Polymer electrolytes based on lithium sulfonate derived from perfluorovinyl ethers; single ion conductors

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Abstract: A new lithium perfluoroakylsulfonate has been synthesized from a commercial perfluorovinylether fitted with a fluorosulfonyl group. By making use of the vinylether group, this species was incorporated into polyurethane networks based either on a poly(ethylene oxide)glycol or on a tri-arm star-poly(ethylene oxide)triol. The results, in terms of ionic conductivities, thermal behaviour and different domains of rigidity (solid-state ¹H NMR), are reported for these single cation conductor polymer electrolytes. When compared to the polymer electrolytes where the same but untethered lithium perfluoroakylsulfonate is dissolved in the same initial networks, a loss of conductivity is observed despite the higher mobility of the ionomers. This loss corresponds to the conductivity attributed to the anionic species. The higher mobility of the ionomeric electrolytes is to be related to the quasi absence of physical crosslinks.

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Keywords: polymer electrolytes; lithium perfluoroakylsulfonate; single cation conductors; crosslinked polyethers; ionomers

INTRODUCTION

The application of ion-conductive polymers to solid electrolytes in high-energy batteries was suggested in 1978.1 Since then, a large number of studies and reviews²⁻⁴ have been devoted to this subject, and the pertinent parameters to achieve important conductivity have been recognized. They are based on the solvating power of the polymer towards the lithium salt to be used and the capability of this salt to dissociate in a medium of low dielectric constant. This determines the number of charge carriers. The mechanism of ion migration requires amorphous character of the polymeric system,⁵ because the mobility of the ionic species is directly related to the segmental motion of the polymer. One of the drawbacks of such systems is the significant decrease in ionic conductivity that occurs under dc polarization, because of cation and anion migration: no active electrode is used for the anionic species, so the local concentration of anions near the anode is increased and, as a consequence, the resistance of the system becomes more important with time.

Several methods have been developed to achieve single cation conductive polymers. According to Tsuchida and co-workers⁴ three general approaches can be identified: (1) a blend of polyelectrolyte and ion-conductive polymer;^{6,7} (2) the copolymerization of ion-conductive monomers and carrier source

monomers;^{8–12} (3) the polymerization of an ionconductive monomer which is also a carrier ion source.¹³ Another approach is the preparation of a polyether network with an ionizable crosslinking agent.^{14,15} Most of the salts used were of sulfonate or carboxylic acid type, and provided modest conductivities (around 10^{-7} S cm⁻¹ at room temperature) due to limited solubilities and dissociation in polyethers. The use of perfluorocarbon moieties adjacent to the sulfonate group increases conductivity because of a better dissociation of the ion-pair.^{16,17} Different strategies have been developed to prepare and copolymerize monomers fitted with such salts and ion-conductive monomers.¹⁷

This work presents the preparation and study of a new type of single ion-conductor obtained from a perfluorovinylether fitted with a fluorosulfonyl endgroup, ie $CF_2 = CF - O - CF_2 - CF(CF_3) - O - CF_2 CF_2 - SO_2 F$.¹⁸ This compound is used as a comonomer in the copolymerization of tetrafluoroethylene to obtain the commercialized "Nafion.¹⁹ It was first transformed by alkaline hydrolysis into lithium sulfonate and its performance as an electrolyte was examined in several polymer matrixes. By making use of the vinyl end-group, a strategy was developed to graft the anion to a polymer and thus prepare a single cation conductor. The vinyl function was transformed into a hydroxyl group and submitted to polycondensa-

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Contract/grant sponsor: Centre National de la Recherche Scientifique

Contract/grant sponsor: Bolloré Technologies

⁽Received 5 August 1999; revised version received 2 February 2000; accepted 15 February 2000)

tion with different functional solvating poly(ethylene oxide)s. To obtain thin film polymer electrolytes with good mechanical stability, polymeric networks were prepared where the perfluoro lithium sulfonates are present as dangling chains attached to a crosslink.

EXPERIMENTAL

Materials

The perfluorovinylether fitted with a fluorosulfonyl group is abbreviated as RFSO₂F. It was graciously given by Dupont and corresponds to the following developed $CF_2 = CF - O - CF_2 - O$ formula: $CF(CF_3)$ —O— CF_2CF_2 — SO_2F . LiOH, mercaptoethanol, azobisisobutyronityrile and poly(ethylene oxide)glycol ($M_n = 600 \,\mathrm{g \, mol}^{-1}$) were purchased from Aldrich. Tris(4-isocyanatophenyl)thiophosphate (Desmodur RFE) was purchased from Bayer. A star-shaped PEO [PEO(OH)₃, trihydroxyl $M_{\rm p} = 3300 \,{\rm g \, mol^{-1}}$] was graciously prepared by Y Gnanou (Laboratoire de Chimie des Polymères Organiques, Bordeaux). All solvents were distilled before used.

