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Novel perfluorinated ionomers and ionenes

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Abstract

Ongoing research in the synthesis and properties of novel polymeric materials containing superacid sulfonimide functions is discussed. Novel perfluorinated ionomers and ionene polymers have been prepared and characterized. These materials have high potential for electrochemical and other applications.

Keywords: Perfluorinated ionomers; Perfluorinated ionenes; Synthesis; Properties; Electrochemical applications

1. Introduction

Perfluorocarbonsulfonyl derivatives of carbon and nitrogen represent an extensive and remarkable class of compounds. Our interest in this area began about 15 years ago in a search for additional nitrogen ligands to bond to xenon [1]. The new acid $(CF_3SO_2)_2NH$ was prepared for this purpose and we were successful in our original goal [2,3]. However, this original work has led to a burgeoning field of new chemistry that has many potential applications.

The acid $(CF_3SO_2)_2NH$ turned out to have remarkable properties with a p*K* value in acetic acid (7.8) much lower than that of many strong oxyacids ($HONO_2$, 10.2). In the gas phase it is a true superacid (several orders of magnitude greater than CF_3SO_3H, $HOSO_2F$, HI, etc.) with a measured acidity exceeded only by other homologues having larger fluorocarbon groups [4]. This remarkable acidity is due mainly to the pronounced delocalization of charge over the O−S−N skeleton and the resultant stabilization of the conjugate base of the acid. The nitrogen is trigonal planar in neutral covalent derivatives of the acid, again due to the delocalization of electron density from nitrogen. The structure of a planar nitrogen compound $CH_3-\quad-N(SO_2CF_3)_2$ is shown in Fig. 1 [5].

Derivatives of the acid exhibit a remarkable reaction chemistry. This is best illustrated by $(CF_3SO_2)_2NF$, which is the best electrophilic fluorination reagent discovered to date. It is effective in the fluorination of activated aromatics [6a], 1,3-dicarbonyl derivatives [6b,e], α-fluorination of functionalized carbonyl compounds [6c], olefins [6h], Wittig reagents [6d] and steroids [6f,g]. Convincing evidence has been obtained that many reactions with organic compounds occur by an electron-transfer mechanism.

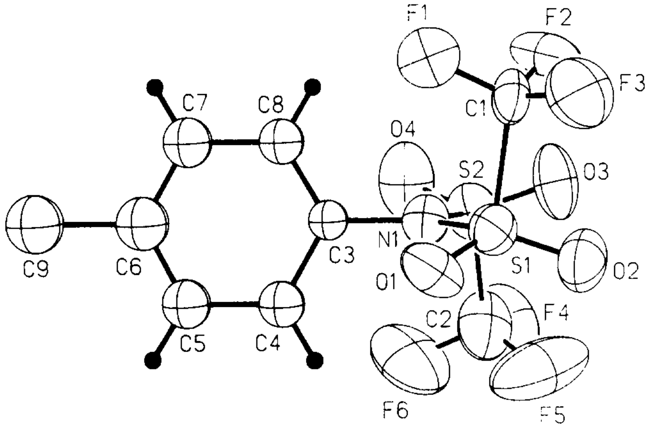
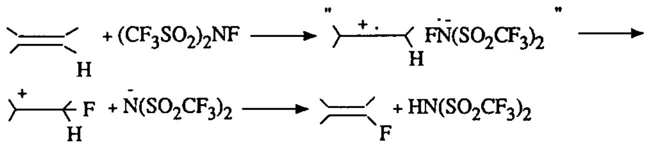


Fig. 1. Structure of *N*-(4-methylphenyl)-bis(trifluoromethylsulfonyl)-imide showing the planar nitrogen geometry.



