



Scheme 2. Synthesis of sulfonate ester-containing poly(arylene perfluorocyclobutane)s (SE-PFCB) by direct polycondensation of a functionalized precursor.

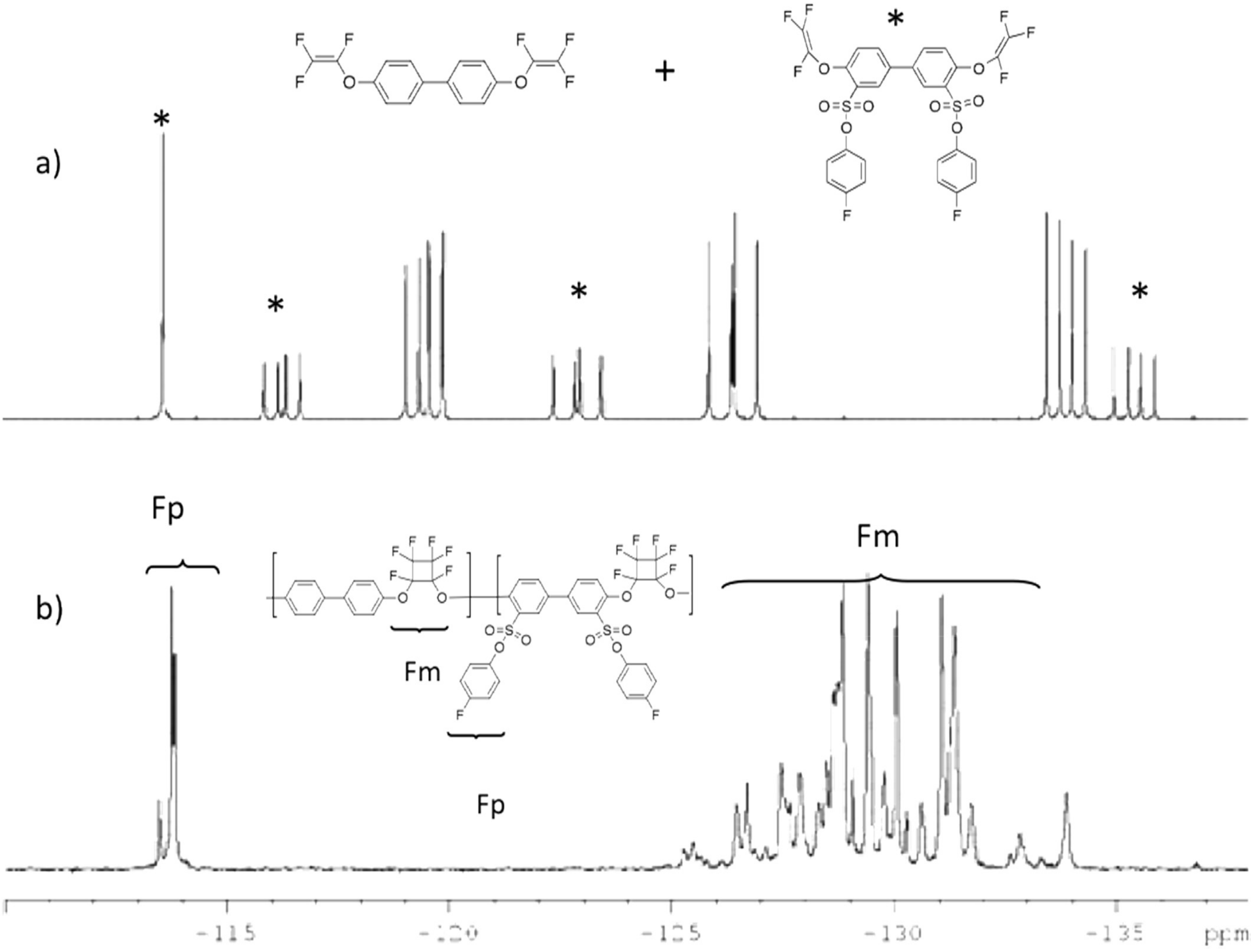


Fig. 8. ^{19}F NMR spectra (diphenyl ether + DMSO-d_6 coaxial) of TFVE monomers initial mixture a) and of the resulting polymer b).

