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Synthesis of Vinylidene Fluoride-Based Copolymers Bearing Perfluorinated Ether Pendant Groups and Their Application in Gel Polymer Electrolytes

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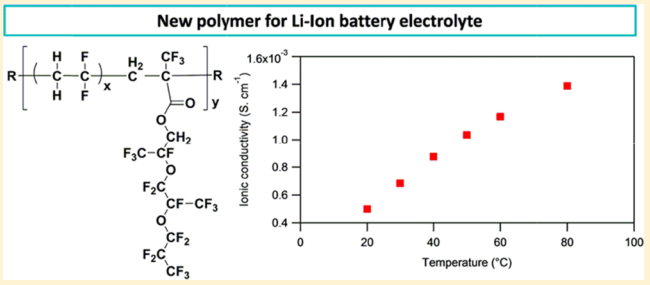
Supporting Information

ABSTRACT: Vinylidene fluoride (VDF)-based copolymers bearing pendant perfluoroalkyl ether groups for potential application in gel polymer electrolytes were synthesized via conventional radical copolymerization of VDF with a 2-trifluoromethacrylate monomer bearing pendant perfluoroalkyl ether groups [2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)propoxy]propyl 2-(trifluoromethyl)-acrylate (MAF-PFE)]. Two kinds of initiators (hydrogenated and a perfluorinated highly branched persistent radical that released $CF_3^{\bullet}$ radical from 80 °C) were used. Molar masses ranged between 35 000 and ca. 50 000 g·mol^{-1}. The synthesized poly(VDF-*co*-MAF-PFE) copolymers were evaluated in gel polymer electrolytes based on ionic liquids. With this aim, the poly(VDF-*co*-MAF-PFE) copolymers were mixed with lithium bis(trifluoromethanesulfonyl)imide and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Homogeneous gels with conductivity values at room temperature reaching up to 3×10^{-3} S·cm^{-1} were obtained, while the transference number of lithium ions was 0.12 at 40 °C. Finally, such electrolytes displayed an electrochemical stability window between 1.5 and 4.4 V as determined by cyclic voltamperometry measurements.



INTRODUCTION

Poly(vinylidene fluoride) (PVDF)[1] and copolymers based on VDF[1] are commonly used in many applications such as coatings,[2] water treatment,[3] medicine (suture wires, controlled drug delivery systems, tissue engineering, microfluidic and artificial muscle actuators, and thermal transducers),[4] backsheets for photovoltaic devices, electroactive devices,[5] and binders and separators for Li-ion batteries[1,6] because of their outstanding physicochemical properties including excellent film-forming ability, long-term reliability, thermal and dimensional stabilities, high chemical and electrochemical stabilities, high dielectric constant due to the polarity of the C−F bonds, and so forth. Therefore, PVDF and VDF-based copolymers are commonly employed as binders in the formulation of electrodes (especially at the cathode), in the design of the separators between electrodes, as well as the polymer component of porous/plasticized solid electrolytes in lithium-ion batteries.[2,6−9] For these applications, VDF has been frequently copolymerized with hexafluoropropylene (HFP) to decrease the crystallinity.[1,10]

Safety issues related to the use of volatile and flammable organic solvents in Li-ion batteries have motivated the search for alternative electrolyte materials.[11−13] To overcome this issue, a first step has been achieved in designing the so-called microporous gel electrolytes.[14] These electrolytes have been generally prepared via the phase inversion method resulting in the formation of phase-separated microstructured materials containing polymer-rich and solvent-rich phases.[15,16] In these materials, the ionic conduction mainly originates from the solvent-rich phase that contains most of the solvent and the dissolved lithium salt. PVDF (alone or in combination with other polymers) has been commonly used for the preparation of these materials.[14,17] Nevertheless, these materials should be regarded more as a microporous membrane soaked by an organic solvent-based electrolyte than as a real physical or chemical gel. The safety risks associated with solvent volatility and chemical and thermal stabilities can be however substantially decreased by using ionic liquids (ILs) as solvents. Indeed, ILs present a negligible vapor pressure and are less flammable than organic solvents, such as alkyl carbonates,

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commonly used in batteries. Therefore, ILs have been advantageously used for the preparation of microporous gel electrolytes based on PVDF.[18,19] These membranes present ionic conductivities close to those of pure ILs and acceptable mechanical properties for use in Li-ion batteries.[18,19]

At the other extreme, solid polymer electrolytes (SPEs) have also been prepared from VDF-based copolymers loaded with lithium salts.[13] For the latter systems, no solvent is present in the electrolyte, and conduction is provided by the motion of Li^+ ions dissolved in the bulk polymer, thanks to the relatively high dielectric constant of PVDF and VDF-based copolymers. In this respect, SPEs have been prepared from poly(VDF-*co*-HFP) copolymers loaded with $LiCF_3SO_3$[20] or Li bis(trifluoromethanesulfonyl)imide.[21] However, these SPEs display rather poor ionic conductivities because of the lack of coordinating atoms for Li^+ ions in the poly(VDF-*co*-HFP) copolymers and accordingly limited solubility of the lithium salts in the polymer matrix. These issues could be partly circumvented by using fluorophilic anions based on perfluorinated pyrazolides and associated with the lithium cations.[22] Acceptable conductivities reaching almost 10^{-3} S cm^{-1} at 50 °C were observed for those SPEs at a very high loading of lithium salt (80 wt %).[22] Under these conditions, the salt is not really dissolved in the polymer, but a polymer in the salt electrolyte is rather formed in which the VDF copolymer chains serve as plasticizers for the lithium salts conferring them a liquidlike behavior and thus promoting ionic conductivity.[13]

An intermediate situation between microporous gel electrolytes and SPEs based on (P)VDF (co)polymers lies in the formation of true physical or chemical gel polymer electrolytes (GPEs) in which the supporting polymer network would be formed either from microphase-separated (the microphase-separated insoluble polymer domains playing the role of physical cross-links) or from chemically cross-linked VDF-based copolymers, and the liquid component swelling the polymer network would be an IL-based liquid electrolyte to minimize safety issues related to traditional organic solvent-based electrolytes.[19] In this context, the formation of GPEs by dissolving VDF-containing copolymers in IL-based electrolytes was investigated recently. Because PVDF displays very poor solubility in the studied ILs, we have focused on the formation of physical gels obtained from microphase-separated VDF-based copolymers in which the PVDF component microphase separates from the IL-based electrolyte and forms physical cross-links, whereas the other polymer component is swollen by the IL-based electrolyte. Practically, oligo(ethylene oxide)[23] or poly(ethylene oxide) (PEO)[24] components were selected to be associated with the insoluble PVDF partner because of their good solubility in IL-based electrolytes and their ability to coordinate with Li^+ cations (they could also contribute to the overall conductivity of the GPE). In those previous studies, GPEs showing ionic conductivities, close to those of pure IL-based electrolytes, and good mechanical properties were obtained allowing their use without any supplementary separator in Li-ion battery prototypes. Nevertheless, addition of silica nanoparticles was required to obtain sufficient mechanical properties in the GPEs obtained from poly(VDF-*co*-trioxa-3,6,9-decyl-2-trifluoromethacrylate) copolymers,[23] whereas the GPEs obtained from polymer conetworks prepared by the interconnection of four-arm star PVDF end-functionalized with benzaldehyde groups and four-arm star PEO end-functionalized with benzaacylhydrazide groups suffered from a tedious synthesis process.[24]