In the metal derivatives of $(CF_3SO_2)_2NH$ and related compounds, the charge delocalization renders the anion a ‘pentadentate ligand’ which leads to unprecedented extended solids. This can only be appreciated by viewing the structure of a typical solid shown in Fig. 2 for

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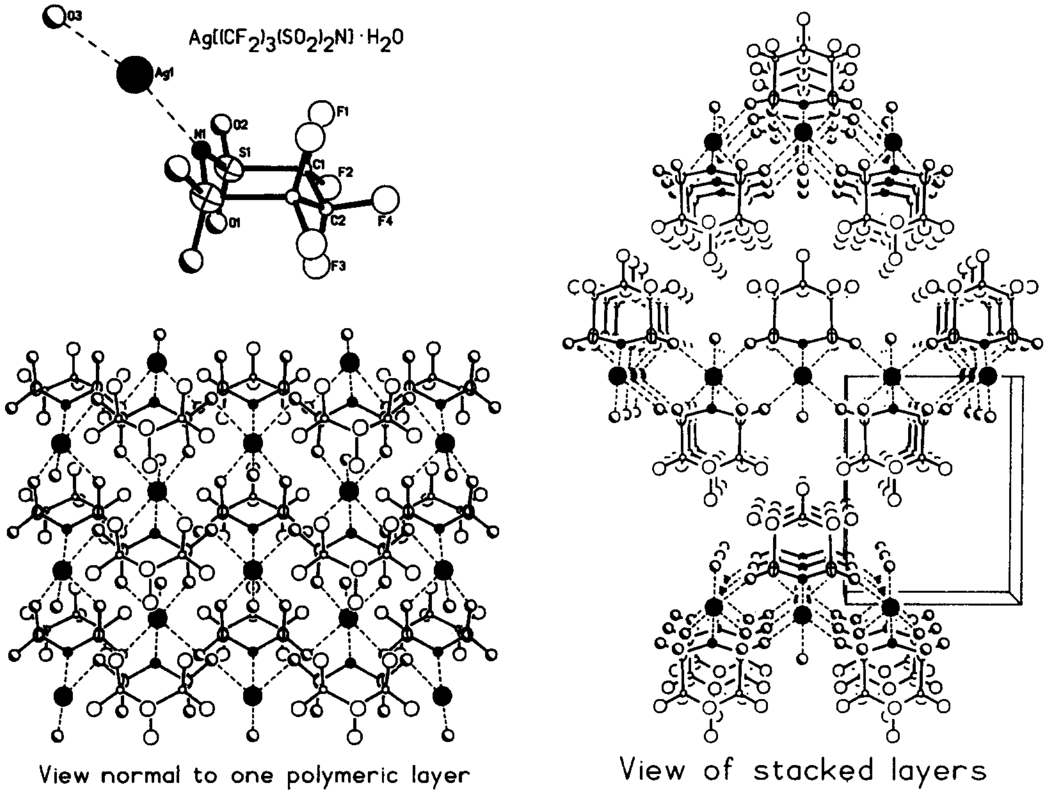


Fig. 2. Structural views of Ag[$\overline{SO_2(CF_2)_3SO_2N}$]·$H_2O$, illustrating the lamellar solid formed by stacking the 2D extended layers.

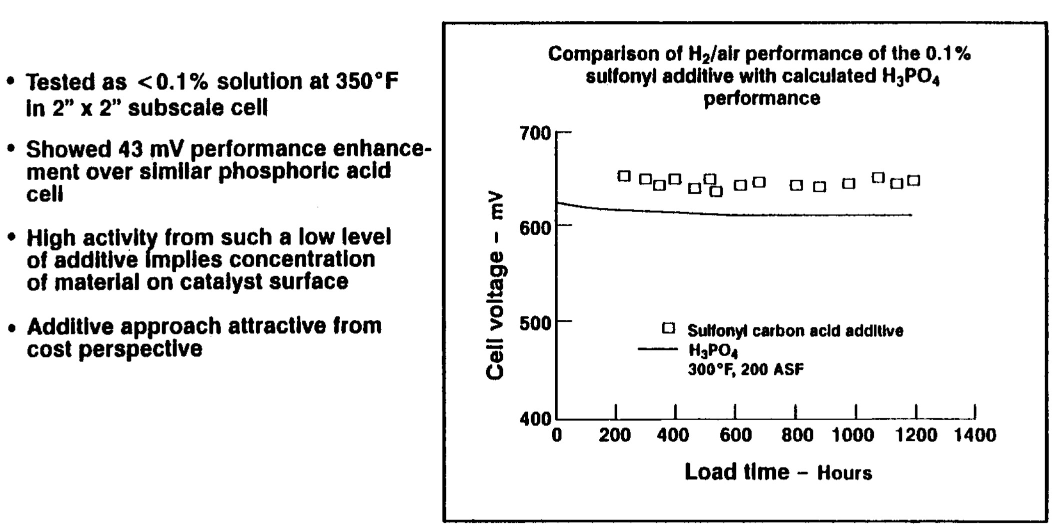
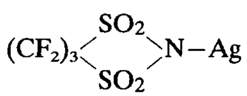

