

# Cationic conductivity in poly(oxyethylene oxide) networks

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## Abstract

New monomer salts with a perfluorosulfonate group were synthesized. These new salts, bearing one or two double bonds, lead to cross-linked solvating ionomers. Preliminary ionic conductivities and thermal characterizations are reported for single-cation conductors polymer electrolytes. The conductivity values of these single-cation conductors are markedly higher than those reported in the literature; the conductivity loss, with respect to the free-salt complexes, corresponds approximately to the expected anionic conductivity. The aim of this communication is twofold: (i) description of the synthesis of new lithium salts, and (ii) presentation of the results obtained with poly-electrolytes having a grafted anion.

**Keywords:** Single cation; Conductivity; Poly(oxyethylene oxide) network

## 1. Introduction

The interest of the scientific community in polymer electrolytes has grown steadily in the past years with regard to their potential applications, especially in solid-state lithium batteries. Recently, the importance of finding a new single-ion polymeric conductor specific to lithium cations has been highlighted. Single-cation polymer electrolytes, despite their fundamental advantages and the expected benefit from their use in batteries, have been the object of scant reports. However, only a few new materials have been prepared, such as poly[oligo(oxyethylene methacrylate)-co-(alkyl-metal methacrylates)] or polyphosphazene with pendent sulfonate groups which both have mobile cations and immobile anions on the polymer chains [1–5]. Unfortunately, due to extensive pairing or even phase separation, their reported conductivity is too low for use as solid polymer electrolytes in batteries operated at room temperature.

If several polymer electrolytes appear to be good candidates for use in lithium batteries providing a high conductivity at the battery-operating temperature and a good electrochemical stability; the important anionic mobility results in the formation of an undesirable salt gradient across the electrolyte membrane which is harmful to the good performances of the batteries. Several ionomers have already been prepared with ionophoretic functions such as sulfonates, phosphates, alkyl or perfluoroalkyl carboxylates, but all these salts behave as

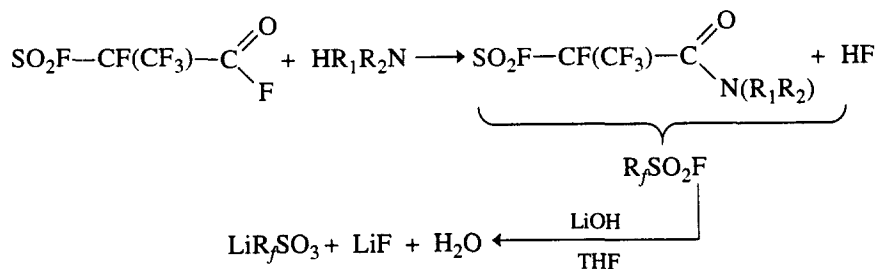
weak electrolytes in low-permittivity polyether solvent [6,7].

Indeed the ionophoretic functions to be attached to the macromolecular backbone must impart strong electrolyte behaviour, yet unknown, and therefore require the synthesis of new salts. As salt homopolymers do not generally meet the mechanical specifications to be shaped in thin membranes and do not own solvating segments, we must prepare a copolymer, incorporating both ionophoretic groups and solvating units. The synthesis and main characteristics of a new perfluorosulfonated salt and the electrochemical properties of a single-cation conductor obtained from its copolymerization have been presented in this paper.

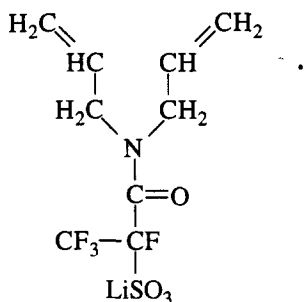
## 2. Experimental

### 2.1. Synthesis of new sulfonate salt

All experiments were performed inside an argon-filled dry box. Hexafluoropropanesultone was slowly added to a stirred ether solution at  $-20^{\circ}\text{C}$  containing a pre-weighted amount of dry Amberlyst A-21 resin (Janssen Chimica) acting as an isomerization catalyst and a scavenger for the hydrogen fluoride produced in the following step. Double bonds are then attached by reacting diallylamine (DAA) (or *N*-methylallylamine (NMAA)), for single double bond sulfonate salt) selectively at the carbonyl fluoride end:



with  $\text{R}_1 = \text{R}_2 = (\text{CH}_2 = \text{CHCH}_2 -)$  as below:



Scheme 1. Lithium *N,N*-diallyl-1-amido-tetrafluoroethane sulfonate  $\text{R}_f\text{SO}_3\text{Li}$ .