(Fig. 7), some differences in chemical shifts of the TFVE peaks clearly appear. Such differences are attributed to the electron-withdrawing effect of the sulfonate ester groups. Based on Spraul [30] correlation between the ^{19}F characterization of trifluorovinyl ethers and their reactivity towards a cyclodimerisation reaction, the lower reactivity of the sulfonate ester-containing monomer is confirmed.

3.2. *Sulfonate ester and sulfonic acid-containing PFCB synthesis and characterization*

When the polymerization was performed in solution in NMP, the reaction was incomplete. This was confirmed by the presence of residual TFVE, even after long reaction times. This is the reason why in this work, polymerizations were performed in diphenylether, which is known for its high boiling point and chemical inertness. High molecular weight sulfonated ester-containing poly(arylene perfluorocyclobutane)s were obtained by a thermal (2π+2π) cyclopolymerization of TFVE monomers, at 250 °C, in diphenylether (Scheme 2).

A first aliquot was directly taken from the homogeneous reaction mixture, at 80 °C, before the polymerization starts. The experimental ratio of the two monomers can be determined by comparing the integral of each TFVE system. ($I_{4,4'\text{-TFVE}}$ and $I_{\text{SE-TFVE}}$) (Fig. 8a)). Then, the evolution of the polymerization was monitored by quantitative fluorine NMR, by relative integration of the ^{19}F peak signal of the TFVE groups compared with the signals assigned to the fluorine atoms involved in hexafluorocyclobutane rings. After 5 h reaction, a quantitative conversion of the aryl TFVE in perfluorocyclobutane rings was evidenced by the complete disappearance of the characteristic peaks assigned to the TFVE groups as well as by the presence of multiplets present in the [-125 ppm; −135 ppm] range, which are ascribed to hexafluorocyclobutane rings (Fig. 8b)). In addition, the incorporation of sulfonate ester groups was proven by the presence of peaks around −114 ppm. The complexity of the spectrum part related to the fluorine atoms belonging to the hexafluorocyclobutane rings is attributed to the presence of different isomers and/or different types of sequences (condensation of 4,4′-TFVE on itself, SE-TFVE condensation on itself or mixed condensation).

The proportion of sulfonate ester groups present in the final polymer was determined by the initial ratio of 4,4'bisTFVE monomer and of its functionalized analogue. A series of polymers bearing different bis TFVE monomers feed ratios was synthesized. For the sake of clarity, polymers will be further named SE-PFCB-X, in which X represents the molar ratio of sulfonate ester precursor. The structure of the polymers has been characterized by ^{19}F NMR (Fig. 9).