- **Tested as <0.1% solution at 350°F in 2" x 2" subscale cell**
- **Showed 43 mV performance enhancement over similar phosphoric acid cell**
- **High activity from such a low level of additive implies concentration of material on catalyst surface**
- **Additive approach attractive from cost perspective**

Fig. 3. Effect of $(CF_3SO_2CH_2SO_2CF_2CF_2)_2$ as an additive to 85% phosphoric acid in a hydrogen/air fuel cell.



$$(CF_2)_3\overset{SO_2}{\underset{SO_2}{<\;>}}N{-}Ag$$

The solid is composed of infinite two-dimensional layers formed by OSNSO–Ag networks with all the silver atoms lying in the same plane. These layers then stack together to form a lamellar structure with the fluorocarbon groups projecting out of the layers [7]. Related structures are found for the isoelectronic carbon analogues [8] and these general structural features have now been observed in the metal derivatives of many different acids.

The electrochemical properties of these acids are fascinating and of considerable commercial interest [9,10]. In Figs. 3 and 4 are shown actual fuel cell tests of $(CF_3SO_2)_2NF$ versus H_3PO_4 and of $(CF_3SO_2CH_2SO_2CF_2F_2)_2$ as an additive to phosphoric acid [1]. Phosphoric acid (85%) is currently the only

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[1] Data obtained by Dr. Donald L. Maricle, International Fuel Cells, South Windsor, CT, USA.

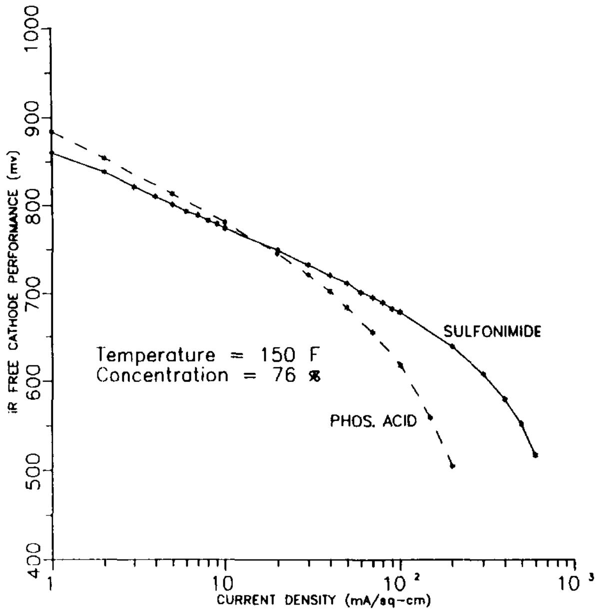


Fig. 4. Half-cell performance of $(CF_3SO_2)_2NH$ versus H_3PO_4 in a 2 in×2 in× hydrogen/air fuel cell.

