REVIEW

Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application[×]

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Abstract

The publication deals with the sulfonation of aromatic polysulfones that results in ionomers intended to be used as membranes for Proton Exchange Membrane Fuel Cells. The mechanical properties and the lifespan of the membranes depend, in particular, on the mode of synthesis of the ionomers and on chemical degradations which can occur and cut the polymeric chains. This article gives a progress report on the various methods giving access to polysulfone ionomers based on sulfonic acid functions. Among these methods, particular attention has been paid to electrophilic substitution from commercially available polysulfone. Although electrophilic sulfonation of aromatic molecules has been known for about one century, its application to the sulfonation of polymers still raises problems, e.g. homogeneity and degradations. A mechanism of chemical degradation is proposed to explain the chain breakings occurring in the course of reaction. The difficulty in passing from the laboratory scale to an industrial production is illustrated from reactions carried out at the pilot scale.

Keywords: Chemical Degradation, Fuel Cell, Ionomer, Membrane, PEMFC, Polysulfone, Proton-Conducting Polymer, Sulfonation

1 Introduction

All the experts agree that there will be an end to the oil supply in the middle to the end of the present century. One environmental concern deals with the CO_2 produced by human activity which is in permanent increase and clearly induces climate changes. In the EU, both National and European programmes try to coordinate research on new energy sources. Similar policies are also being carried out in Japan and in USA, where they are supported, in particular, by the D.O.E. (Department Of Energy) and the D.O.D. (Department Of Defense). In the field of electrochemical energy sources, batteries and Fuel Cells are able to provide the necessary energy, and may be considered, in a first approach, as competing for future markets, e.g. electrical and hybrid vehicles, U.P.S. (Uninterruptible Power Sources) etc. However a decrease in size will also allow fuel cells to be used as energy sources for portable applications, i.e. the 4 C market (Computers, Camcorders, Cellular phones, Cordless tools). In the field of automotive applications, PNGV (Partnership for New Generation Vehicles) aims at developing a prototype based on a passenger Sedan with an equivalent energy consumption of 80 miles per gallon. PNGV therefore has funded various programmes exploring several ways to decrease the energy consumption with respect to thermal vehicles, such as hybrid vehicles, already on the market, but also of prototypes of fuel cell vehicles.

For all the applications, including the production of electricity, Proton Exchange Membrane Fuel Cells, PEMFC, seem to be the most promising fuel cell owing to their modularity. Many problems have to be solved, however, in particular: price, operating temperature range, fuel selection and supplies. The polymer electrolyte membrane is indisputably one

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Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application **Fuel Cells**

REVIEW

of the identified problems, while MEAs (Membrane Electrode Assemblies) are identified as the most costly components in view of large scale production [1].

As in PEMFC operating at $T < 100$ °C, liquid water is continuously produced and removed, the anionic functions must be attached to the macromolecular backbone by covalent bonds.

Perfluorosulfonic ionomers as Nafion® are the most conductive polymer electrolytes, they have a high chemical and electrochemical stability but (i) they are by far too expensive, (ii) their environmental impact is questionable and (iii) their highest operating temperature is close to 80 °C.

Fluorine-less or non-fluorinated ionomers proposed to replace Nafion® consist mainly of alkyl or arylsulfonic acids attached to various polymer backbones, such as polysiloxane [2–6], polyphosphazene [7–12], polyvinylidene fluoride [13, 14], polystyrene-polyethlene-polystyrene triblock copolymers [15], polytrifluorostyrene [16, 17], polybenzimidazole [18, 19], polyimide [20–22], polyether-ether-ketone [23–26], polyparaphenylene [27], polybenzoxazoles [28, 29] polysulfone [30–33] etc. As alkyl or arylsulfonic functions are less dissociated than the perfluoroalkylsulfonic acid ones present in Nafion®, an increase in sulfonic acid concentration is necessary. This results in an increase of the membrane swelling and often affects its mechanical properties. This paper will focus on the chemical aspects of the sulfonation of aromatic polysulfones and on its possible consequences on the chain breakings. In addition, the relationship between sulfonated polysulfone structure and membrane swelling is reported. Some aspects on the stability and degradation of sulfonated polysulfone are presented.