The aim of the present study is to design a GPE based on a copolymer containing VDF and a comonomer bearing a perfluoroalkyl ether side chain as the polymer component and an IL-based electrolyte as the liquid component. We are targeting a GPE not needing additional silica nanoparticles such as our previous system[23] and with a much more simple macromolecular design than the system reported based on polymer conetworks.[24] To reach this goal, statistical copolymers based on VDF and perfluorooligoether 2-trifluoromethylacrylate [2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)propoxy]propyl 2-(trifluoromethyl)acrylate (MAF-PFE)] have been synthesized with varying compositions and molar masses. It can be expected that the PVDF component will microphase-separate and will provide chemical and mechanical stabilities to the resulting system, whereas the perfluoroether (PFE) side groups will allow a good swelling with the IL-base electrolyte and promote the formation of a gel. Moreover, perfluoropolyether main-chain polymers have demonstrated to display chemical inertness and acceptable ionic conductivities in the solid state, very high transference numbers for Li^+ ions, nonflammability, and good mechanical properties.[25−28] On the basis of the previous results, we could also anticipate an involvement of the perfluorooligoether side chains swollen by the IL and the dissolved lithium salt in the overall ionic conductivity of our GPE.

EXPERIMENTAL SECTION

Materials. The reagents involved in this work were used as received unless mentioned. 2-Trifluoromethyl acrylic acid (MAF), 2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)-propoxy]-1-propanol, VDF (1,1-difluoroethylene), and 1,1,1,3,3-pentafluorobutane were generously given by Tosoh Finechem Corporation (Shunan, Japan), Unimatec Company (Ibaraki, Japan), Arkema (Pierre Bénite, France), and Solvay Fluor (Hannover, Germany), respectively. Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) was offered by Dr. Taizo Ono, NIAIST (Nagoya, Japan), whereas *tert*-butyl peroxypivalate (Tbppi, purity 75%) was supplied by AkzoNobel (Chalons sur Marne, France). Dimethyl carbonate (purity >99%), thionyl chloride, pyridine, and laboratory reactants such as methanol were obtained from Sigma-Aldrich. Deuterated acetone (acetone-d_6), requested for nuclear magnetic resonance (NMR) spectroscopic analysis, was bought at Euroiso-top (Grenoble, France) (purity >99.8%). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI) were bought from Solvay and Tokyo Chemical Industry, respectively.

Synthesis of 2-(Trifluoromethyl)acryloyl Chloride. MAF was chemically modified into 2-(trifluoromethyl)acryloyl chloride (MAF-COCl) in the presence of thionyl chloride. In a typical procedure, MAF (5.00 g, 35 mmol) and $SOCl_2$ (3 mL, 43.0 mmol) were stirred in a 50 mL round-bottom flask connected to a cooling system equipped with an oil bubbler on top of it to check the evolution of the gases (HCl and SO_2) and thus the reaction progress. The reaction was considered complete when the gas release stopped. The formed product, MAF-COCl, was purified by fractional distillation to yield a yellowish liquid.

Synthesis of 2,3,3,3-Tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)propoxy]propyl 2-(Trifluoromethyl)-acrylate. 2,3,3,3-Tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]-1-propanol (17.5 g, 35 mmol) and pyridine (3.1 mL, 3.1 mmol) were transferred into 1,1,1,3,3-pentafluorobutane (20 mL) in a two-necked round-bottom flask equipped with a dropping funnel. Under a nitrogen atmosphere, the mixture was cooled to −10 °C and purged in the inert medium for at least 20 min. MAF-COCl (5.64 g, 35 mmol) was injected into the dropping funnel under a nitrogen atmosphere and slowly added into the above mixture (the procedure took ca. 30 min), keeping the

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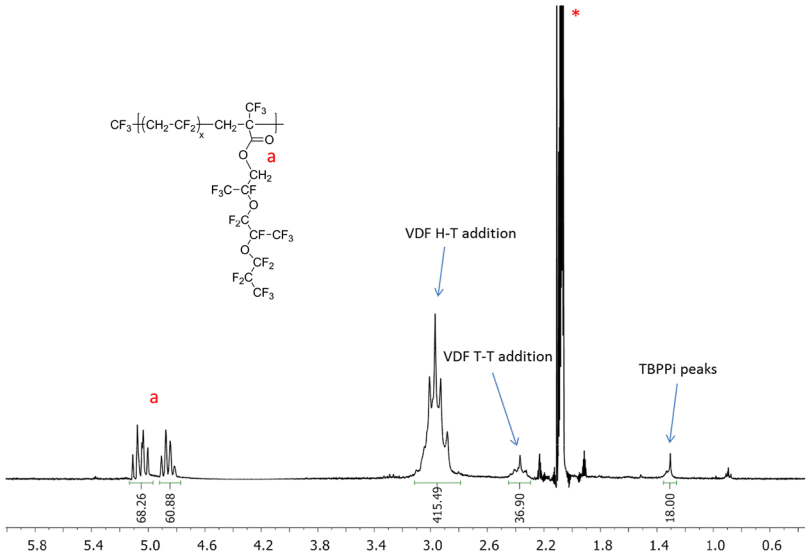

Figure 1. ^{1}H NMR spectrum of the poly(VDF-*co*-MAF-PFE) copolymer (P3, Table 1) prepared by free radical copolymerization of VDF and MAF-PFE initiated by Tbppi in 1,1,1,3,3-pentafluorobutane at 74 °C, recorded in d_6-acetone (*) at 20 °C.