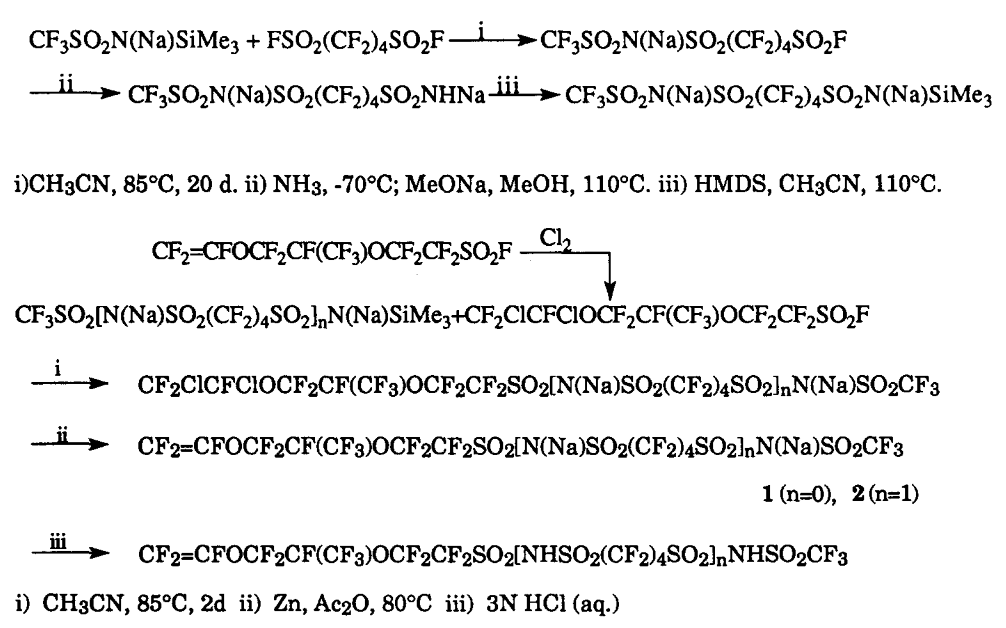
practical electrolyte for large-scale commercial fuel cells, although the efficiency rapidly falls off at high current densities. The improvement shown by $(CF_3SO_2)_2NH$ is dramatic under the conditions shown, but unfortunately the acid volatilized out of the cell at a more practical operating temperature of 200 °C. The additive effect was originally noted by Yeager and coworkers [10]. This result confirms it in a more representative fuel cell. Clearly if this improved performance could be realized in practical fuel cells over an extended lifetime, the improvements in the technology could be considerable.

There is much interest in the development of new polymeric materials for use as solid polymer electrolytes or capable of incorporation into the electrode structures to provide improved oxygen reduction kinetics while continuing to use phosphoric acid as the bulk electrolyte [11]. In a different but related application, $LiN(SO_2CF_3)_2$ has been shown to be one of the highest conducting 1:1 lithium electrolytes and it is presently undergoing long-term testing in proprietary lithium batteries [12–15]. It is now offered commercially by the 3M Corporation.

2. Current research—ionomers

The above brief background has led to a major effort to incorporate the bis[(perfluoroalkyl)sulfonyl] superacid function into polymers. Many new monomers have been successfully prepared and copolymerized with tetrafluoroethene to make new ionomer materials. Preliminary and ongoing evaluations of membranes prepared from these new ionomers are very encouraging. Some examples of monomers and copolymers obtained are given in Table 1. In this work there is an unprecedented opportunity to vary the microstructure of the ionomer and thereby modify the transport properties of the membranes. We are very optimistic that ionomers with improved properties for use in fuel variable fuel cells can be developed.