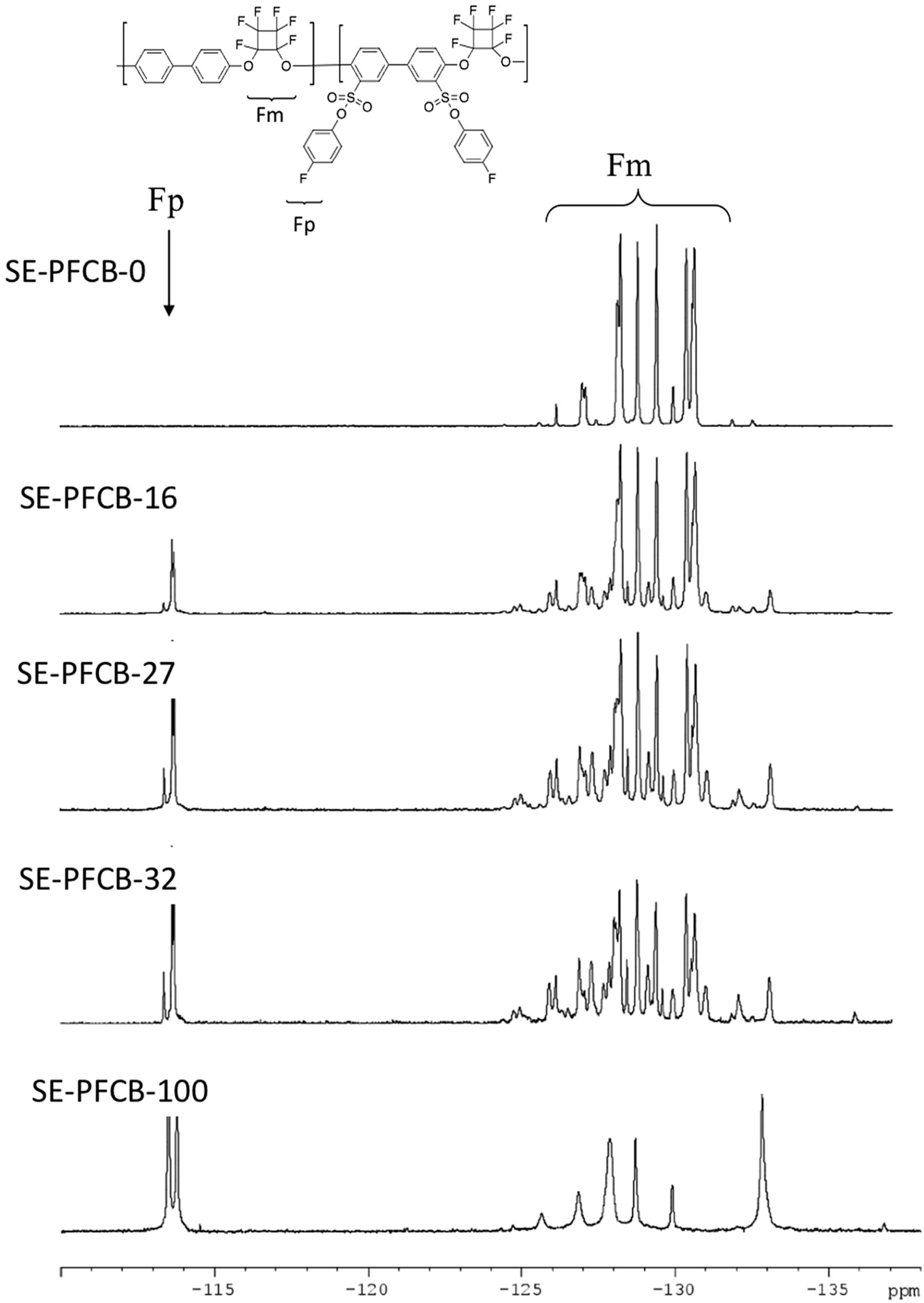


Fig. 9. ^{19}F NMR spectra ($CDCl_3$) of SE-PFCB-X (X: 0, 16, 27, 32, 100).

Table 1
Physico-chemical characterization of SE-PFCB and SA-PFCB.

SE-PFCB (sulfonate ester form)							SA-PFCBK (potassium salt form) and SA-PFCBH (sulfonic acid form)		
Acronym	% Th SE-TFVE	% Exp[a] SE-TFVE	$Td_{5\%}$[b] (°C)	Tg[c] (°C)	M_{nPS} (g/mol)	M_{wPS}[d] (g/mol)	Acronym	$Td_{5\%}$[b] (°C)	Tg[c] (°C)
SE-PFCB-0	0	0	> 450	151					
SE-PFCB-16	16	16	365	146	22 500	56 900	SA-PFCBK-16 SA-PFCBH-16	393	125
SE-PFCB-27	27	27	355	143	10 600	55 600	SA-PFCBK-27 SA-PFCBH-27	343 315	143
SE-PFCB-32	32	30	356	140	17 800	44 400	SA-PFCBK-32 SA-PFCBH-32	349 293	192
SE-PFCB-100	100	100	344	115[e]	nd	nd	SA-PFCBK-100	288	>250

[a] Experimental (^{19}F NMR).
[b] $T_{d5\%}$: 5% weight los temperature (TGA).
[c] T_g (DSC).
[d] (SEC in THF, PS calibration).
[e] This value was under-estimated, due to some residual diphenyl ether in the sample.