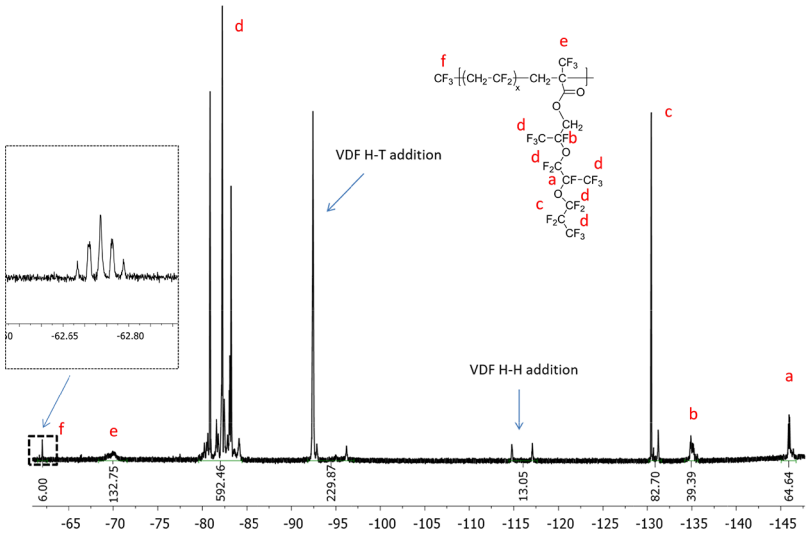

Figure 2. ^{19}F NMR spectrum of the poly(VDF-*co*-MAF-PFE) copolymer (P2, Table 1) prepared by free radical copolymerization of VDF and MAF-PFE initiated by PPFR in 1,1,1,3,3-pentafluorobutane at 74 °C, recorded in d_6-acetone.

medium temperature at −10 °C, then for additional 30 min, and then at room temperature (RT)for 16 h. Finally, the reaction mixture was washed with 40 mL of distilled water, 40 mL of diluted HCl, and then with water. The collected organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed under 0.001 atm to get 18 g of brownish viscous liquid in 85% yield. Such a monomer, MAF-PFE, was characterized by ^{1}H and ^{19}F NMR spectroscopies.

^{1}H NMR (400 MHz, acetone-d_6, δ ppm, Figure S1): 4.83 and 5.14 (complex AB system, 2H, −C(O)−O−CH_2−CF), 6.83 and 6.94 (2s, 2H, $\underline{H}_2C$═C(CF_3)CO_2CH_2−).

^{19}F NMR (376 MHz, acetone-d_6, δ ppm, Figure S2): peak centered at −66.0 (s, 3F, H_2C═C(CF_3)CO_2CH_2−), complex signals between −80.0 and −85.0 (m, 13F, −CO−O−CH_2−CF($C\underline{F}_3$)−O−$C\underline{F}_2$−CF($C\underline{F}_3$)−O−$C\underline{F}_2$−CF_2−$C\underline{F}_3$), −131.0 (m, 2F, −O−CF_2−$C\underline{F}_2$−CF_3), −135.0 (m, 1F, O−CH_2−$C\underline{F}$(CF_3)−), −146.0 (m, 1F, −O−CF_2−$C\underline{F}$(CF_3)−).

Radical Copolymerization of VDF with MAF-PFE in an Autoclave. The radical copolymerization of VDF with MAF-PFE was carried out in a 50 mL Hastelloy autoclave Parr (HC 276) system equipped with a mechanical Hastelloy anchor, a manometer, a rupture disk (2000 PSI), outlet and inlet valves and a Parr electronic controller (to monitor both heating and stirring). Prior to transfer in the autoclave, first, a mixture of Tbppi (0.335 g, 1.924 mmol) and MAF-PFE (15.5 g, 25.66 mmol) in 1,1,1,3,3-pentafluorobutane (30 mL) was bubbled under a nitrogen flow for ca. 35 min. Second, the autoclave was pressurized with 30 bar nitrogen to identify any possible leaks. Then, the vessel was placed under 0.0005 atm vacuum for 35 min to ensure the absence of oxygen. The solution was vacuum-injected into the vessel through a funnel securely connected to the introduction valve of the reactor. Then, it was frozen into liquid nitrogen, followed by transferring VDF gas (6.5 g, 102.64 mmol) into the vessel and controlling its weight. Further, the reactor was progressively heated up to 75 °C under stirring mechanically, and the evolutions of temperature and pressure (P_{max} = 19 bar) were monitored. After 16 h (P_{final} = 11 bar), the reaction was considered complete by cooling the autoclave to RT and then in ice. The unreacted VDF was vented off carefully by opening the outlet valve and stirring smoothly. Then, the vessel was opened, and the solvent was removed under vacuum. The total product mixture was then dissolved in methyl ethyl ketone or acetone, precipitated from cold pentane (or hexane), and centrifuged. Then, the waxy bottom part was dried under vacuum (0.001 atm at 60 °C) for 14 h. The

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copolymerization yield was assessed gravimetrically from the ratio of weight of the obtained copolymer/weight of the transferred monomers in the reactor. The yield was 23% of an off-white wax. The produced poly(VDF-*co*-MAF-PFE) copolymer was analyzed by ^{1}H and ^{19}F NMR spectroscopies.

^{1}H NMR (400 MHz, acetone-d_6, δ ppm, Figures 1, S3, and S5): 2.3 to 2.5 ppm (m, $-CF_2CH_2-CH_2CF_2-$ reverse VDF−VDF tail-to-tail (T−T) dyad addition); 2.8 to 3.2 ppm (m, $-CH_2CF_2-CH_2CF_2-$, normal VDF−VDF head-to-tail (H−T) dyad addition and $C\underline{H}_2CF_2-CH_2C(CF_3)(CO_2CH_2)$ in VDF−MAF-PFE dyad); 2.9 ppm (m; $-C\underline{H}_2C(CF_3)(CO_2CH_2)$ in MAF-PFE); 4.8 and 5.2 ppm (complex system, 2H, $-O-C\underline{H}_2-CF(CF_3)$ in MAF-PFE).

^{19}F NMR (376 MHz, DMSO-d_6, δ ppm, Figure 2): −62.7 (qi, 6F, $^{3}J_{FH} = {}^{4}J_{FF} = 10$ Hz, $-CF_3$ end groups) when PPFR was used as initiator; −70.0 (s, 3F, $-CF_3$ of MAF-PFE in the copolymer); signals between −80.0 and −85.0 (m, 13F, $-CO-O-CH_2-CF(C\underline{F}_3)-O-C\underline{F}_2-CF(C\underline{F}_3)-O-C\underline{F}_2-CF_2-C\underline{F}_3$); −92.5 ($-CH_2CF_2-CH_2CF_2-$ normal VDF−VDF head-to-tail dyad addition); −96.0 ($-CF_2$ of VDF in the alternating VDF−MAF-PFE dyad); −114.8 ($-CH_2C\underline{F}_2-CF_2CH_2-CH_2$, reverse VDF−VDF H−H dyad addition); −117.0 ($-CH_2CF_2-C\underline{F}_2CH_2-CH_2$, reverse VDF−VDF H−H dyad addition); −130.5 (m, 2F, $-O-CF_2-C\underline{F}_2-CF_3$); −134.9 (m, 1F, $O-CH_2-C\underline{F}(CF_3)-$); −146.0 (m, 1F, $-O-CF_2-C\underline{F}(CF_3)$).