There are many challenges in this synthetic work that must be met in order to successfully achieve our goals. First, there is the problem of obtaining pure monomers for polymerization. The copolymerization employed by us involves an aqueous redox initiation system for the emulsion polymerization. The function-



$$CF_3SO_2N(Na)SiMe_3 + FSO_2(CF_2)_4SO_2F \xrightarrow{i} CF_3SO_2N(Na)SO_2(CF_2)_4SO_2F$$

$$\xrightarrow{ii} CF_3SO_2N(Na)SO_2(CF_2)_4SO_2NHNa \xrightarrow{iii} CF_3SO_2N(Na)SO_2(CF_2)_4SO_2N(Na)SiMe_3$$

i)CH_3CN, 85°C, 20 d. ii) NH_3, -70°C; MeONa, MeOH, 110°C. iii) HMDS, CH_3CN, 110°C.

$$CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F \xrightarrow{Cl_2}$$

$$CF_3SO_2[N(Na)SO_2(CF_2)_4SO_2]_nN(Na)SiMe_3 + CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2SO_2F$$

$$\xrightarrow{i} CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2SO_2[N(Na)SO_2(CF_2)_4SO_2]_nN(Na)SO_2CF_3$$

$$\xrightarrow{ii} CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2[N(Na)SO_2(CF_2)_4SO_2]_nN(Na)SO_2CF_3$$

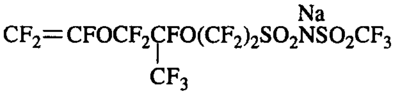
1 (n=0), **2** (n=1)

$$\xrightarrow{iii} CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2[NHSO_2(CF_2)_4SO_2]_nNHSO_2CF_3$$

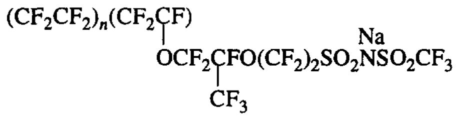
i) CH_3CN, 85°C, 2d ii) Zn, Ac_2O, 80°C iii) 3N HCl (aq.)

Scheme 1.

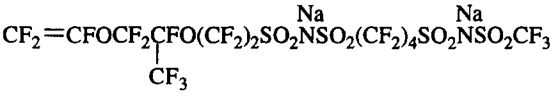
Table 1
Examples of sulfonimide monomers and copolymers with TFE



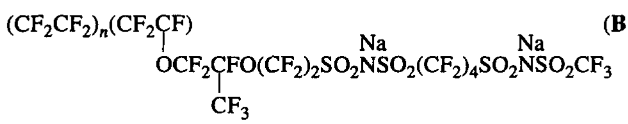
$CF_2{=}CFOCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2CF_3$ (1)



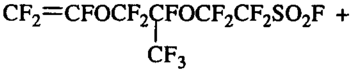
$(CF_2CF_2)_n(CF_2\underset{OCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2CF_3}{C}F)$ (A)



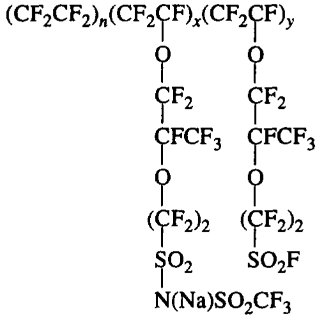
$CF_2{=}CFOCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2(CF_2)_4SO_2\overset{Na}{N}SO_2CF_3$ (2)



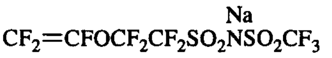
$(CF_2CF_2)_n(CF_2\underset{OCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2(CF_2)_4SO_2\overset{Na}{N}SO_2CF_3}{C}F)$ (B)



$CF_2{=}CFOCF_2\underset{CF_3}{C}FOCF_2CF_2SO_2F$ + 1 (3)

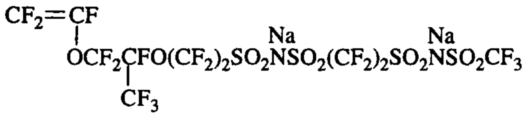


(C)

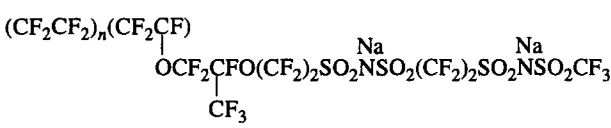


$CF_2{=}CFOCF_2CF_2SO_2\overset{Na}{N}SO_2CF_3$ (4)