2 Polymer Backbone Selection

Most of the alternatives to perfluorosulfonic ionomers deal with polyaryl skeletons. Such polymers are known as high performance polymers and most of them may be roughly considered as thermostable polymers. Even if thermostability, owing to the chemical modification of aromatic groups, cannot be retained, a high stability vs. oxidation may be expected from such polymeric backbones. Obviously, due to the aromatic rings, such polymeric backbones open up a wide window of chemical modification opportunities, through

electrophilic substitutions e.g. chloromethylation, nitration and sulfonation, but also through metalation. Electrophilic sulfonation is well known and widely used in chemical industry for many applications, such as the production of surface active agents, detergents, ion-exchange resins etc. Among the commercial polymers which can be sulfonated are polyether-ketone (PEK), polyether-ether-ketone (PEEK), polysulfone (PSU) and polyphenylsulfone (PPSU), polyphenylenesulfide (PPS), etc. In order to evaluate the electrochemical stability of aromatic polymeric backbones Maréchal et al. prepared model molecules mimicking PEEK, PSU, PPSU and PPS and performed, in sulfolane, their comparative electrochemical study by cyclic voltammetry. The main advantage of the use of model molecules is that it allows high concentration to be obtained; thus enhancing the signal associated to a possible degradation. Sulfolane was selected as the solvent as (i) it dissolves both the neutral molecules and their sulfonic derivatives, (ii) its electrochemical window includes that of water and is sufficient to explore a wide potential range and (iii) it has a high boiling point allowing the cyclic voltammetries to be performed at 80 °C i.e. at the operating temperature of most of the PEMFC. Investigations were performed both on the neutral and ionic forms of the model molecules at ambient and 80 °C, under argon, hydrogen or oxygen atmosphere. From the results obtained with the model molecules it may be inferred that both PSU and PPSU have the widest electrochemical stability window [34] that is not modified by their sulfonation. PPS is sensitive to oxidation. As for PEEK, it shows a good stability to oxidation but is less stable in reduction than PSU and PPSU [35]. However, it may be assumed that this instability, which occurs at low potential, should not affect its long-term stability in fuel cell application.

High redox stability in a wide temperature range, high glass-transition temperatures, solubility in organic solvents useful for chemical modifications and thermal stability are indisputable assets for PSU and PPSU. Below are gathered, in Table 1, the main characterizations of commercially available polysulfones.

In addition, as contrary to PEK, PEEK and PPS, these polymers are fully amorphous, their mechanical strength does not depend on crystallinity ratios and on melting temperatures which are very sensitive to the nature of chemical modifications and to their extent. Lastly, polysulfones have been

Table 1 Characteristics of commercial polymers.

Properties	Unit	polysulfone		polyethersulfone			polyphenylsulfone
		UDEL (SOLVAY)	ULTRASON S (BASF)	RADEL A (SOLVAY)	ULTRASON E (BASF)	SUMIKA PES (SUMITOMO)	RADEL R (SOLVAY)
Glass transition	°C	190	187	220	225	225	220
Specific gravity		1.24	1.24	1.37	1.37	1.37	1.29
Thermal expansion	10^{-5} / °C	5.6	5.5	4.9	5.9	5.5	5.6
Tensile strength	MPa	70	80	83	90	84	70
Elongation at break	%	> 50		> 50		40–80	> 50
Flexural strength	MPa	106		111		129	91
Flexural modulus	MPa	2,690	2,600	2,900	2,700	2,550	2,410
Melt flow index (2.16 kg)	g / 10 min	2–9 (343 °C)	5–15 (343 °C)	9–15 (380 °C)	7–30 (355 °C)		9–14 (365 °C)

Fuel Cells Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application
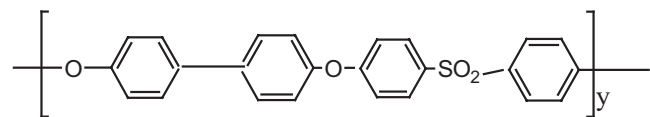
REVIEW

widely used in membrane applications, e.g. filtration, ultrafiltration [36–39], pervaporation [40, 41], electrodialysis [42, 43]. Below are the formulas of some polysulfones:
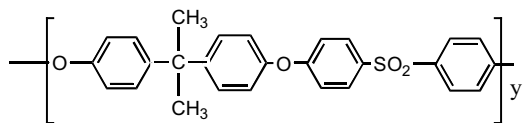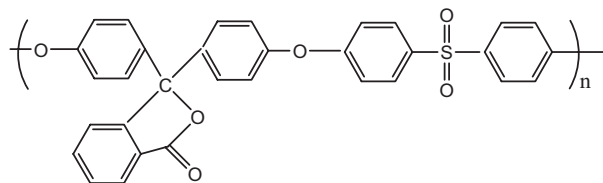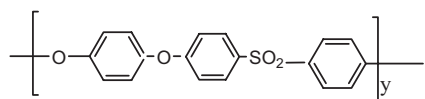
Polysulfone (PSU)
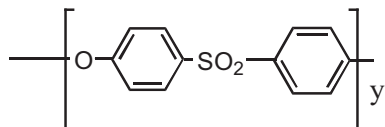
Polyethersulfone (PESU)