## 2.2. Preparation of electrolytes

All the following preparations were also performed in the argon-filled dry box. After mechanical stirring for several hours in order to obtain homogeneous solutions, the polyelectrolyte films were prepared by the conventional solvent casting method in a glass ring on polytetrafluoroethylene plate paper. After slow evaporation of the solvent under argon for 1 day at room temperature, the films were stored in a dry glove box, and the remaining film on a Teflon plate was heated for several hours at 70 °C in order to perform complete drying and thermal polymerization.

A complete copolymerization was confirmed by soxhlet extracts of insoluble films using dimethyl ketone as solvent. The percentage extracts of insoluble films was determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as eluent.

## 3. Material characterization

### 3.1. Gel permeation chromatography

GPC analysis was performed on a Waters 590 GPC, equipped with a differential refractometer Waters 410 and a Waters 745B 'data module'. The solvent (THF) previously filtered and degassed is used at flow rates of 0.7 ml/min through two ultra-styragel columns of 100 Å and 1.2 ml/min through three ultra-styragel columns of 10<sup>4</sup>, 10<sup>3</sup> and 500 Å, respectively, for salt and polymer analysis. The resulting separation of poly-

mers, oligomers, monomers and solvents is very efficient and is therefore very sensitive to low molecular weight variation.

### 3.2. Thermal analysis

A Netzsch STA 409 differential scanning calorimeter (DSC) was used to determine the glass-transition ( $T_g$ ) and melting ( $T_m$ ) temperatures. Thermograms were recorded at a rate of 10 °C min<sup>-1</sup> under a helium atmosphere. Each sample was first heated from -120 to 150 °C, quenched or cooled to -120 °C and then heated again up to 150 °C. The thermal stability of the samples was studied by heating in an air atmosphere at the rate of 10 °C min<sup>-1</sup> from room temperature to 400 °C.

### 3.3. Conductivity measurements

The ionic conductivity of the POE–polyelectrolyte mixtures were determined by the impedance spectroscopy method with blocking electrodes, using a HP 4192 A analyser in the range from 13 MHz to 5 Hz under dynamic vacuum. The cell was handled in a dry box for samples to be sandwiched between two stainless-steel electrodes after which, it was submitted to heating/cooling cycles. The conductivity was measured at various temperatures, after an equilibrium time of 1 h at each temperature.

### 3.4. Infrared and RMN characterizations

The infrared spectrum was performed with a Nicolet 710 Fourier-transform infrared spectroscopy (FT-IR) coupled to a microcomputer. The spectrum was collected over the 4000–400 cm<sup>-1</sup> range by averaging 200 scans with a resolution of 4 cm<sup>-1</sup>. The salt  $\text{R}_f\text{SO}_3\text{Li}$  was analysed as a dispersion in a KBr pellet.

The <sup>19</sup>F NMR spectrum was recorded with a Bruker spectrometer operating at 200 MHz for fluorine resonance.

### 3.5. Cyclic voltammetry

The electrochemical stability was studied, using both micro- and macroelectrodes, by voltamperometry. We

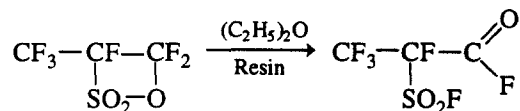
finally selected the microelectrodes for the study of our polyelectrolyte systems. Indeed, one of the main advantages [8–10] of microelectrodes is related to the very weak currents which are useful for the highly resistive polyelectrolytes, as the use of macroelectrodes encountered large uncompensated *IR* effects. A two-electrode configuration experimental cell was used. The working electrode is a metallic microdisc of platinum (diameter = 25  $\mu\text{m}$ ) and nickel (diameter = 50  $\mu\text{m}$ ) sealed in soft glass. Lithium metallic foil pressed on a stainless-steel collector served as auxiliary electrode which can be used as the reference electrode without detectable perturbation of its potential since low currents are measured.

The scanning rates used were 2 and 4  $\text{mV s}^{-1}$  and the temperature of the sample was fixed at 80  $^{\circ}\text{C}$ .

## 4. Results and discussion

### 4.1. Salt synthesis and characterizations

The new lithium sulfonate is synthesized from perfluorosultones. The latter are usually prepared by condensation of sulfur trioxide on perfluoroalkenes, here, on hexafluoropropene. Hexafluoropropanesultone undergoes a rapid isomerization in the presence of catalytic amounts of a nucleophilic reactant such as diethyl oxide. Isomerization results in an acyclic compound, the perfluoro-2-fluorosulfonyl-propionyl fluoride, bearing two fluoride-acid functions, COF and  $\text{SO}_2\text{F}$ , as shown below [11,12]:



The two functions COF and  $\text{SO}_2\text{F}$  can react with the amine function giving an amide or a sulfonamide product, respectively. Nevertheless, since the COF function is much more reactive than  $\text{SO}_2\text{F}$ , the amide, by thorough addition of the amine on the isomerized sultone, can be selectively obtained. Thus, the isomerized sultone is always in excess with respect to the amine. The resulting product will be abbreviated as  $\text{R}_f\text{SO}_2\text{F}$ .