Syntheses

Preparation of $RFSO_2F$ derivatives and characterization $\mathbf{RFSO}_3\mathbf{Li}$ (perfluorovinylether lithium sulfonate) was obtained by reacting 1.16g (2.6×10^{-3} mol) of \mathbf{RFSO}_2F dissolved in 5ml of THF and 1.7ml of aqueous LiOH (3.4moll⁻¹). The solution was continuously stirred at room temperature for 15h. After evaporation of the solvent, the product was again dissolved in tetrahydrofuran (THF), centrifuged and filtered to eliminate the excess of LiOH and LiF. After evaporation of THF, the product was dried under vacuum (10^{-3} mmHg) for 48 hours. A yellow solid was obtained (about 92% yield) and washed with chloroform to extract unreacted \mathbf{RFSO}_2F . It was characterized as follows:

$$(1) F \xrightarrow{O-CF_2-CF_3} O-CF_2CF_2SO_3Li$$

$$(2) F \xrightarrow{(3)} F \xrightarrow{(d)} (d) = (b) (e)$$

$$(1) F \xrightarrow{(d)} (d) = (cF_2) CF_2CF_2SO_3Li$$

$$(1) F \xrightarrow{(d)} (f) = (cF_2) CF_2CF_2SO_3Li$$

¹⁹F NMR (acetone- d_6) δ (ppm): -72.8 (m, 5F, b+c); -77.7 (m, 2F, d); -106.9 (dd, 1F, CF₂=, 1); -111.1 (m, 2F, e); -115 (dd, 1F, CF₂=, 2); -129.3 (dd, 1F, CF=, 3); -138.3 (m, 1F, f).

IR: (SO_2) asym vibr 1309 cm^{-1} (strong), sym vibr 982 cm^{-1} (weak).

The elemental analysis was made on a sample that could not be dried completely because of its very high hygroscopy: C (%) 18.95 (calculated 18.66), Li (%) 1.66 (calculated 1.55). However, the slight excess of Li and C is to be attributed to traces of impurities, presumably lithine or LiF and organic by-products.

HO—**RF**—SO₂F (ω -hydroxy derivative of **RF**SO₂F) was obtained by reacting 5.14g (0.015 mol) of **RF**SO₂F, 1.8g (0.023 mol) of mercap-

toethanol and 0.378g of azobisisobutyronitrile (AIBN) in 15ml of THF solvent, within a glass tube. After oxygen removal, the reaction was run under static vacuum at 70 °C for 8h. A first distillation under vacuum (10mmHg) allowed the solvent and non-reacted species to be removed. A colourless, viscous product was obtained at about 80 % yield by distillation under 10^{-4} mmHg vacuum and characterized as follows:

$$\begin{array}{c} (c) \\ CF_{3} \\ HO-CH_{2}CH_{2}-S-CF_{2}-CFH \\ (d) \\ (f) \\ (b) \\ (e) \\ (a) \end{array} + \begin{array}{c} (c) \\ CF_{3} \\ (-CF_{2}-CF_{3}-CF_{2}-CF_{2}-CF_{3}-$$

¹HNMR (CDCl₃) δ (ppm): 6 (dt, 1H, --CFH---); 3.57 (t, 2H, --CH₂O---); 3.08 (t, 2H, --CH₂S---).

¹⁹FNMR (CDCl₃) δ (ppm): +47.88 (m, 1F, -SO₂F, a); -77 (m, 2F, b); -77.6 (m, 3F, c); -82 (m, 2F, d); -86.5 (m, 2F, F1+F2); -109.6 (m, 2F, e); -136.9 (d, 1F, 3); -142.6 (m, 1F, f).

IR (film): (SO_2) asym vibr 1415 cm⁻¹ (strong), sym vibr 982 cm⁻¹ (strong).