Polyphenylsulfone (PPSU)

Polyethersulfone cardo (PESU-C)

Polyether ethersulfone (PEESU)

Diaryl ether provides flexibility to the polymer chains. In addition, due to their lone pair, oxygen atoms may interact both with protons and water. Isopropylidene moiety also provides flexibility to the polymer but, above all, enables the polymer to be dissolved in various solvents; this is an asset when carrying out chemical modifications. As for diaryl sulfone moieties, it has been reported by Cerfontain et al. [44, 45] that half-protonation of diphenyl sulfone requires the use of oleum (103% in H_2SO_4) while that of benzene sulfonic acid $C_6H_5\text{-}SO_3H$ only requires 81% H_2SO_4. This means that it is easier to obtain $C_6H_5\text{-}SO_3H_2^+$ than to obtain $C_6H_5\text{-}SO_2H^+\text{-}C_6H_5$. These results clearly demonstrate that, despite their oxygen atoms, SO_2 groups cannot interact with protons in the operating conditions of fuel cells. On the other hand, diaryl sulfone moiety should improve the thermal and electrochemical stabilities.

3 Selection of the Ionic Function

Ionic conductivity is proportional to ion concentrations (anion and cation) and to their respective mobility. In lithium-polymer batteries, the anion mobility is prevalent and the cationic transport number t_+ ranges generally between 0.1 and 0.5. Obviously, ionomers with an anion attached to the polymer backbone are single-cation conducting polymers ($t_+ = 1$). Due to the loss of the predominant anionic conductivity, even optimized lithium ionomers have conductivities markedly lower than those obtained when both anion and cation are mobile. On the contrary, proton conductivity in water is mainly governed by the proton, which has a transport number close to 0.9 [46]. Thus, a comparison at 298 K in diluted aqueous solutions (0.1 N) of M^+Cl^- shows that t_+ decreases according to H^+ (0.83) > K^+ (0.49) > Na^+ (0.39) > Li^+ (0.32) [46]. This means that the penalty induced by the anion immobilization should be lower in Fuel Cell Ionomeric electrolytes than in Lithium Batteries ones. The conductivity also depends on the proton concentration, i.e. the concentration in ionic groups. This obviously depends on the ionic exchange capacity but also on the acid dissociation. The organic anions, therefore, have to be selected from among the conjugated bases of strong acids or superacids. For example, sulfonic acids are much more acidic than carboxylic ones. Among the sulfonic acids, aryl sulfonic acids are more acidic than alkyl sulfonic ones, while the more acidic ones are the perfluoroalkylsulfonic groups whose synthesis is not easy and whose chemistry is expensive. Now, the dissociation occurs in water which, due (i) to its high permittivity and (ii) to its high solvating ability *vs.* cations high DN (Donor Number) and anions high AN (Acceptor Number), should exert, to some extent, a levelling effect on the dissociation of strong acids. The Linear Free Energy Relationship (LFER) principle is an approach proposed early on by Hammett and deeply detailed in his book entitled "Physical Organic Chemistry" [47] to evaluate the effects of electron-donating and electron-withdrawing aromatic substituents on the transition state and, therefore, on the rate constant of reactions occurring in aromatic positions or in the alpha position of an aromatic ring. An efficient sensor of both inductive and resonance electronic effects is the acidity constant of substituted benzoic acids. σ is the difference between the *pKa* of unsubstituted benzoic acid and that of substituted benzoic acids. Plotting the *pKa* of aryl acids as phenols or aryl bases as anilines *vs.* σ often leads to linear correlations, the slope being referred to as ρ. This explained the well-known relation $\rho\sigma$. The higher the slope, the higher the electronic effect is. Cerfontain et al. found a low value, 0.7 for the slope ρ [44], the *pKa* values ranging between – 6.85 and – 6.3 for aryl sulfonic acids. So they conclude that the acidity is only weakly influenced by the substituents present on the aromatic ring. These *pKa* values rank their acidity between that of the 1st acidity of H_2SO_4 and that of HCl. Another crucial criterion for the anion selection is its redox stability. We checked by cyclic voltammetry, performed in sulfolane on model molecules of Na sulfonated

Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application **Fuel Cells**

REVIEW

polymers, that the electrochemical window of arylsulfonate anions is much wider than that required for PEM fuel cells [35]. This means that no electrochemical degradation, related to the arylsulfonate anion, should occur in a PEM fuel cell.