$^{19}\text{F}$  NMR of  $\text{R}_f\text{SO}_2\text{F}$  in  $\text{CD}_3\text{Cl}_3$  show the expected product with three singlets at, respectively,  $-152.6$  ppm (CF),  $-73.2$  ppm ( $\text{CF}_3$ ), and  $+46.8$  ppm ( $\text{SO}_2\text{F}$ ) reference  $\text{CF}_3\text{Cl}$ .

The infrared spectrum agrees well with the expected molecular structure and shows very intense bands in the  $1280\text{--}1076$   $\text{cm}^{-1}$  region for the  $\text{SO}_2$  group, an absorption in the  $1360\text{--}1300$   $\text{cm}^{-1}$  region for the  $-\text{CF}_3$ , while the  $1676\text{--}1640$   $\text{cm}^{-1}$  region is related to the  $-\text{CO}$  of the amide function. Several other bands connected

Table 1  
Fourier-transform infrared absorption spectrum frequencies in  $\text{cm}^{-1}$  of the new salt of  $\text{R}_f\text{SO}_2\text{F}$

| Group                           | =CH <sub>2</sub> | -CH  | -CH <sub>2</sub> | -C=O | S=O  | S-F  | S-O  |
|---------------------------------|------------------|------|------------------|------|------|------|------|
| Absorption ( $\text{cm}^{-1}$ ) | 3091             | 3022 | 2922             | 1640 | 1255 | 1045 | 1076 |
|                                 | 2992             |      | 1476             |      | 1141 |      |      |

Table 2  
Glass-transition temperatures ( $T_g$ ) of several samples MPOE/ $\text{R}_f\text{SO}_3\text{Li}$  determined from differential scanning calorimetry; heating rate = 10  $\text{K min}^{-1}$

| O/Li                         | 5   | 14  | 16  | 18  |
|------------------------------|-----|-----|-----|-----|
| $T_g$ ( $^{\circ}\text{C}$ ) | -30 | -52 | -52 | -52 |

to the  $-\text{CH}$  and the  $=\text{CH}_2$  groups are summarized in Table 1.

The lithium salt is obtained by mixing a THF solution of  $\text{R}_f\text{SO}_3\text{Li}$  with an excess of lithium hydroxide for several hours.  $^{19}\text{F}$  NMR performed in a  $\text{CD}_3\text{CN}$  show the disappearance of the signal at  $+46.8$  ppm, confirming the reaction of  $\text{SO}_2\text{F}$ .

### 4.2. Synthesis of single-cation conductor and characterizations

#### 4.2.1. Synthesis

A good way to obtain a single-cation conductor consists in cross-linking a POE unsaturated copolymer, called modified POE (MPOE) with  $\text{R}_f\text{SO}_3\text{Li}$ . The cross-linked films were prepared by homogeneous copolymerization of MPOE and  $\text{R}_f\text{SO}_3\text{Li}$ , using a small amount of free-radical initiator such as benzoyl peroxide. The membranes were then thoroughly washed either by swelling and washing the membranes several times with dimethyl ketone or by soxhlet extraction. In any case, we did not recover free-salt, as evidenced by infrared and by GPC analysis of the extracts.

$\text{R}_f\text{SO}_3\text{Li}$  appeared therefore to react completely and to be covalently bonded to MPOE chains.

#### 4.2.2. Thermal analysis

$T_m$  and  $T_g$ , from DSC analysis, are listed in Table 2. Amorphous network ionomers were obtained for all salt compositions at ambient temperature; the crystalline phases exhibit temperatures lower than 20  $^{\circ}\text{C}$ . The  $T_g$  values are markedly lower than those obtained by salt dissolution in the same network and are almost independent of the salt concentration, except for the highest salt concentrations.

#### 4.2.3. Conductivities

Prior to investigate single-cation conductors we checked the  $\text{R}_f\text{SO}_3\text{Li}$  behaviour, when dissolved in a

usual solvating polymer, i.e. POE  $5 \times 10^6$ . Fig. 1 reports the best Arrhenius plots obtained for POE/ $R_7SO_3Li$ , POE/ $CF_3SO_3Li$  and POE/ $LiClO_4$ , and shows that the  $R_7SO_3Li$  complexes are markedly more conductive than the triflate one, while only slightly more conductive than the perchlorate complex. According to its conductivity in POE complexes, the salt may be bonded to the polymer to provide single-cation conductors.