Mass spectrum: M/e = 524, parent peak for $C_0H_6O_5F_{14}S_2$

Synthesis of the polymer electrolyte network NTPEO₆RFSO₃Li (O/Li=18)

The reaction was carried out in a glove box under nitrogen atmosphere. 1.38g $(2.3 \times 10^{-3} \text{ mol})$ of PEG600 (poly(ethylene oxide)glycol), $M_{\rm p} = 600 \,{\rm g}$ mol^{-1}) (Aldrich), 0.75g (1.43×10^{-3} mol) of HO—**RF**SO₂F and 1.00g $(2.15 \times 10^{-3} \text{ mol})$ of tris(4-isocyanatophenyl)thiophosphate (Desmodur RFE, Bayer) $S=P(OC_6H_4N=C=O)_3$ were dissolved in THF. 1,4-Diazo-[2,2,2]-bicyclooctane catalyst was added at 0.3% of the total mass of PEG and monohydroxylated HO-RF-SO₂F. The critical conversion p_c to reach the gel point was previously calculated^{20°} to be 0.84 using the equation $p_c = 1/[r(f_{w,OH}-1) (f_{w,NCO}-1)]^{0.5}$, where r = [OH]/[NCO] = 0.935, and $f_{w,OH}$ and $f_{w,NCO}$ are the weightaverage functionalities of the hydroxyl and isocyanate containing molecules. Thus, it is established that a network can be formed that would fully incorporate the monohydroxy derivative of the fluorosulfonyl perfluorovinylether.

The solution was poured in a Teflon mould to obtain a thin film. It was kept at ambient temperature for 48h and then raised to 60 °C and kept at this temperature for 3h. The resulting gel was washed in methanol until constant weight was obtained: 2% by weight of soluble species were extracted and showed to be mainly isocyanate oligomers. Thus one can consider that practically all PEG 600 and HO—**RF**—SO₂F are present and reacted in stoichiometric amounts with the triisocyanate.

Subsequently the gel was swollen in water in the presence of LiOH ([LiOH]/[HO $-RF-SO_2F$]=2.2) for 2h to transform the pendant $-SO_2F$ group into

 $-SO_3Li$. It was washed with water to remove LiOH and LiF and then with methanol. The film obtained was dried under vacuum (10^{-3} mmHg) at 80°C for 24h.

Synthesis of the polymer electrolyte network *NTPEO*₃₃*RFSO*₃*Li* (*O*/*Li*=17.5)

The same procedure was used to obtain the NTPEO₂₃RFSO₂Li network. A trihydroxyl starshaped \overrightarrow{PEO} [$\overrightarrow{PEO}(OH)_3$, $M_n = 3300 \text{ g mol}^{-1}$] was prepared by Y Gnanou using the anionic polymerization technique.²¹ 0.23 g (7×10^{-5} mol) of this functional polymer was reacted with 0.15 g(2.86×10⁻⁴ mol) of HO—**RF**—SO₂F and 0.080 g $(1.72 \times 10^{-4} \text{ mol})$ of tris(4-isocyanatophenyl)thiophosphate in THF solution. The critical conversion p_c to reach the gel point was calculated to be 0.78, so that HO-RF-SO₂F should be fully incorporated into the network. By washing, some 2% by weight of soluble species [isocyanate oligomers and some tri-star PEO(OH)₂] were extracted, so that again one can consider that practically all PEO(OH)3 and HO-**RF**—SO₂F are present and reacted in stoichiometric amounts with the triisocyanate. The alkaline hydrolysis was run in the same way as previously.

Polymer electrolyte characterization by thermal analysis, ionic conductivity and solid state ¹HNMR measurements

The different polymer electrolytes were obtained as films or membranes from a solution of salt and polymer in acetonitrile, prepared in a Teflon mould. After evaporation of the solvent they were dried at 80 °C under vacuum for several days and then kept in a dry nitrogen atmosphere.

The thermal analysis was performed by a Perkin Elmer DSC 7 apparatus on tight aluminium capsules containing the polymer electrolyte samples. To determine the glass transition temperature T_g of the amorphous systems, the samples were first quenched to -110 °C, then heated to 150 °C at a rate of 20 °C min⁻¹. This cycle was repeated several times to check reproducibility. When the systems were semicrystalline, the rate of heating was changed to 40 °C min⁻¹ from -110 to 30 °C and to 10 °C min⁻¹ from 30 °C to 220 °C, to determine T_g and the melting temperature T_m , respectively.

To measure the ionic conductivity, the films were sandwiched between stainless-steel electrodes and heated at 50 °C under vacuum for 48h. AC conductivity measurements were carried out under dynamic vacuum using a Solartron 1260 impedance analyser (Schlumberger Technologies), from room temperature up to 85 °C over the frequency range 5Hz to 32 MHz. When some flow was observed, the conductivity values were corrected by using the appropriate dimensions of the sample.

To determine domains of different rigidity, solid state ¹HNMR measurements were carried out on a Bruker SXP spectrometer operating at 60 MHz (¹H).