$(CF_2CF_2)_nCF_2\underset{OCF_2CF_2SO_2\overset{Na}{N}SO_2CF_3}{C}F$ (D)



$CF_2{=}\underset{OCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2(CF_2)_2SO_2\overset{Na}{N}SO_2CF_3}{C}F$ (5)



$(CF_2CF_2)_n(CF_2\underset{OCF_2\underset{CF_3}{C}FO(CF_2)_2SO_2\overset{Na}{N}SO_2(CF_2)_2SO_2\overset{Na}{N}SO_2CF_3}{C}F)$ (E)

alized monomers must be in salt form both so that the pH is properly controlled and to allow solubility in H_2O. Optimization of the synthetic methods leading to these monomers is very challenging. As an example, monomer **2** has a formula weight of 962 in the Na form and is prepared as shown in Scheme 1. At present, it is necessary to purify monomer **2** by acidifying, followed by a difficult short-path distillation with considerable loss of material. The monomer is then neutralized carefully with $NaHCO_3$ to return it to the Na form for polymerization. Attractive alternative routes are being developed to prepare monomers such as **2** employing fewer steps.

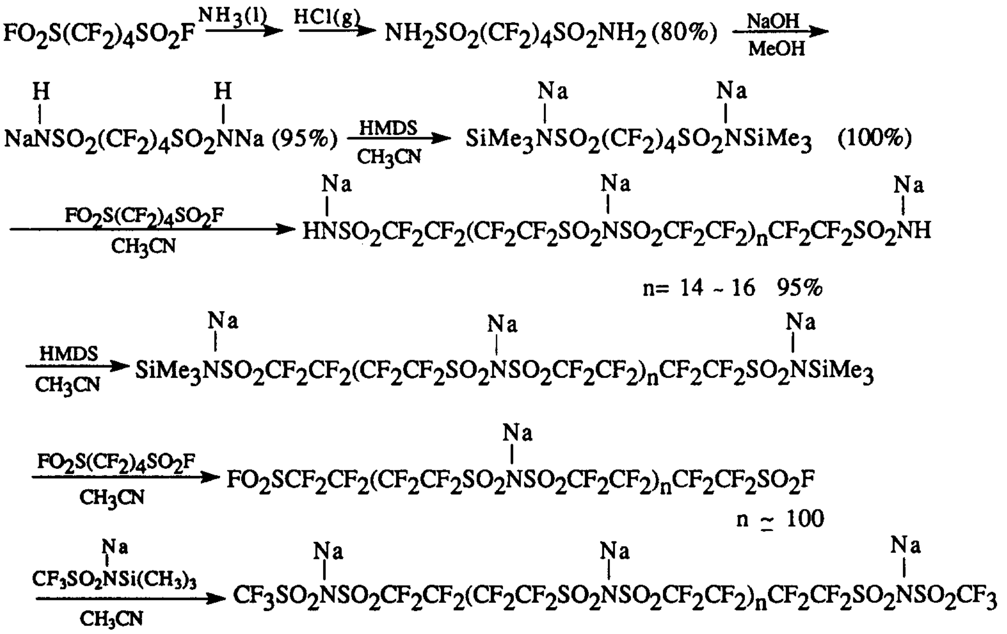
The polymerization of various monomers including those listed in Table 1 has been carried out successfully by aqueous emulsion polymerization. Some typical polymerizations involving monomer **1** are listed in Table 2.

The resultant white polymer in acid form can be solution-cast or hot-pressed into membranes. These

Table 2
Some typical copolymerizations of monomer **1**

Reactants and conditions	Experiment No. [a]			
	1	2	3	4
Water (ml)	300	300	300	300
$C_7F_{15}CO_2Na$ (g)	2.1	2.1	2.1	2.1
$Na_2HPO_4\cdot 7H_2O$ (g)	3.5	3.5	3.5	3.5
$Na_2S_2O_8$ (g)	0.7	0.8	0.8	0.8
$NaHSO_3$ (g)	0.7	0.8	0.8	0.8
TFE pressure (psi)	75–80	78–81	70–75	70–75
Monomer (g)	5.0	8.0	7.5	7.5
Temperature (°C)	21	21	21	21
Stirring speed (rpm)	450	450	600	650
TFE drops (psi)	38	45	46	55
Weight of copolymer (g)	5.3	6.2	7.0	7.7
IEC (mg H g^{-1})	0.52	0.64	0.94	0.96
Eq. wt.	1933	1562	1063	1042
TFE/1	13.5	10	4.9	4.8