4 Aromatic Sulfonation

Several research groups have investigated polysulfone, sulfonated on the aromatic rings of the macromolecular backbone, in particular for fuel cell applications. Two main procedures have been reported for the sulfonation of polysulfone. The first one deals with the classical polymer sulfonation by an electrophilic substitution, while the second one proceeds through the metalation of aromatic rings.

4.1 Electrophilic Substitution

4.1.1 Reactivity and Orientation

The polysulfone may be sulfonated up to two sulfonic groups per monomer repeat unit. As usual the orientation of the electrophilic substitution is greatly influenced by the electron-donating or electron-withdrawing substituents present on the aromatic ring. The latter, as SO_2, decreases the reactivity, while the former increases the sulfonation rate. The reactivity and the orientations are both influenced by the inductive (I) and resonance (M) effects of these substituents. Due to the electron-withdrawing effect of SO_2 which cumulates both –I and –M effects, sulfonation will not take place on the phenyl sulfone but on the phenyl ether. Indeed, the ether exerts an inductive electron-withdrawing effect –I, which is overcompensated in the ortho and para positions by its resonance electron-donating effect +M. The sulfonation will mainly occur, therefore, at the ortho position of the ether function.

4.1.2 Reagents and Solvents for Polymer Sulfonation

The sulfonation of aromatic organic molecules can be performed with a variety of sulfonation reagents and in different solvents, the aromatic molecule often being used both as substrate and solvent. On the other hand, due (i) to the polymer and ionomer solubilities and (ii) to possible chain degradations, the choice of an experimental procedure is much more restricted in the case of the sulfonation of polymers. Some studies have reported direct polymer sulfonation being carried out using sulfuric or chlorosulfonic acid both as solvent and as sulfonation reagent [48–54]. This process seems attractive, in particular when the sulfonation is performed in concentrated sulfuric acid i.e. 98 wt.-%, as it avoids the use of organic solvents. Blanco et al. succeeded in sulfonating PESU from Victrex® and PESU-C® in concentrated sulfuric acid [52] and reported that degradation by chain breakings occur rapidly in the sulfonation of PESU while it is slowed down greatly in the sulfonation of PESU-C [52].

PSU and PPSU, on the other hand, can be dissolved in chlorinated solvents well-adapted to electrophilic substitutions. Thus the sulfonation of PSU, insoluble in sulfuric acid