The resonance field was monitored with a field frequency lock (Drusch, NMR gaussmeter and regulation unit TAO2) within 2μ T. The free induction decay (FID) signal, following a $\pi/2$ pulse of 4μ s generated by a Hewlett-Packard pattern generator 8175A, was digitized with a LeCroy 6810 with 12 bits (accuracy 1/2000) at a fastest sampling rate of 5 MHz, and finally averaged and treated on an IBM-PC compatible ACER-1100. Numerical computations were performed in Asyst language. The FID can be fitted with a linear combination of exponential functions. Extrapolation of the signal to the middle of the pulse (t=0) through the dead time of the receiver (5µs) provides the relative amount of each component. Owing to a ratio of at least three for the time constants, the fractions deduced from the FID can be considered as significant.

RESULTS AND DISCUSSION

Various polymer electrolytes were synthesized in order to achieve an O/Li ratio (molar ratio of solvating ether oxygens to lithium salt) of around 18, which corresponds to a domain of salt concentration showing usually high conductivity values, and thus allow comparison at the same or close salt content. A limited availability of the starting material (perfluorovinylether) did not allow us to explore a larger range of lithium salt concentration.

Thermal behaviour and ionic conductivity of polymer electrolytes containing lithium sulfonate RFSO₃Li, derived from perfluorovinyl ether

effectiveness of $CF_2 = CF - O - CF_2 - O$ The $CF(CF_3)$ —O— CF_2CF_2 — SO_3Li (referred to as RFSO₃Li) as an ionic conductive salt was examined when dissolved in a semi-crystalline high molecular weight poly(ethylene oxide) (PEO) $(M_n = 9 \times 10^5 \text{ g})$ mol⁻¹). Two samples were prepared with an O/Li content of 20 and 30, ie respectively 0.75 mol and 0.56 mol of salt per kilogram of polymer electrolyte. Their DSC analysis revealed the presence of both a crystalline ($T_{\rm m}$ =67 °C) and an amorphous phase $(T_{\sigma} = -35 \,^{\circ}\text{C} \text{ and } -37 \,^{\circ}\text{C}, \text{ respectively}).$ This is reflected in the Arrhenius conductivity plots (Fig 1) which exhibit a shoulder below 60°C when the crystalline phase appears and where low conductivity values are obtained.⁵ When measurements were run at decreasing temperatures a retardation to crystallization would account for the higher conductivity as shown in the case of O/Li = 20. Conductivities of about $10^{-4} \mathrm{S \, cm^{-1}}$ were obtained at $60\,^{\circ}\mathrm{C}$ which compare with data obtained for $CF_3SO_3Li_2^{2}$ at close O/Li ratios, although reports for the $C_nF_{2n+1}SO_3Li$ series indicate some dependence of conductivity on the size of the perfluoro entity.²³

To avoid the interference of crystallinity and in order to compare $\mathbf{RFSO}_3\mathbf{Li}$ with the most performing $(\mathbf{CF}_3\mathbf{SO}_2)_2\mathbf{NLi}$,²⁴ the two salts were dissolved in an amorphous polyurethane network \mathbf{NTPEO}_6 , prepared



Figure 1. Dependence of conductivity on reciprocal temperature for PEO $(M_{\eta}=9 \times 10^5 \text{ g mol}^{-1})/\text{RFSO}_3\text{Li}$ electrolytes for two compositions during cooling $(\bigtriangledown, O/\text{Li}=20; \blacklozenge, O/\text{Li}=30)$ and during heating $(\triangle, O/\text{Li}=20)$.

from stoichiometric amounts of poly(ethylene oxide)glycol (PEG) $(M_n = 600 \text{ g mol}^{-1})$ and an aromatic triisocyanate, $S = P(OC_6H_4N = C = O)_3$, yielding two polymer electrolytes, $NTPEO_6/RFSO_3Li$ $(O/Li = 26; T_g = +4°C)$ and $NTPEO_6/(CF_3SO_2)_2NLi$ $(O/Li = 27; T_g = +6°C)$. A preliminary study showed conductivity values about three times higher for the sulfonimide at the same temperature. Because these measurements were performed at close segmental mobility of the polymeric matrix and close solvated lithium content, the higher conductivity of the latter salt is to be related to some better dissociation properties.