[a] Conducted in a 450-ml capacity magnetically stirred Parr autoclave.



$$\mathrm{FO_2S(CF_2)_4SO_2F} \xrightarrow{\mathrm{NH_3(l)}} \xrightarrow{\mathrm{HCl(g)}} \mathrm{NH_2SO_2(CF_2)_4SO_2NH_2\ (80\%)} \xrightarrow[\mathrm{MeOH}]{\mathrm{NaOH}}$$

$$\mathrm{Na\overset{H}{N}SO_2(CF_2)_4SO_2\overset{H}{N}Na\ (95\%)} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{HMDS}} \mathrm{SiMe_3\overset{Na}{N}SO_2(CF_2)_4SO_2\overset{Na}{N}SiMe_3\ (100\%)}$$

$$\xrightarrow[\mathrm{CH_3CN}]{\mathrm{FO_2S(CF_2)_4SO_2F}} \mathrm{H\overset{Na}{N}SO_2CF_2CF_2(CF_2CF_2SO_2\overset{Na}{N}SO_2CF_2CF_2)_nCF_2CF_2SO_2\overset{Na}{N}H}$$

$$n = 14 \sim 16 \quad 95\%$$

$$\xrightarrow[\mathrm{CH_3CN}]{\mathrm{HMDS}} \mathrm{SiMe_3\overset{Na}{N}SO_2CF_2CF_2(CF_2CF_2SO_2\overset{Na}{N}SO_2CF_2CF_2)_nCF_2CF_2SO_2\overset{Na}{N}SiMe_3}$$

$$\xrightarrow[\mathrm{CH_3CN}]{\mathrm{FO_2S(CF_2)_4SO_2F}} \mathrm{FO_2SCF_2CF_2(CF_2CF_2SO_2\overset{Na}{N}SO_2CF_2CF_2)_nCF_2CF_2SO_2F}$$

$$n \simeq 100$$

$$\xrightarrow[\mathrm{CH_3CN}]{\mathrm{CF_3SO_2\overset{Na}{N}Si(CH_3)_3}} \mathrm{CF_3SO_2\overset{Na}{N}SO_2CF_2CF_2(CF_2CF_2SO_2\overset{Na}{N}SO_2CF_2CF_2)_nCF_2CF_2SO_2\overset{Na}{N}SO_2CF_3}$$

Scheme 2.