The molar fraction of SE-TFVE (y) effectively incorporated in the polymers was determined by ^{19}F NMR, by comparing the integral (Ip) of fluorine atoms present on the sulfonate ester groups (Fp) and the integral Im of the fluorine assigned to the hexafluorocyclobutane rings (Fm), according to the following equation (eq 1):

$$y = \frac{3 \times I_p}{I_m} \tag{1}$$

The experimental values are in good agreement with the expected theoretical ones (Table 1).

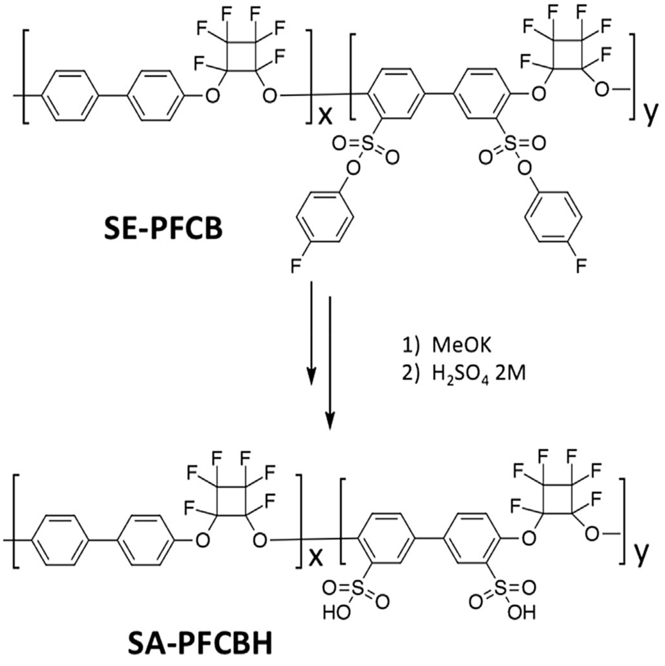
The thermal properties of SE-PFCB were investigated by TGA, under nitrogen. The resulting thermograms (supporting information S2) suggest a high thermal stability of these structures up to 300 °C. The incorporation of increasing proportions of sulfonate results in a slight stability decrease at high temperatures. However, this does not jeopardize the thermal stability of the polymers. Indeed, the 5% weight loss temperatures are in all cases higher than 343 °C (Table 1). No additional thermo-oxidative degradation was evidenced when experiments were performed under air. The glass transition temperature of these polymers were determined by DSC. No melting endotherm are observed, which suggest an amorphous nature for the polymers. The glass transition temperatures is lower than 151 °C. (corresponding to the Tg of the non functionalized PFCB). Not surprisingly, a slight plasticizing effect is observed with increasing proportions of bulky fluorophenol sulfonate ester side-chains. The polymers are soluble in common organic solvents (THF, Chloroform, NMP, DMAC…), as reported for many various poly(arylene perfluorocyclobutane)s. Mean molecular weights were determined by size exclusion chromatography, in THF. Analyses show monomodal distributions for all polymers (Supporting information Figure S3). The reported values in Table 1 were assessed from a polystyrene calibration curve. High molecular weight polymers were obtained, which was confirmed by the elaboration of thin tough membranes from 20% weight polymer solutions in DMAC, by a conventional solvent casting method.

It is worth noting that attempts to regenerate sulfonic acid functions on the polymer preliminary cast into thin membranes failed. ^{19}F NMR spectra of a thin film refluxed in MeOK and of pristine SE-PFCB are identical. One probable reason is related to the extremely low swelling availability of these membranes in methanolic potassium hydroxide. Sulfonic acid containing PFCB were therefore produced by basic hydrolysis of their sulfonate ester containing analogues before the elaboration of membranes (SA-PFCBK) and subsequent re-acidification (SA-PFCBH). The precursors were dissolved in NMP and potassium methanolate was added to the solution (Scheme 3).

The deprotection reaction was monitored by ^{19}F NMR. This reaction was quantitative in less than 10 min. The fluorine atom present on the sulfonate ester group, initially present at −113 ppm, completely disappears. In the meantime, the fluorophenate characterized by the apparition of a new singlet at −137 ppm appears (Fig. 10).

Upon deprotection of the sulfonate ester groups, a drastic change of polymer solubilities occur. Indeed, SA-PFCBK-X are no longer soluble in chlorinated solvents, THF or even DMSO. They can be however dissolved in DMAC, cyclopentanone or NMP. Because of the high proportion of sulfonic acid groups incorporated in SA-PFCBK-100, this polymer is even soluble in water.