Polymer networks with pendant lithium perfluoroalkyl sulfonates: synthesis, thermal properties, ionic conductivity, structuring effect Synthesis of ionomeric networks with pendant lithium perfluoroalkyl sulfonates

The perfluorinated ω -hydroxy-sulfonyl fluoride HO— **RF**SO₂F was obtained from the initial perfluorovinylether **RF**SO₂F (Scheme 1) and further incorporated into a solvating polymer backbone by formation of a polyurethane network (Scheme 2). The polymer samples were carefully extracted with methanol to remove soluble species. After hydrolysis of the sulfonyl

$$CF_2$$
=CF-O-CF₂-CF(CF₃)-O-CF₂CF₂-SO₂
HS-CH₂CH₂OH ↓ AIBN, 70 °C
HO-CH₂CH₂-S-CF₂-CF(H)-O-
CF₂-CF(CF₃)-O-CF₂CF₂-SO₂F

Scheme 1. Synthesis of HO-RFSO₂F.

fluoride group into lithium sulfonate by lithium hydroxide and subsequent extraction by water to eliminate excess of alkali, the polymeric networks were expected to be single cation conductors.

A first sample was obtained from a HO– $\mathbf{RFSO}_2F/$ PEG600 mixture (0.622 molar ratio) and a stoichiometric amount of triisocyanate to yield a molar ratio of solvating ether oxygens over SO₂F groups ([O]/ [-SO₂F]) equal to 18. Thus after alkaline hydrolysis, the same ratio of [O]/[-SO₃Li] equal to 18 is obtained, which is within the domain where best conductivities are usually observed. If one assumes that only one ionomer is attached to a triurethane knot, 71% of those knots would have a pendant **RFSO**₃Li group whereas 29% would be true crosslinks, ie connected to elastic poly(ethylene oxide) chains.

A second sample was made from a HO—RFSO₂F/ PEO(OH)₃ 3300 mixture (4.09 molar ratio) and stoichiometric amount of triisocyanate so as to yield after hydrolysis a molar ratio $[O]/[-SO_3Li]$ of solvating ether oxygens over SO₃Li groups equal to 17.5. In this network 29% of the junction points stem from PEO(OH)₃ and are true crosslinks, whereas 71% come from the triisocyanate. The latter junctions are connected to an average of 1.6 pendant RFSO₃Li groups per knot and thus form only a small amount of real crosslinks.

The features of these networks and other systems made from by incorporation of unterhered lithium salts are reported in table 1.

Properties of the tridimensional polymer electrolytes made from poly(ethylene oxide)glycol PEG600

The first network, referred as NTPOE₆RFSO₂F



Scheme 2. Formation of the polyurethane (PUR) networks.

	Polymer network	Polymer electrolyte	Т _д (°С)	O/Li	mol salt/kg of polymer electrolyte
	NTPEO ₆ RFSO ₂ F		-13.5		
	0 2	NTPEO ₆ RFSO ₃ Li	-11.5	18	0.47
		NTPEO6RFSO2F	-4	15	1.59
		+ RF SO ₃ Li	-5	21	1.42
Table 1. Lithium salt content and glass transition		NTPEO6RFSO2F	0	15	1.82
temperatures of NTPEO6RFSO2F and		$+ (CF_3 SO_2)_2 NLi$	-1	25	1.38
NTPEO ₃₃ RFSO ₂ F polymer networks and networks	NTPEO33RFSO2F		-40		
made from them containing either tethered		NTPEO33RFSO3Li	-35	17.5	0.63
(NTPEO ₆ RFSO ₃ Li and NTPEO ₃₃ RFSO ₃ Li) or		NTPEO33RFSO2F	-25	16.8	0.50
untethered (RF SO ₃ Li) lithium perfluorosulfonates or (CF ₃ SO ₂) ₂ NLi		+ RF SO ₃ Li			

before hydrolysis, totally amorphous is $(T_g = -13.5 \,^{\circ}\text{C})$. After hydrolysis, the network $(NTPEO_6 RFSO_3 Li; O/Li=18)$ is still amorphous but has a slightly higher $T_{\rm g}$ (-11.5 °C). Its Arrhenius conductivity plot is shown in Fig 2. To compare the results with a system where the same but untethered lithium salt is present, RFSO₃Li was dissolved in the same initial network ie NTPEO₆RFSO₂F, at two different O/Li ratios (15 and 21) which raise its T_{σ} to -4 °C and -5 °C, respectively. Figure 2 shows that the latter polymer electrolytes are more effective in the same range of temperature and O/Li ratio. To check whether this can be related to the absence of the anionic contribution, the conductivity values were plotted versus $100/(T-T_g)$, ie at reduced temperature (Fig 3). Indeed, the ionic conductivity of an amorphous system, above glass transition temperature, is related to its free volume: it was shown that the logarithm of conductivity is inversely proportional to $(T - T_g)$, as postulated by the Williams, Landel and Ferry equation.²⁵ Now comparison can be made at equivalent mobility between the grafted and nongrafted sulfonates, in the same range of O/Li ratio. It is