98 wt.-% [52], was carried out in chlorinated solvents, using chlorosulfonic acid at temperatures ranging from 263 to 298 K. Although PSU is perfectly soluble in these solvents, the resulting ionomer precipitates as soon as it is obtained [31, 38, 55–58]. Baradie et al. reported that sulfonation of PSU by chlorosulfonic acid leads to chain breakings [58]. Blanco et al. [52] assumed that chlorosulfonic acid leads to chain breakings on PSU. PPSU was sulfonated in dichloromethane using SO_3 [59]. Again, the ionomer precipitates and the sulfonation degree is uncontrolled. Indeed, both reagents lead directly to arylsulfonic acid groups which modify the solubility parameter of the polymer and results in the ionomer precipitation. In addition to degradations by chain breakings, the homogeneity of such ionomers, owing to their partial precipitation during the reaction, is questionable. Indeed, the precipitation may affect in priority the longest polymer chains, the shortest remaining soluble. As the reaction rate is probably dramatically slowed down in the precipitate, it may be assumed that the shortest chains, which remain in solution, might be much more sulfonated than the precipitated ones. A possible selective dissolution of these highly sulfonated short chains may therefore occur in the operating conditions of the fuel cells and would therefore lower the actual exchange capacity of the resulting polymer, thus affecting the membrane conductivity. Other studies have proposed the sulfonation of polymers in dichloroethane in the presence of SO_3-triethylphosphate complex, which has been reported to be more reliable and to minimize side reactions [30, 60, 61]. However, the toxicity and high reactivity of SO_3, plus the very exothermic reaction with triethylphosphate make it difficult to use.
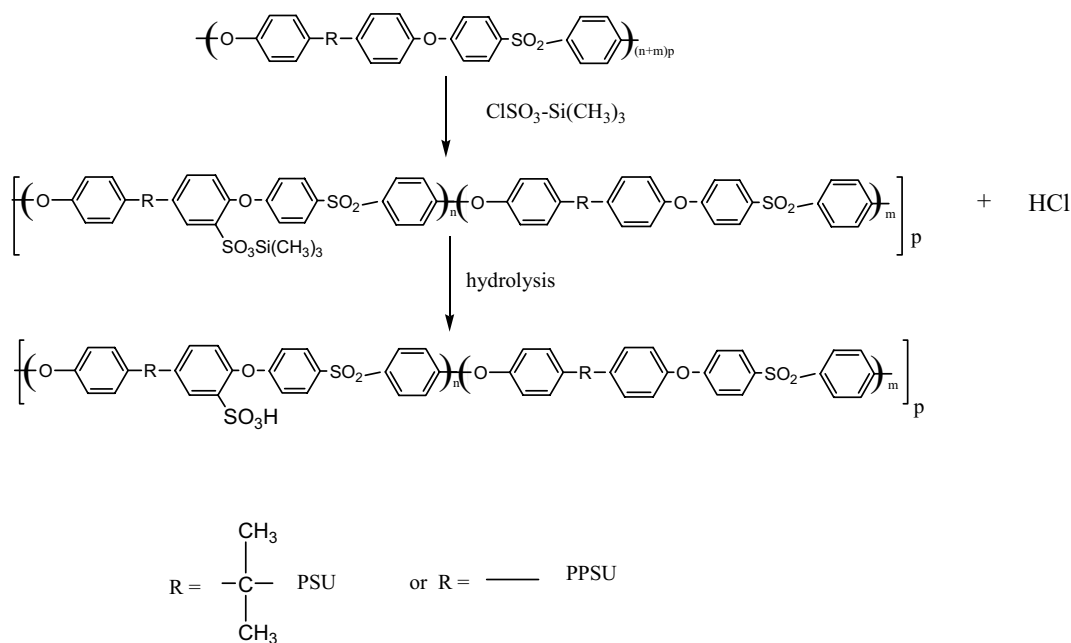
4.1.3 Polysulfone Sulfonation by Trimethylsilyl Chlorosulfonate (TMSCS)

Advantages: Homogeneity and Limitation of Chain Scission

An alternative method that we also selected is the sulfonation based on trimethylsilyl chlorosulfonate (Scheme 1) [31, 59, 62–64]. Due to the formation of a trimethylsilyl sulfonic ester, the hydrophobic character of the sulfonated polymer is retained. This means that the solubility parameter of the starting polymer is probably retained and, therefore, the sulfonated polymer remains soluble in the solvent used for the reaction, namely methylene chloride or dichloroethane. Up to high sulfonation degrees and provided the reaction medium is kept perfectly anhydrous, the reaction mixture remains perfectly homogeneous. In addition, the trimethylsilyl ester prevents side-reactions reported with chlorosulfonic acid. Lastly, from a comparison of sulfonation performed with chlorosulfonic and trimethylsilylchlorosulfonate reagents, it has been reported [62] that chain breakings are decreased and even suppressed with the latter.

Kinetic Aspects

From a kinetic point of view it must be emphasized that the reaction rate greatly decreases when chlorosulfonic acid

Fuel Cells Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application

REVIEW

Scheme 1 Sulfonation of PSU or PPSU by TMSCS.

is replaced by trimethylsilyl chlorosulfonate. As the reactions were performed in the same solvents, the explanation cannot be related to the dielectric constant. It may be assumed that the electrophilicity of chlorosulfonic acid is much higher than that of the trimethylsilyl ester form.