Radical Copolymerization of VDF with MAF-PFE in Carius Tubes. As the PFE chain degrades in metal containers at high temperatures,[28,29] the copolymerization of VDF and MAF-PFE was also initiated by PPFR and performed in borosilicate thick Carius tubes (internal diameter 10 mm, length 130 mm, and thickness 2.5 mm for a total volume of ca. 8 mL) connected to a manifold. In a typical copolymerization, the solution of different reactants including the initiator, PPFR (1.5 mol % with respect to the monomers), and MAF-PFE in 1,1,1,3,3-pentafluorobutane were first injected in the tubes. They were degassed by four thaw−freeze cycles and then frozen in a liquid nitrogen bath. Further, VDF was transferred while checking the drop of pressure from a separate VDF container (a beforehand calibration "curve weight of VDF vs the drop of gas pressure" was established). Subsequently, the tubes were sealed under vacuum while keeping the medium frozen in liquid nitrogen and then inserted in metallic tubes placed in a heating and stirring oven regulated at the desired temperature (80 °C). After reaction, the tube was frozen into liquid nitrogen and broken, and the total product mixture was dissolved in acetone and precipitated from chilled pentane. After recovering the waxy product and drying, the copolymer was analyzed by ^{1}H and ^{19}F NMR spectroscopies. The spectra were similar to those characterized above with an additional quintet ($^{3}J_{FH} = {}^{4}J_{FF} = 10$ Hz) centered at −62.7 ppm assigned to $-CF_3$ end groups adjacent to a CH_2CF_2 unit.

Preparation of GPEs. The GPEs were prepared by sequential dissolution in acetone of the calculated amounts of copolymer, lithium salt, and IL. First, 0.20 g of poly(VDF-*co*-MAF-PFE) copolymer was weighed and dissolved in 1600 μL of acetone at reflux for 3 h and ultrasound for 30 min. In parallel, a given amount of lithium salt (LiTFSI) was dissolved in the calculated acetone amount to achieve a specific concentration, so that the targeted molar Li^+ ion/MAF-PFE unit ratio was reached when adding 400 μL of this solution into the copolymer solution. A calculated amount of IL (EMIM TFSI) was weighed simultaneously with the Li^+ salt to obtain an ionic mixture with an IL/Li^+ molar ratio of 9:1. The GPE was then readily obtained by evaporation of acetone at reflux followed by overnight drying under vacuum at RT.

NMR Spectroscopy. The determination of the microstructures and compositions of the copolymers was achieved by ^{1}H and ^{19}F NMR spectroscopies by means of a Bruker AC 400 spectrometer (400 MHz for ^{1}H and 376 MHz for ^{19}F) utilizing acetone-d_6 as the solvent. The chemical shifts and coupling constants are given in parts per million (ppm) and hertz (Hz), respectively. The experimental conditions for recording ^{1}H [or ^{19}F] NMR spectra were as follows: acquisition time 4.5 s [or 0.7 s], number of scans 32 [or 64], flip angle 90° [or 30°], pulse delay 2 s [or 5 s], and a pulse width of 5 μs for ^{19}F NMR.

Thermogravimetric Analysis. The thermal stability of the purified copolymers was analyzed using a TGA 51 apparatus from TA Instruments at a heating rate of 10 °C min^{-1} under air from RT to 600 °C.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) analyses of the poly(VDF-*co*-MAF-PFE) copolymers were carried out using a Mettler Toledo DSC 823e instrument under a N_2 atmosphere. The DSC instrument was calibrated with indium metals (T_m = 156.6 °C). Heating ranged between −60 and 140 °C using a 20 °C min^{-1} scanning-rate.

Ionic Conductivity Measurements. Ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) with a Biologic VMP300 apparatus. The GPEs were placed as a sandwich between two stainless steel electrodes, and the thickness was controlled by a poly(tetrafluoroethylene) spacer (thickness = 260 μm, internal diameter = 1.5 cm, and external diameter = 1.9 cm). The temperature dependence measurements were performed from 20 to 80 °C by increasing the temperature gradually in steps of 10 °C with an equilibration time of ca. 1 h between each step. The electrochemical response of the electrolytes was measured at RT in the 1 mHz to 1 MHz frequency range with an ac excitation voltage varying between 5 and 1000 mV.

Electrochemical Stability. The electrochemical stability was assessed on a Biologic VMP300 apparatus by cyclic voltammetry. The GPE (thickness of 260 μm) was sandwiched between a stainless steel working electrode and a lithium foil as the counter and reference electrode. The Swagelok cell was assembled in a glovebox under argon and cycled at a scan rate of 0.1 mV/s from 0.5 to 5 V versus Li/Li^+.

Transference Number. A Li/GPE/Li symmetrical cell was assembled in a glovebox under argon and equilibrated at 40 °C for 24 h before measurement. The dc polarization and the impedance measurements were achieved on a Biologic VMP300 apparatus with a dc bias of 10 mV (9.2 mV in practice) at 40 °C.

■ RESULTS AND DISCUSSION

Achieving novel copolymers bearing a PVDF backbone and PFEs as dangling groups is challenging. Actually, PVDF is endowed with outstanding properties (chemical, mechanical, thermal, and electrochemical stabilities),[1−6] whereas perfluoropolyethers possess quite low glass transition temperatures, are thermal and electrochemical stable, and enable lithium conductivity.[25−28] Advantageously, the PFE grafts could be swollen by the IL-based electrolyte and enable the formation of a GPE. The strategy used in the present study is first to synthesize a new PFE comonomer to be further copolymerized with VDF under radical initiation. Then, the thermal and electrochemical properties of the resulting copolymers are investigated.

Synthesis of MAF-PFE. The synthesis of MAF-PFE was achieved by esterification reaction of MAF with 2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)-propoxy]-1-propanol (Scheme 1) in 75% overall yield. The purified MAF-PFE was characterized by ^{1}H (Figure S1) and ^{19}F (Figure S2) NMR spectroscopies (see Supporting Information).

Synthesis of Poly(VDF-*co*-MAF-PFE) Copolymers. The radical copolymerization of VDF with MAF-PFE was carried out in various comonomer feed ratios (Scheme 2) in 1,1,1,3,3-pentafluorobutane to solubilize all reactants and to avoid any transfer. It was initiated by R$^{\bullet}$ radical originated from the thermal dissociation of Tbppi at 74 °C or from PPFR at 80 °C that released a $^{\bullet}CF_3$ radical.