As reported in Table 1, the thermal stability of sulfonic acid-containing PFCB (in their potassium salt (SA-PFCBK)) has been investigated (supporting information Figure S4). The results



Scheme 3. Sulfonate ester poly(arylene perfluorocyclobutane)s hydrolysis leading to sulfonic acid-containing poly(arylene perfluorocyclobutane)s.

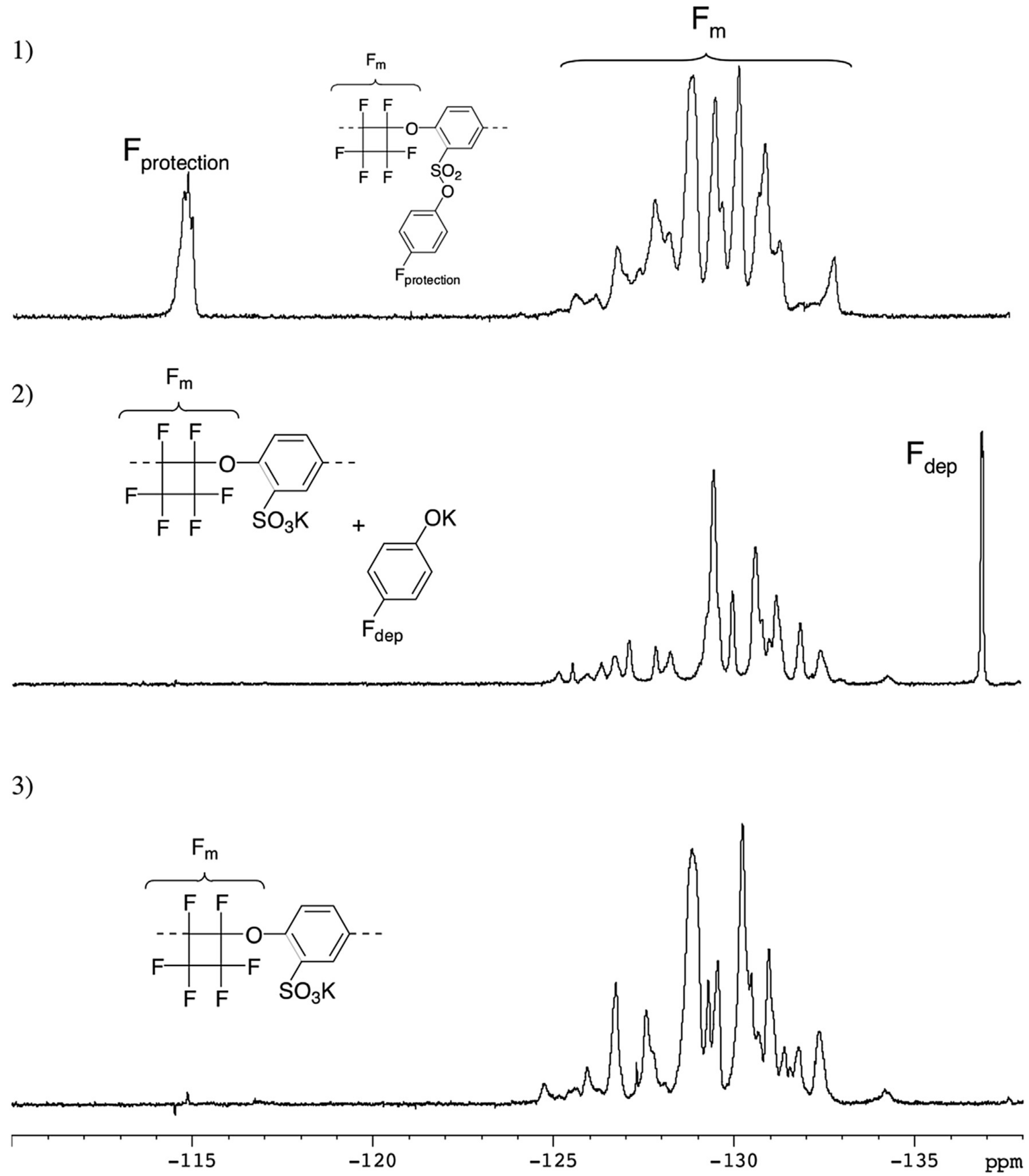


Fig. 10. Deprotection of sulfonate ester groups. ^{19}F NMR spectra (NMP + coaxial DMSO-d_6) (1) SE-PFCB, (2) in-situ deprotection reaction, with MeOK, (3) isolated SA-PFCBK.