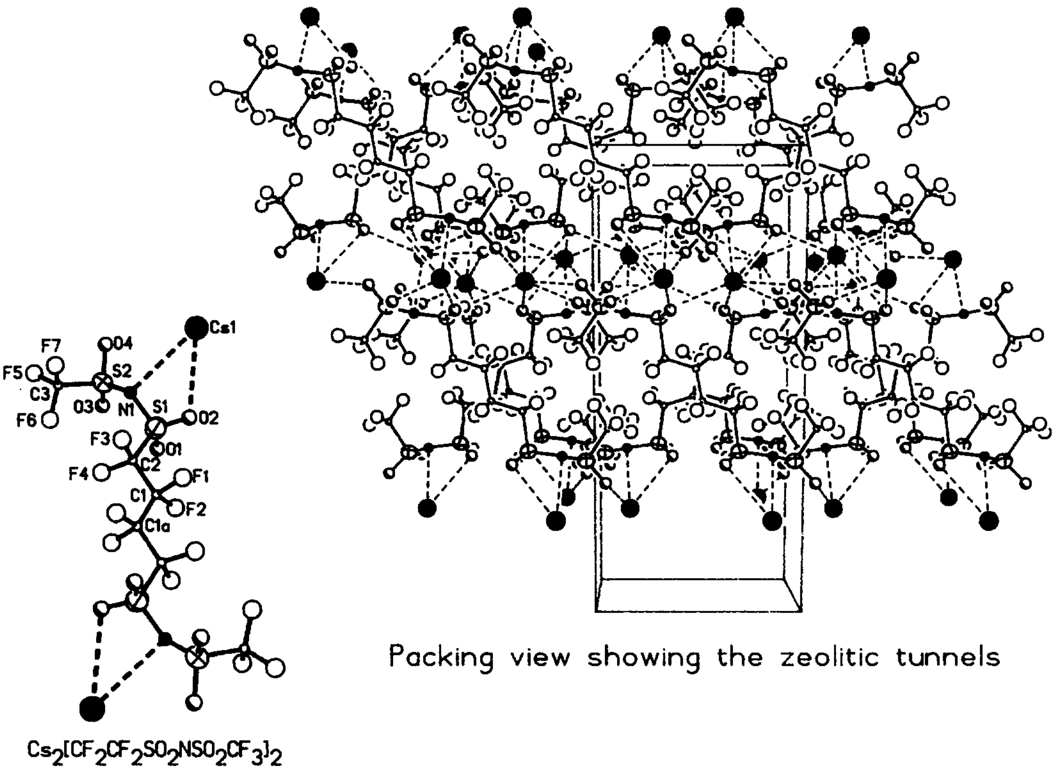


Fig. 5. Structural view of $\mathrm{Cs_2[(CF_3SO_2NSO_2CF_2CF_2)_2]}$ showing the extended 3D solid consisting of ionic and fluorocarbon domains.

materials exhibit many of the same properties as commercial ionomers containing sulfonic acid functions [16].

3. Current research—ionenes

The ionene polymers we have prepared possess very intriguing molecules. A publication has appeared on this work which demonstrates that these compounds have good electrochemical properties but are temperature-limited [17]. This publication, unfortunately, does not point out that the purity of the polymer tested was modest at best. Ionene polymers of this type are unique and no examples of strong acid polymers of this type are possible with oxygen, and none have been reported for any other possible acid systems. The synthetic methodology for the synthesis of these compounds is shown in Scheme 2. Again, in these systems, one has an unprecedented opportunity to vary the nature of this polymer by including different acid functions in the chain and by varying the separation of the acid groups within the chain.

This work on ionenes is extremely challenging from a synthesis point of view. On paper it looks easy, but in practice it is anything but. However, the basic methodology works and it is a matter of making it work better to give high molecular weight materials. In this work the polymers are unlikely to have average molecular weights exceeding 60–70 kDa, due to the statistics of step-reaction polymerization and the limits on the degree of polymerization.

Apart from their potential in fuel cells, these ionenes may have very interesting applications as ionic conductors in solid-polymer electrolytes for lithium batteries. As mentioned in the Introduction, $LiN(SO_2CF_3)_2$ is of considerable interest in this regard [12–18]. From the structures in Figs. 2 and 5, the self-assembly of these materials in the solid state into ionic and fluorocarbon domains is evident. The structure of $Cs_2[CF_3SO_2NSO_2(CF_3)_4SO_2NSO_2CF_3]$ depicted in Fig. 5, shows that this self-assembly gives an extended solid with the difunctional materials and probably multifunctional materials, although we have no structures beyond the difunctional compounds and no lithium structures as yet.

With a little imagination one can envisage that these materials might lead to a high lithium mobility in an ionene dissolved in a suitable polymer electrolyte. It may be reasonable to assume that the lithium ion can migrate (hop) from one sulfonimide group to another, akin to proton migration in sulfuric acid for example. The transport mechanism of the ionic species in various lithium battery systems (e.g. the $Li/PEO–LiClO_4/V_6O_{13}$ composite) is not well understood [19] and work to test our ideas is in progress.

Acknowledgments

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