All conductivities were performed on extracted membranes, in order to remove the soluble materials, i.e., remaining soluble polymers and possibly traces of  $R_7SO_3Li$ . By changing the host linear polymer-POE for MPOE, the salt must copolymerise by a thermal free-radical polymerization process with MPOE dangling double bonds. Thin films prepared by the thermal polymerization of allyl monomers were flexible. Fig. 2 reports a conductivity comparison between several MPOE/ $R_7SO_3Li$  networks. The Arrhenius conductivity plots exhibit a free-volume behaviour except for the composition O/Li=5. In order to determine the con-

ductivity loss inherent to the anion fixing, preliminary measurements have been performed to value the ionic conductivities of linear and cross-linked MPOE- $R_7SO_3Li$  complexes. Thus, in cross-linked MPOE- $R_7SO_3Li$  complexes, MPOE is previously cross-linked without any salt, the membrane is then washed to remove the residual peroxide,  $R_7SO_3Li$  is at that time incorporated in the membrane from an acetonitrile  $R_7SO_3Li$  solution. After the removal of acetonitrile the weight difference allows the salt composition to be determined. The conductivities of cross-linked MPOE- $R_7SO_3Li$  are lower than those obtained with the same lithium salt concentration using linear MPOE- $R_7SO_3Li$  complexes (Fig. 3).

The best conductivities were observed for a salt concentration O/Li=14 and reach  $10^{-7} S cm^{-1}$  at 25 °C and  $10^{-5} S cm^{-1}$  at 75 °C, a good result for a single cation conductor.

Moreover, the best conductivity values of these single-cation conductor ionomers approach those obtained for free  $R_7SO_3Li$  dissolved (and non-bonded) in the same cross-linked network. The ratio between the best conductivity levels of single-cation and free salt is close to 0.3, this discrepancy probably being related to the loss of anionic contribution.

#### 4.2.4. Electrochemical stability

The electrochemical stability was checked by cyclic voltammetry using microelectrodes (Figs. 4 and 5) which are characterized by their small surfaces ( $6 \times 10^{-6} cm^2$ ). The use of platinum microelectrodes allows the electrochemical stability during oxidation up to 4 V versus Li/Li<sup>+</sup> to be characterized, but the formation of a lithium-platinum alloy and intermetallic phase mask the lithium plating/stripping; on the contrary, nickel and copper microelectrodes allow the electrolyte behaviour in solution to be characterized.

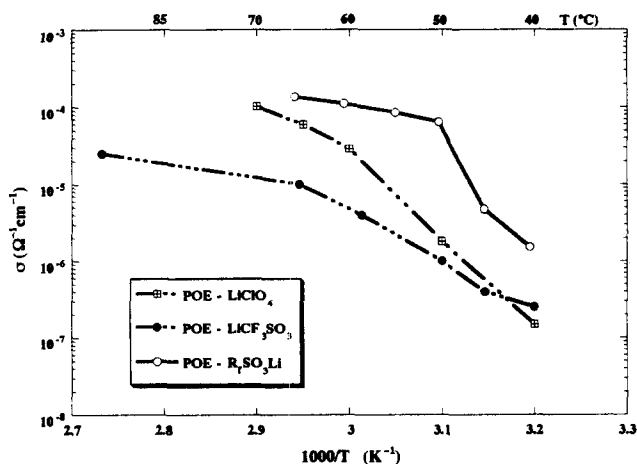


Fig. 1. Conductivity vs. reciprocal temperature for complexes  $P(OE)_n-R_7SO_3Li$  compared with triflate and perchlorate. First cooling cycle.

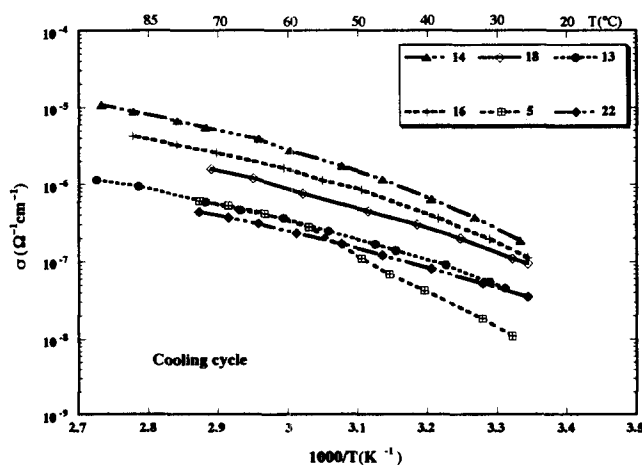


Fig. 2. Conductivity vs.  $T^{-1}$  of the grafted anion networks for several concentrations.