Since VDF is a gas, the radical copolymerizations were carried out in high pressure autoclaves when using Tbppi as an initiator. However, due to the degradation of perfluorinated ethers in contact with the metal at high temperatures (above

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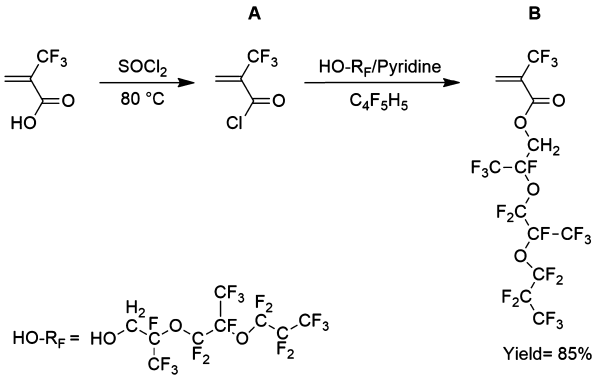
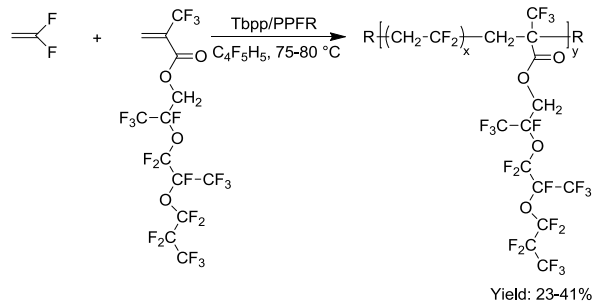
Scheme 1. Synthesis of MAF-PFE from the Esterification Reaction of MAF with 2,3,3,3-Tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]-1-propanol



Scheme 2. Radical Copolymerization of VDF with MAF-PFE Initiated by Tbppi or PPFR



Tbpp: tertiary butyl peroxypivalate
PPFR: Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistant radical

75 °C),[28,29] two other copolymerizations were carried out in thick borosilicate Carius tubes. All polymerizations (Table 1) were achieved in 1,1,1,3,3-pentafluorobutane as the solvent,[30,31] with yields ranging between 23 and 41%. Similar to all MAF esters, which are known not to homopolymerize (reactivity ratio $r_{MAF} = r_{MAF\text{-}TBE} = 0$),[31,32] MAF-PFE behaves the same way.

After precipitation and drying, the poly(VDF-*co*-MAF-PFE) copolymers, as white waxes, were characterized by NMR spectroscopy (see below), and the comonomer contents were calculated from eqs 1 and 5. Because of the insolubility of the resulting poly(VDF-*co*-MAF-PFE) copolymers in dimethylformamide, tetrahydrofuran, $CHCl_3$, or dimethyl sulfoxide, the molar masses (M_ns) and dispersities ($Đ$s) could not be determined by size exclusion chromatography. That is why the PPFR persistent radical (Scheme 3) was used because it led to copolymers terminated by CF_3 end groups as valuable labels to assess the M_n by ^{19}F NMR spectroscopy. Actually, such a PPFR generates a $^{\bullet}CF_3$ radical that can react onto the methylene group of VDF and initiate the polymerization.[33−36]

Characterization of Poly(VDF-*co*-MAF-PFE) Copolymers by ^1H and ^{19}F NMR Spectroscopies. The purified poly(VDF-*co*-MAF-PFE) copolymers were characterized by ^1H and ^{19}F NMR spectroscopies (Figures 1 and 2). The ^1H NMR spectrum of the poly(VDF-*co*-MAF-PFE) P3 copolymer (Figure 1) mainly exhibits five characteristic signals: (i) in the 2.3−2.5 ppm range attributed to the reverse (tail-to-tail, T−T) addition of VDF repeat units ($-CF_2CH_2-CH_2CF_2-$);[32−35] (ii) a signal at 2.9 ppm assigned to the [$-CH_2CF_2-C\underline{H}_2C(CF_3)CO_2CH_2R_F$]; (iii) a broad one ranging between 2.80 and 3.20 ppm corresponding to normal (head-to-tail, H−T) addition of VDF ($-CH_2CF_2-CH_2CF_2-$);[35−38] (iv) two multiplets at 4.8 and 5.2 ppm attributed to the two anisochronous protons in $-CH_2C(CF_3)-CO_2C\underline{H}_2CF(CF_3)$ since such a methylene group is adjacent to an asymmetric carbon atom.

Thus, the molar percentage of VDF can be determined from the integral of the signals characteristic of VDF and MAF-PFE (Figure 3, eq 1). In addition, ^1H NMR spectrum allowed us to get a rough estimation of the molar mass, M_n, of the copolymer initiated by Tbppi using eqs 1−4 (Figure 3), taking into account the signal centered at 1.30 ppm assigned to the *tert*-butyl end group. Since the termination occurs by recombination,[35−37] such a poly(VDF-*co*-MAF-PFE) copolymer displays two *tert*-butyl end groups (e.g., 18 protons). Using eq 2 (Figure 3), the actual number of MAF-PFE units (64) in the copolymer chains can be determined. Following the same strategy, the VDF number was 162 using eq 3. Finally, eq 4 enables to assess the M_n value.

The microstructure of the resulting copolymer was also evidenced by ^{19}F NMR spectroscopy. For example, Figure 2 displays the ^{19}F NMR spectrum of the poly(VDF-*co*-MAF-PFE) copolymer that mainly exhibits the following characteristic features: (i) a quintet ($^3J_{FH} = {}^4J_{FF} = 10$ Hz) centered at −62.7 ppm corresponding to CF_3 from PPFR initiator in $-CF_2-CH_2-CF_3$ as evidence of the regioselectivity of addition of $^{\bullet}CF_3$ radical onto the less hindered site of VDF;[32−35] (ii) a broad signal centered at −70.0 ppm assigned to $-CF_3$ of $H_2C-C(CF_3)-$ in MAF-PFE units;[38] (iii) signals between −80.0 and −85.0 characteristic of the 13 fluorine atoms in the perfluorinated side chain ($-CO-O-CH_2-$

Table 1. Experimental Conditions and Characteristic Features of the Copolymers Resulting from the Radical Copolymerization of VDF with MAF-PFE[a]

	VDF mol %									
entry	feed	copolymer[b]	P_{max}[c] (bar)	ΔP[d] (bar)	yield (%)	$M_{n,NMR}$[e]	initiator	$T_{d10\%}$[f] (°C)	T_g (°C)	T_m[g] (°C)
P1[h]	70	72	n.d.	n.d.	33	36 400	PPFR	142	n.d.	n.d.
P2[h]	75	73	n.d.	n.d.	41	35 000	PPFR	141	n.d.	n.d.
P3	80	87	15	8	23	49 100	Tbppi	281	−15	n.d.

[a]Initiator: Tbppi or PPFR; solvent: 1,1,1,3,3-pentafluorobutane; temperature: 75 °C; time: 16 h. Conditions: solvent used = 30 mL; initiator = 1.5 mol % with respect to the total monomer. [b]Copolymer compositions were assessed by ^{19}F NMR spectroscopy using eq 5. [c]P_{max}: maximum pressure observed during the polymerization. [d]ΔP: pressure drop observed in the autoclave between the maximum pressure and the pressure at the end of the polymerization. [e]Molar masses (M_ns) were determined either by ^1H NMR (when Tbppi initiated the copolymerization, P3, using eqs 2−4, Figure 3) or by ^{19}F NMR (when PPFR was used, P1−P2, from eq 6) spectroscopy. [f]$T_{d10\%}$ stands for 10 wt % loss, assessed by TGA under air; 10 °C/min. [g]Determined by DSC. [h]Reactions performed in Carius tubes; n.d. stands for not observed.