Figure 2. Dependence of conductivity on reciprocal temperature for ionomeric network NTPEO₆RFSO₃Li (■, O/Li=18) and NTPEO₆RFSO₂F/ RFSO₂Li network with untethered perfluorinated lithium sulfonate added (⊠, O/Li=15; □, O/Li=21).

clear that the non-grafted salt system is about 4-8 times more conductive. Thus the anionic contribution predominates over the cationic one for this type of salt. Similar observations have been reported in the literature.^{26,27} This phenomenon can be related to the lower solvation of the anion compared to the strong solvating interaction of Li⁺ with the ether oxygen atoms.^{24,26–28}

Properties of the tridimensional polymer electrolytes made from the three-arm trihydroxypoly(ethylene oxide) PEO(OH), 3300

The second network, referred to as NTPOE₃₃RFSO₂F before hydrolysis, was designed to improve the mobility of the polymeric segments by the increase of the average length of the polymer chains joining two crosslinks. Therefore PEG600 was replaced by a hydroxy-terminated three-arm poly(ethylene oxide) star $PEO(OH)_3 3300 \ (M_n = 3300 \text{ g mol}^{-1})$, which was reacted with the same triisocyanate in the presence of HO—**RF**SO₂F. The network **NT**POE₃₃**RF**SO₂F obtained also differs from the previous one because some of the polar urethane crosslinks are changed to non-



Figure 3. Comparison of conductivities at reduced temperature between $\textbf{NT}\text{PEO}_{6}\textbf{RFSO}_{2}\text{F}/\textbf{RFSO}_{3}\text{Li network with unterhered perfluorinated lithium}$ sulfonate added (⊠, O/Li=15; □, O/Li=21) and NTPEO₆RFSO₃Li ionomeric network, made from the previous one by hydrolysis of -SO2F groups into —SO₃Li (■, O/Li=18).



Figure 4. Dependence of conductivity on reciprocal temperature for $PEO(OH)_3 3330$ - and PEG 600-based networks containing either tethered $NTPEO_{33}RFSO_3Li (\bullet, O/Li=17.5)$ and $NTPEO_6RFSO_3Li (\bullet, O/Li=18)$ or untethered $NTPEO_{33}RFSO_2F/RFSO_3Li (\bigcirc, O/Li=16.8)$ lithium sulfonates.

polar ones. It appears to be amorphous, although the poly(ethylene oxide) star is semicrystalline, and is much more flexible than the previous network (Table 1). The ionomeric network NTPOE₃₃RFSO₃Li (O/Li=17.5) obtained after hydrolysis shows only a slightly increased T_g (from -40 °C to -35 °C). Figure 4 compares the Arrhenius conductivity plots of the two (NTPOE₃₃RFSO₃Li ionomeric systems and NTPOE₆RFSO₃Li) at very similar O/Li ratios (O/Li=17.5 and 18, respectively, for the PEG3300and PEG 600-based networks). The conductivities are highest for the most flexible system and reach values of around 2×10^{-5} S cm⁻¹ at 80 °C, comparable to that of networks bearing other lithium perfluorosulfonates.¹⁷ The difference in values is even higher at lower temperature due to the increase of the difference $T-T_{g}$ between the two electrolytes. Figure 4 also compares the Arrhenius conductivity plots of the ionomeric NTPOE33RFSO3Li network and the one obtained when RFSO₃Li is added to the same initial network, ie NTPOE₃₃RFSO₂F at similar O/Li ratios (O/Li=17.5 for the ionomer and 16.8 for the nonbonded salt). Despite its higher rigidity ($T_g = -25 \,^{\circ}\text{C}$), the untethered salt polymer is more conductive. Plotting the conductivity values versus $100/(T-T_{o})$ (Fig 5) allows comparison at the same mobility between two ionomeric systems that differ slightly in their O/Li ratios, but where the chemical structures of the salt and of the polymer are identical, except that the NTPOE₃₃RFSO₃Li system contains 29% of hydrocarbon-type junctions and 71% of urethanetype junctions. It is clear that the conductivity increases with the number of charge carriers, which in turn depends both on the O/Li ratio and the nature of the junctions. Such an influence of the nature of the crosslinks on the mobility of the lithium salts has already been mentioned and attributed to their bulkiness or stiffness.^{29,30} Figure 5 shows a conductivity about four times lower for the NTPOE₃₃ RFSO₃Li ionomeric network than for the same initial

network but with untethered salt (NTPOE₃₃RFSO₂F/ RFSO₃Li;O/Li=16.8). Assuming that the ionomeric system represents the cationic conductivity of the latter, the anionic transport number of the NTPOE₃₃RFSO₂F/RFSO₃Li electrolyte can be calculated to be in the range 0.7–0.8, which compares well to the values reported in the literature.^{26,27}