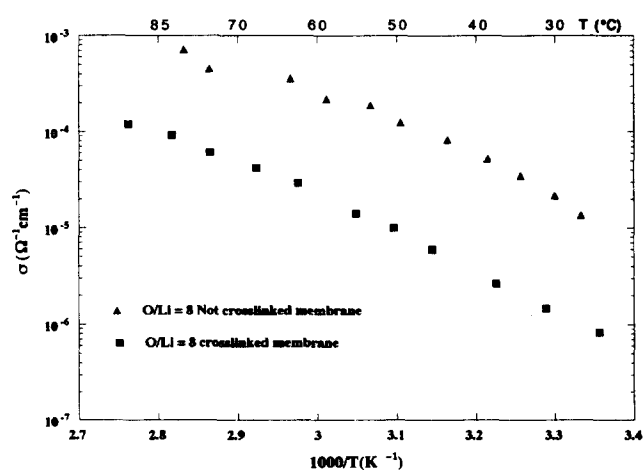


Fig. 3. Conductivity vs. reciprocal temperature for complexes MPOE- $R_7SO_3Li$  for the same concentration using both linear and cross-linked modified POE (MPOE).

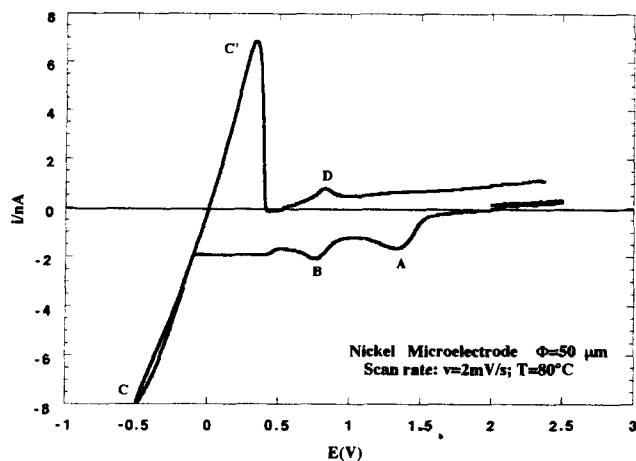


Fig. 4. Voltammogram of the electrochemical stability of the MPOE/ $R_7SO_3Li$  network at 80 °C on a nickel microelectrode, diameter = 50  $\mu m$ ; scan rate = 2  $mV s^{-1}$ .

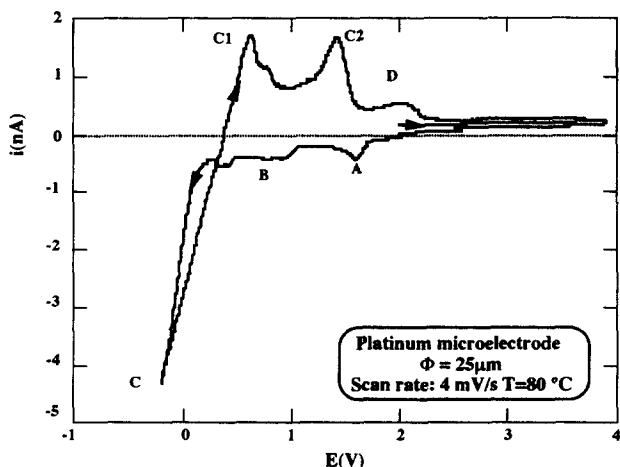


Fig. 5. Voltammogram of the lithium plating/stripping process from the MPOE/ $R_7SO_3Li$  network at 80 °C on a platinum microelectrode, diameter = 25  $\mu m$ ; scan rate = 4  $mV s^{-1}$ .

## 5. Conclusions

A new class of single-cation polymeric conductors has been found. Synthesis leads to salts in which the sulfonate anionic charge is adjacent to a strongly at-

tracting moiety (perfluorocarbon + amide group) and is more compatible in polyether-based electrolytes and more dissociated in such a medium than the non-fluorinated sulfonates and carboxylates, or even than the perfluorocarboxylates.

Our first attempt was successful, insofar as the conductivity values of these single-cation conductor polymer electrolytes are higher than those reported in the literature. Nevertheless, progress must be made in order to increase their conductivities, which may probably be increased by more than one order of magnitude.

The electrochemical properties of this new ionomer are in progress.

## Acknowledgements

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