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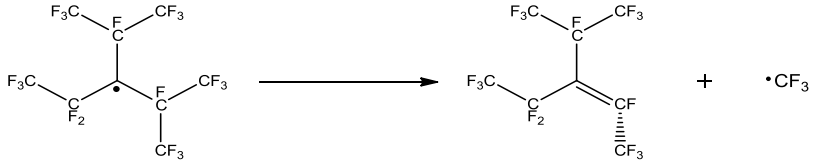
Scheme 3. β-Scission Elimination Mechanism for the Generation of $^{\bullet}CF_3$ from PPFR[33−36]



$$mol\%\ VDF\ in\ copolymers\ by\ ^1H\ NMR = \frac{(\int_{2.3}^{2.5} I_1 + \int_{2.8}^{3.2} I_2) - \int_{4.7}^{5.2} I_3}{\int_{2.3}^{2.5} I_1 + \int_{2.8}^{3.2} I_2} \times 100 \quad (1)$$

$$number\ of\ MAF-PFE\ units = \frac{\int_{4.7}^{5.2} I_3/2}{\int_{1.2}^{1.4} I_4/18} = 64 \quad (2)$$

$$number\ of\ VDF\ units = \frac{\left(\int_{2.3}^{2.5} I_1/2 + \int_{2.8}^{3.2} I_2/2\right)}{\int_{1.2}^{1.4} I_4/18} - number\ of\ MAF-PFE = 162.2 \quad (3)$$

$M_n = 2M_{tBu} + M_{VDF}$ x number of VDF + $M_{MAF-PFE}$ x number of MAF-PFE = 49000 g.mol^{-1} (4)

$$mol\%\ VDF\ in\ copolymers\ by\ ^{19}F\ NMR = \frac{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2}{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2 + \int_{-66}^{-71} CF_3/3} \times 100 \quad (5)$$

$M_n = 2M_{CF_3} + M_{VDF}$ x number of VDF + $M_{MAF-PFE}$ x number of MAF-PFE (6)

Figure 3. Equations for the determination of (1) the molar percentage of VDF in the poly(VDF-*co*-MAF-PFE) P3 copolymer from the ^{1}H NMR spectrum (Figure 1), (2) the number of MAF-PFE units in the polymer chains from ^{1}H NMR, (3) the VDF number from ^{1}H NMR, (4) the molar mass of the copolymer from ^{1}H NMR, and (5) the molar percentage of VDF in the copolymer from ^{19}F NMR. $\int_x^y I_a$ stands for the integral of signal assigned to I_a group ranging between x and y ppm in the NMR spectra. M_{tBut}, M_{VDF}, $M_{MAF-PFE}$, and M_{CF_3} are 57, 64, 604, and 69 g·mol^{-1}, respectively.

$CF(CF_3)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-CF_3$); (iv) at −92.5 ppm attributed to the normal or head-to-tail (H−T) VDF−VDF dyads ($-CH_2CF_2-CH_2CF_2-$) of the PVDF chains;[39] (v) at −96.0 ppm corresponding to the fluorine atoms of the $-CF_2$ groups of VDF in VDF−MAF-PFE alternating dyads;[34,38] (vi) at −114.8 and −117.0 ppm characteristic of the reverse or H−H VDF−VDF dyads ($-CH_2C\underline{F}_2-C\underline{F}_2CH_2-$); (vii) at −130.5 ppm assigned to both fluorine atoms in $-O-CF_2-C\underline{F}_2-CF_3$, (viii) at −134.9 ppm for the F atom in $O-CH_2-C\underline{F}(CF_3)-$; and (viii) at −146.0 for that in $-O-CF_2-C\underline{F}(CF_3)-$.

Thermal Properties of Poly(VDF-*co*-MAF-PFE) Copolymers. The thermal stabilities of the poly(VDF-*co*-MAF-PFE) copolymers were assessed by thermogravimetric analysis (TGA) under air (Figure 4). First, a small loss was observed at 140 °C for all polymers because of the degradation of the ester group in the MAF-PFE group, as observed in other poly(VDF-*co*-MAF) copolymers[30,32,40] where the lower the MAF content the higher the thermal stability of the copolymer. Hence, this loss is steeper for P1 and P2 copolymers (containing 27−28 mol % MAF-PFE) than for P3 possessing 13 mol % (Table 1). This is also attributed to the lower molar masses of P1 and P2, which may evaporate rather than degrade. Actually, this first weight loss corresponds to the MAF-PFE amount in the copolymer. It is noted that between 140 and 200 °C, a loss of P1−P2 corresponds to 19 and 27−28%, whereas it is only 5% for P3. A second degradation is also observed at ca. 350−380 °C mainly attributed to the decomposition of the fluorinated polymer backbone.

The determination of the glass transition (T_g) and melting (T_m) temperatures of the copolymers was attempted by DSC. As expected, for PVDF or copolymers containing a high VDF amount, the glass transition temperature, T_g, was observed with difficulty. T_g was only detected for the P3 sample with values of −15 °C (Figure S8). However, to our surprise, all

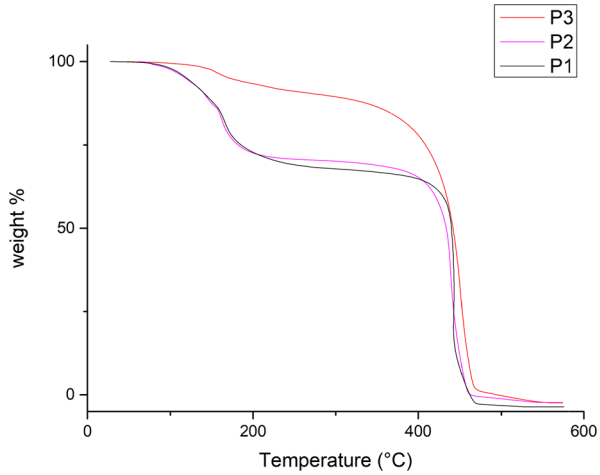


Figure 4. TGA thermograms of poly(VDF-*co*-MAF-PFE) copolymers heated at 10 °C min^{-1} under air (where P*i* compositions are supplied in Table 1).

copolymers showed no melting transition too (Figure S8). This may arise from the introduction of a high amount of bulky MAF-PFE pendant groups that hinder the organization of PVDF moieties and thus reduce the crystalline zone brought by PVDF until the polymer totally loses its crystallinity, thus behaving like an amorphous copolymer. This is in agreement with poly(VDF-*co*-HFP) copolymers.[10,15] The lack of crystalline domains could be beneficial to the ionic conductivity but could at some point be detrimental for the mechanical properties.[41]

Preparation of GPEs. Because the direct dissolution of poly(VDF-*co*-MAF-PFE) copolymers in the IL-based electrolytes was difficult, all components of the GPE were dissolved in a common solvent, that is, acetone. Acetone was then