Effect of tethered and untethered lithium sulfonates on polymer electrolyte structure

When the initial networks (containing the fluorosulfonyl groups) are hydrolyzed to form ionomeric electrolytes only a slight increase in $T_{\rm g}$ is observed. Similar behaviour was reported for other ionomeric networks.¹⁷ However, when a non-bonded salt such as **RF**SO₃Li or $(CF_3SO_2)_2NLi$ is added to the same initial network, this increase becomes several times more important for similar O/Li ratios (Table 1). An important increase of T_g has also been reported by Lenest et al²⁸ when untethered salts are dissolved in polymeric networks. It was related to the presence of ionic associations playing the role of a physical crosslink; these crosslinks are reversible and disappear above 40 °C. However, there is no definite explanation for the rather slight increase in T_{σ} observed for the polymer electrolytes with tethered salts. The major difference in the present system is the reduced mobility of the anion attached to a junction point between two polymer segments and the steric hindrance generated by its enhanced bulkiness, thus preventing a closer approach of neighbouring chains to solvate the cation. This might also affect the equilibria between the different ionic species (simple ions, triplets, etc) and paired species, and as a consequence the association process of polymer chains by the electrolyte.

To compare the stiffening in these amorphous networks containing either tethered or untethered salts, a solid-state ¹HNMR study has been performed on the ionomeric network $NTPEO_6RFSO_3Li$ (O/Li=18) and on the same initial $NTPEO_6RFSO_2F$



Figure 5. Comparison of conductivities at reduced temperature between PEO(OH)₃3300- and PEG 600-based networks containing either tethered NTPEO₃₃RFSO₃Li (\bullet , O/Li=17.5) and NTPEO₆RFSO₃Li (\bullet , O/Li=18) or untethered NTPEO₃₃RFSO₂F/RFSO₃Li (\bigcirc , O/Li=16.8) lithium sulfonates.



Figure 6. ¹HNMR free induction decay signal of the ionomeric network NTPEO₆RFSO₃Li (O/Li=18).

network with $\mathbf{RFSO}_3\mathbf{Li}$ added at two different concentrations (O/Li=15 and 21). Figures 6 and 7 show the free induction decay signals corresponding, respectively, to the ionomeric network $\mathbf{NTPEO}_6\mathbf{RFSO}_3$ -

volts

Li (O/Li=18) and to the $\mathbf{NTPEO}_6\mathbf{RFSO}_2\mathbf{F}/\mathbf{RFSO}_3\mathbf{Li}$ (O/Li=15) network with unterhered salt. Their decomposition in two domains of different mobilities is shown in Table 2. The fast decay is to be related to



Figure 7. ¹HNMR free induction decay signal of NTPEO₆RFSO₂F network containing untethered RFSO₃Li (O/Li=15).

Table 2. ¹ HNMR free induction decay decomposition of polymer electrolyte networks with tethered (NT PEO ₆ RF SO ₃ Li) and untethered (NT PEO ₆ RF SO ₂ F / RF SO ₃ Li) lithium		Fast decay domain		Slow decay domain	
	Polymer electrolyte	T ₂ (μs)	¹ H (%)	T ₂ (μs)	¹ H (%)
	$\begin{split} \mathbf{NT} PEO_6 \mathbf{RF} SO_3 Li(O/Li=18) \\ \mathbf{NT} PEO_6 \mathbf{RF} SO_2 F / \mathbf{RF} SO_3 Li (O/Li=15) \\ \mathbf{NT} PEO_6 \mathbf{RF} SO_2 F / \mathbf{RF} SO_3 Li (O/Li=21) \end{split}$	66 49 50	34 60.5 59	472 303 304	66 39.5 41

the rigid part of the material, whereas the slower one represents a more mobile region, each being characterized by a spin-spin relaxation time T_2 . The absence of additional spin-spin relaxation time in the untethered system excludes any phase separation due to some less homogeneous distribution of the per-fluoroalkyl groups. The percentage of protons corresponding to the rigid region varies from 34% for the ionomeric network to about 60% for the non-bonded salt network.