indicate a high thermal stability, with a 5% weight loss temperature above 288 °C. Concerning DSC analyses, increasing proportions of sulfonic acid groups (in their potassium salt form) induce a Tg increase. This result is not surprising as a similar behaviour has been observed on different polymer backbones (sulfonated polyimides, sulfonated polarylethers…). For the polymer based exclusively on the functionalized monomer (SA-PFCBK-100), no Tg could be determined in the temperature range investigated.

The polymers (in their sulfonic acid, potassium salt form) were cast into thin films, from 20% weight DMAC solutions. Surprisingly, only thin 30 µm thick membranes were successfully elaborated, while thicker membranes had fair mechanical properties. Further experiments dedicated to understand this phenomenon are currently under investigations. The thin membranes were re-acidified in 2 M H_2SO_4. The deprotected and re-acidified polymers present ionic exchange capacities ranging from 0.86 meq H+/g of dry polymer (for SA-PFCBH-16) to 4.1 meq ion/g of dry polymer, (for SA-PFCBH-100) as assessed by the following equation (eq (2)):

$$IEC = \frac{2y}{y \times M_{sulfonated} + x \times M_{non\ sulfonated}} \times 1000$$

$$IEC = \frac{6 \times I_p}{(I_m - 3I_p) \times M_{non\ sulfonated} + 3I_p \times M_{sulfonated}} \times 1000 \qquad (2)$$

with $M_{sulfonated} = 506.364$ g mol^{-1} and $M_{non\ sulfonated} = 346.224$ g mol^{-1}.

The stability of the materials in their SO_3H acidic form (SA-

PFCBH-X) against desulfonation reactions was evaluated by thermogravimetry analysis. The results obtained (supporting information S5) are consistent with typical desulfonation reactions of aromatic sulfonic groups (above 250 °C).

Preliminary proton conductivity measurements were performed on a membrane cast from a 1,4 meqH$^+$g^{-1} polymer solution (SA-PFCBH-27). The value measured at 90 °C and under 95% of relative humidity reached 138 mS cm^{-1}. In analogous conditions, the well-known Nafion has a proton conductivity of 270 mS. cm^{-1}. This result is coherent with the proton conductivity of sulfonated block PFCB obtained by post-sulfonation (106,9 mS @80 °C for a 2 meqH$^+$g^{-1} sulfonated PFCB) reported by Park [7].

4. Conclusion

In this work, we have successfully prepared a sulfonate ester-containing bis TFVE precursor by a multi-step synthesis. The physico-chemical properties of this monomer were investigated (structural characterization by ^{1}H and ^{19}F NMR, thermal properties by TGA and DSC). A series of sulfonate ester-containing perfluorocyclobutanes were then synthesized by direct copolymerization of the functionalized monomer with 4,4′-TFVE. Increasing sulfonate ester-containing units were obtained by adjusting the molar ratio of the two monomers. These polymers were soluble in common organic solvents and were proven to be highly thermostable. Upon basic treatment in the presence of KOH/MeOH, the sulfonate ester protecting groups were hydrolysed, producing sulfonic acid-containing polymers, in their potassium salt form. After the elaboration of thin membranes from solution casting method and re-acidification in 2 M H_2SO_4, the proton conductivity of the materials was evaluated. Promising results were obtained (138 mScm^{-1} @90 °C–95% RH). To the best of our knowledge, this is the first example of the synthesis of sulfonated PFCB by the direct cyclodimerisation of a functionalized monomer precursor. This opens new perspectives for the synthesis of original sulfonated perfluorocylobutane architectures (sulfonated multiblock copolymers).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.11.061.

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