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evaporated to yield the GPEs. The aspect of the resulting materials was strongly depending on the used poly(VDF-*co*-MAF-PFE) copolymer. For P1 and P2, deliquescent materials were obtained showing macroscopic domains. Changing the copolymer/IL/LiTFSI composition of the initial blend did not help to obtain homogenous materials. However, homogenous, transparent, and colorless gels withstanding the tube inversion test were readily observed when the P3 copolymer was used. The latter gels were observed under an optical microscope to confirm the lack of macrophase separation of the P3 copolymer in the IL-based electrolytes as well as the absence of LiTFSI clusters. Those observations confirm our picture of a GPE formed by nanosized microphase-separated PVDF-rich domains dispersed in a continuous phase formed by alternating oligo(VDF-*alt*-MAF-PFE)-rich segments swollen in the IL-based electrolyte. These results emphasize the importance of the poly(VDF-*co*-MAF-PFE) characteristic features on the final properties of the material. Obviously, poly(VDF-*co*-MAF-PFE) should have a sufficiently high molar mass and a high VDF content (see characteristics of P3 in Table 1) to allow the formation of GPE. In addition, the reactivity ratios of VDF and MAF-PFE comonomers suggest that the distribution of these two comonomers is not fully random in the copolymer chains.[32,40] Moreover, a dispersity in the comonomer distribution among polymer chains should also exist beside the dispersity in chain lengths. On this basis, one can assume that some part of the polymer chains will be enriched in the PVDF segment while others will mainly contain MAF-PFE ones, that is, oligo(VDF-*alt*-MAF-PFE) moieties. These compositional heterogeneities could be essential for the microphase separation to occur between VDF-rich segments and MAF-PFE ones and could certainly be a key feature for the formation of a gel structure. Obviously, the delicate balance between the different components of the system could only be achieved in the case of the P3 copolymer. To give credit to our hypothesis that PVDF-rich segments are responsible for the formation of insoluble domains in the GPE, a solubility test of PVDF homopolymer was performed in the IL-based electrolyte used in the present study by following the same experimental procedure as the one described for the formation of the GPE from the P3 sample. After evaporation of acetone, it was observed that no gel was formed and that insoluble PVDF was found in the IL-based electrolyte. Thus, the presence of MAF-PFE segments is mandatory for the formation of the gel.

Because the preparation of GPEs involved the use of a common solvent (acetone), the determination of the swelling factor of poly(VDF-*co*-MAF-PFE) copolymer by the IL-based electrolytes was meaningless. Therefore, fixed swelling ratios were investigated in the following that may not correspond to the maximum equilibrium swelling ratio, which could be reached by the GPE.

Ionic Conductivity Measurements. EIS was therefore conducted on the GPEs prepared from the P3 copolymer and containing various amounts of doping LiTFSI salt and EMIM-TFSI IL in a IL-to-Li^+ molar ratio always fixed to 9:1. Quantitative information about ionic conductivity, σ, can be derived from the bulk resistance measured by EIS, R, the thickness, d, and the surface area, S, of the GPE—the latter two parameters being set by the use of a ring spacer between the electrodes in the Swagelok cell—via equation $\sigma = \frac{1}{R} \times \frac{d}{S}$.

As presented in Table 2, the investigated GPEs exhibit interesting ionic conductivities at an ambient temperature between 10^{-6} and 10^{-3} S cm^{-1} depending on the Li^+ content. Actually, we have calculated the Li^+ content according to the amount of oxygen atoms in the P3 copolymer. According to the previous literature on perfuoroalkyl polyethers,[25−28] Li^+ ions could indeed bind to ether oxygens in MAF-PFE and contribute to the global ionic conductivity of the GPE. Nevertheless, the main contribution to the ionic conductivity is believed to originate from LiTFSI dissolved in the EMIM-TFSI IL. This hypothesis is confirmed by the data plotted in Table 2 because the values obtained for MAF-PFE/Li^+ ratios of 5 and 2 are close to those that we previously measured for the pure LiTFSI/EMIM-TFSI electrolytes containing similar amounts of Li^+ ions (Figure S9 in ref 24). The GPE with the lithium content for which MAF-PFE/Li^+ = 5 was selected for deeper analysis.

Table 2. Conductivity at RT of the GPE Prepared from Poly(VDF-*co*-MAF-PFE) P3 and EMIM-TFSI IL Depending on the MAF-PFE/LiTFSI Molar Ratio

nMAF-PFE/$n$$Li^+$	conductivity (S cm^{-1})
20	4×10^{-6}
5	7×10^{-4}
2	3×10^{-3}

The ionic conductivity of the GPE with MAF-PFE/Li^+ = 5 increases with temperature and reaches values over 10^{-3} S cm^{-1} at 80 °C (Figure 5a). This ionic conductivity increases with temperature is generally attributed to an enhanced mobility of the charge carriers.[42] These competing conductivities result from the low activation energy (E_a = 1.12 kJ/mol) of the electrolyte calculated with the Vogel−Tamman−Fulcher (VTF)[43] model, as presented in Figure 5b.

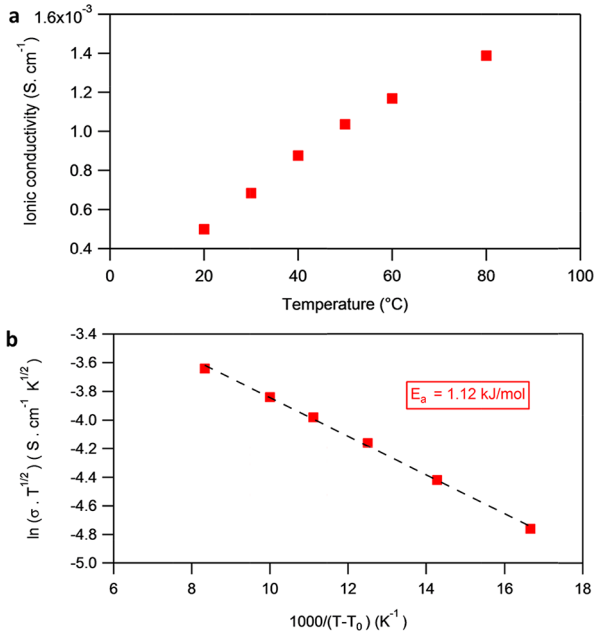

Figure 5. (a) Ionic conductivity of the GPE prepared from the poly(VDF-*co*-MAF-PFE) P3 copolymer with MAF-PFE/Li^+ = 5 in EMIM-TFSI IL vs temperature. (b) Temperature dependence of the ionic conductivity using the VTF model.

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The rather low value noted for the activation energy indicates that the Li^+ ions move easily in the investigated GPE. This was expected because LiTFSI is well-dissolved and dissociated in the EMIM-TFSI IL. This observation confirms that the ionic conductivity is due to the LiTFSI salt dissolved in the EMIM-TFSI IL.