To identify the hydrogen atoms which belong to the rigid part, their experimental percentage has been compared with various calculated ones, assuming that the closer to the crosslink the more rigid they would be. Considering that a junction point of the ionomeric network will not be connected to more than one pendant perfluorosulfonate group, one calculates that about 29% of them constitute effective crosslinks, ie are connected to three elastic chains: the corresponding protons, resulting from the triisocyanate aromatic groups, will be rigid in terms of NMR and will account for about 5% of the total number of protons, which is far below the experimental value of 34% of rigid protons. Now, if one considers that the aromatic protons of all the junctions are rigid, this percentage rises to 16%. Thus, it should also be assumed that among the CH₂ groups of the PEG elastic chains and of the perfluorinated sulfonate branches, some will have their movement frequency reduced due to the vicinity of the junction with the urethane groups. Assuming that only the CH₂ groups closest to those junctions will become rigid the total amount of rigid protons is raised to 24%. However, if the rigidity is extended to the two CH22 groups closest to the crosslinks, ie if the [CH₂CH₂O] units closest to the junctions become rigid, then the total number of rigid protons would account for 32 % of the total number of protons. This value compares well with the experimental one.

The two systems where the $\mathbf{NTPEO}_6\mathbf{RFSO}_2\mathbf{F}$ network contains $\mathbf{RFSO}_3\mathbf{Li}$ at two different concentrations (O/Li=15 and 21) show an almost identical decomposition of the free induction decay, indicating no fundamental change in the rigidity in this range of concentration. The experimental value of rigid hydrogens is around 60%, meaning that a new type of segmental stiffening has appeared and is directly due to the presence of the $\mathbf{RFSO}_3\mathbf{Li}$ salt. This can be related to the formation of transient physical crosslinks between the elastic PEG chains by the electrolyte, where the 'rigid' protons are close to the transient crosslinks. One can calculate that in addition to the $[CH_2CH_2O]$ units closest to the junctions some four or five supplementary units present rigid protons. Taking into account the concentration of **RFSO**₃Li, this would indicate that about 6–11 repeat units are stiffened by one molecule of salt. Because there is a quasi absence of stiffening for the tethered network, it can be assumed that the formation of transient crosslinks is notably decreased, probably due to some steric effect of the bulky anion that would hinder the association process.

CONCLUSIONS

Polymer electrolytes containing the lithium perfluoroakylsulfonate **RFSO**₃Li, derived from a commercial perfluorovinylether fitted with a fluorosulfonyl group, show conductivity values close to those of lithium trifluoromethanesulfonate. Single cation conductors were obtained by incorporation of RFSO₃Li into polyurethane networks where the perfluorosulfonates are covalently bound to the crosslinks. The best conductivities $(2 \times 10^{-5} \text{ S cm}^{-1} \text{ at } 80 \,^{\circ}\text{C}, \text{ for O/Li}$ ratios close to 18) are obtained with the ionomeric network NTPOE33RFSO3Li, based on the tri-arm star-poly(ethylene oxide)triol [PEO(OH)₃3300], as compared to the NTPEO₆RFSO₃Li network, based on a linear poly(ethylene oxide)glycol (PEG 600). On top of a higher mobility of the former network, this difference is also to be related to the presence in the PEO(OH)₃-based polymer electrolyte of a slightly higher content of solvated lithium cations and a lower amount of bulky junctions.

The conductivity values of these ionomeric systems are below those obtained by the same but nonhydrolysed networks, where **RF**SO₃Li is added at the same O/Li ratio. This shows the predominant effect of the anionic contribution. However, at lower temperatures the gap of conductivity is reduced due to the higher flexibility of the ionomers. The difference in flexibility results from a stiffening when RFSO₃Li is introduced into the non-hydrolysed networks (NTPEO₆RFSO₂F or NTPEO₃₃RFSO₂F) as shown by solid-state ¹HNMR and thermal analysis; this stiffening is due to the formation of physical crosslinks that involve the untethered salt and the solvating polymer chains. In contrast, no important stiffening is observed in the case of ionomeric polymers, when the SO₂F group is hydrolysed to SO₃Li: this is possibly

related to the greater hindrance for neighbouring polymer chains to solvate the lithium cation of the bound salt.

ACKNOWLEDGEMENTS

The authors express their thanks to Electricité de France (EDF) which has provided financial support of part of this work in the framework of a partnership with the French National Research Center (C N R S) and Bolloré Technologies. The Agence de l'Environnement et de la Maîtrise de l'Energie (A D E M E) is acknowledged for a scholarship given to SB and Dupont de Nemours for having graciously provided us with perfluorovinylether samples.

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