Transference Number. The lithium ion transference number (tLi^+) represents the fraction of current carried by lithium ions and varies from 0 to 1 with 1 being the best value. Figure 6 shows the time dependence of current flowing

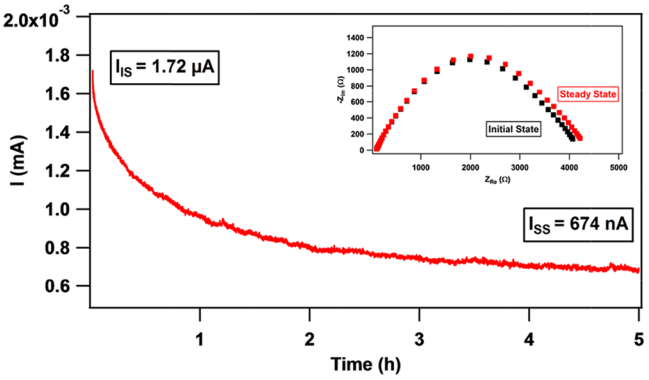

Figure 6. Time-dependent response of dc polarization for a Li/GPE/Li symmetric cell configuration at an applied dc bias of 10 mV (practical bias of 9.2 mV) and at 40 °C. The GPE is the poly(VDF-*co*-MAF-PFE) P3 copolymer with MAF-PFE/Li^+ = 5 in the EMIM-TFSI IL. The inset shows the impedance spectra at the initial (black) and steady (red) states of the cell.

through the P3-based GPE at 40 °C. The inset in Figure 6 displays the impedance measurements performed at the initial and steady states. The lithium ion transference number of the GPE was estimated to be 0.12 at 40 °C. This value is in the range of the tLi^+ values reported for PEO-based electrolytes[44−46] and does not reach a higher value as observed for some electrolytes based on ILs.[47] This observation is somewhat disappointing and could be due to a too strong coordination of the lithium ions on the MAF-PFE segments.

Electrochemical Stability. The electrochemical stability window of the GPE was investigated by cyclic voltammetry between 0.5 and 5 V versus Li/Li^+ at a scan rate of 0.1 mV/s (Figure 7). The GPE appears to be electrochemically stable in a wide range of potentials varying from 1.5 to 4.0 V versus Li/Li^+. Degradation is observed above 4.0 V and might be

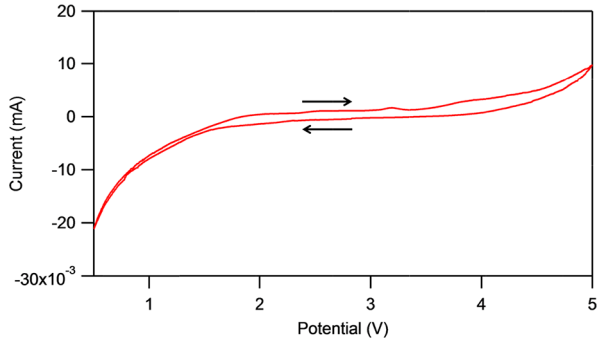

Figure 7. Cyclic voltammetry performed on the GPE at a scan rate of 0.1 mV/s. The GPE is the poly(VDF-*co*-MAF-PFE) P3 sample with MAF-PFE/Li^+ = 5 in the EMIM-TFSI IL.

attributed to the oxidation of MAF-PFE groups at the interface with the electrodes and oxidative corrosion of the stainless steel working electrode. For potentials below 1.5 V versus Li/Li^+, the pyrrolidinium cation reduction in the IL is probably occurring.[24]

CONCLUSIONS

This work represents a first step in the study of novel fluorinated copolymers as components for GPEs based on low vapor pressure ILs. The originality of the investigated materials lies in the design of original random copolymers obtained from VDF and a 2-trifluoromethacrylate monomer bearing pendant perfluoroalkyl ether groups (MAF-PFE). Three copolymers were synthesized with VDF molar ratios of 72, 73, and 87 mol %. DSC experiments revealed the lack of T_m, confirming the lack of crystalline domains in the copolymers. TGA measurements indicated that the most thermally stable system was the one containing the lowest MAF-PFE comonomer content, confirming that thermal degradation started from the decomposition of ester functions.

GPEs were prepared by swelling poly(VDF-*co*-MAF-PFE) copolymers in the IL-based electrolytes. Only the copolymer sample with the highest molar mass and containing the highest VDF content could lead to homogenous, transparent, and colorless gels, emphasizing the importance of the copolymer composition on the physicochemical properties of the system. On the one hand, MAF-PFE segments are mandatory for the formation of the GPE because a PVDF homopolymer alone could not lead to the formation of a GPE. In this respect, the solubility of MAF-PFE in the LiTFSI/EMIM-TFSI mixture is a key feature for the formation of the gel. On the other hand, one could hypothesize that VDF-rich domains insoluble in the IL-based electrolyte are formed and act as cross-linking knots at the origin of the GPE structure.

For the optimized GPE, conductivity values at RT reached up to 3×10^{-3} or 7×10^{-4} S·cm^{-1} for a MAF-PFE/LiTFSI molar ratio of 2 or 5, respectively. The temperature dependence of the conductivity was studied to calculate the activation energy (as low as 1.12 kJ·mol^{-1}) associated with the motion of lithium ions via the VTF model. These observations point out an ionic conduction essentially originating from the lithium salt dissociated in the IL component of the GPE. We believe that the low value of the transference number results from a strong coordination of Li^+ ions to the ether oxygens of the MAF-PFE units. Finally, such electrolytes displayed a decent electrochemical stability window.

Moreover, in addition to a deeper electrochemical characterization, mechanical analysis of the different samples will be essential to get further insight into their rheological behavior. This will provide a better understanding of the effects of the lithium salt and IL on the cohesion of the material. In addition, further work on reaching higher VDF amount is under progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00355.

^{1}H and ^{19}F NMR spectra of the MAF-PFE comonomer and poly(VDF-*co*-MAF-PFE) copolymers and DSC

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thermogram of the poly(VDF-*co*-MAF-PFE) P3 copolymer (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DSC, differential scanning calorimetry; EMIM TFSI, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; GPEs, gel polymer electrolytes; HFP, hexafluoropropylene; IL, ionic liquid; LIBs, lithium ion batteries; LiTFSI, lithium bis-(trifluoromethanesulfonyl)imide; MAF, 2-trifluoromethyl acrylic acid; NMR, nuclear magnetic resonance spectroscopy; PEO, poly(ethylene oxide); PPFR, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical; PVDF, poly(vinylidene fluoride); PFE, perfluoroalkyl ether; SPEs, solid polymer electrolytes; Tbppi, *tert*-butyl peroxypivalate; TGA, thermogravimetric analysis; VDF, vinylidene fluoride

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