In an attempt to follow the sulfonation kinetic, we previously investigated the sulfonation of PSU and reported [65] that the evolution of the real sulfonation degree displays three main stages of the reaction. Sulfonation is rapid over the first 5 h and reaches 0.615 mol H$^+$ mol^{-1}, namely 61,5% of the theoretical conversion after 48 h (Figure 1).
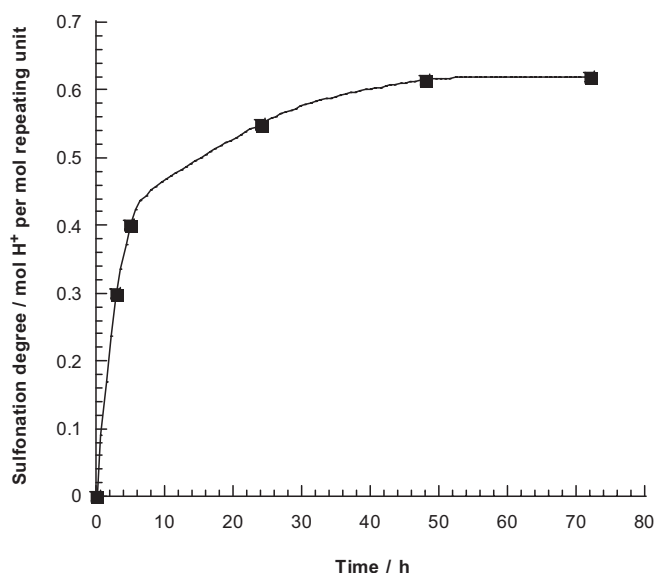

Fig. 1 Sulfonation degree *vs.* reaction time. Operating conditions: sulfonation of PSU with TMSCS, mol TMSCS per mol repeating unit = 1, θ = 35 °C, under argon flow.

After 48 h the sulfonation level reaches a plateau at 0.62 mol H$^+$ per mol repeating monomer unit. Recent investigations have shown that an additional amount of trimethylsilyl chlorosulfonate (0.15 mol TMSCS per mol repeating unit) allows the plateau to be shifted towards higher ionic exchange capacity (from 0.62 mol H$^+$ per mol repeating unit to 0.7 mol H$^+$ per mol repeating unit) [65]. Several assumptions might explain these results: (i) a partial precipitation of the ionomer or a poor interaction between ionomeric silylester and the solvent, both decreasing the sulfonation rate; (ii) a decrease in the remaining reactive aromatic rings; (iii) a reversible reaction and (iiii) a contribution to the dielectric constant of the trimethylsilylchlorosulfonate reagent.

Indeed, up to very high sulfonation degrees, the ionomer, under its silylester form, remains soluble in halogenated solvents and the reactions were performed under very drastic conditions to avoid partial hydrolysis of the sulfonate silyl ester which would lead to its precipitation. On the contrary, the increase in the solution viscosity with the conversion yield indicates a better interaction of the ionomeric ester with the halogenated solvents than that of the starting polymer.

The second assumption, a decrease in reactivity of aromatic rings, cannot explain the slowing down of the reaction, as the plateau may be reached from a sulfonation degree of 0.6 mol per mol repeating unit while very reactive aromatic positions still remain.

As for the third assumption, aromatic sulfonation is of course a reversible reaction but according to previous reports [66] the reverse reaction is very slow and the forward reaction may be considered as practically irreversible. In addition, we observed that an increase of argon flux, which increases the removal of the HCl produced during the sulfonation, decreases the reaction yield where it should increase the yield of a reversible reaction.

Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application **Fuel Cells**

REVIEW

The last assumption is perhaps the most realistic. Indeed, the rate-determining step of electrophilic substitution of aromatic rings is the formation of the sigma complex (or Wheeland complex) in which the positive charge is delocalized on the aromatic ring. It is well known that reaction rates increase with the solvent polarity in the case of neutral substrates and reagents when the transition state is partly ionic. In the sulfonation of polysulfones by trimethylsilylchlorosulfonate, not only both reagent and substrates are neutral but the transition state has a high ionic character, favoured by the delocalization of the positive charge on the aromatic ring. A high increase in reaction rate is, therefore, expected from an increase in solvent polarity. The dielectric constant of usual halogenated solvents ranges from 5 to 10, but a high dielectric constant may be expected for trimethylsilylchlorosulfonate and would allow the overall polarity of the medium to be increased. This influence progressively decreases with its consumption in the reaction. Addition of fresh reagent therefore allows the polarity of the medium to be increased.

In order to check the sulfonation efficiency, several experiments were carried out using the same reaction conditions i.e. same solvent, polymer concentration in solvent, inert atmosphere, inert gas flow, stirring rate but varying the reagent concentration (Figure 2). The real sulfonation degree per monomer unit increases with the theoretical sulfonation degree per monomer unit but the efficiency (conversion *vs.* sulfonating reagent) decreases with the increase of the theoretical sulfonation degree.

Despite the rate decrease, as compared to the reaction performed with chlorosulfonic acid, the sulfonation performed with the silylester form must be preferred. Indeed, (i) the side reactions are limited; in particular, the chain breakings which affect the lifetime of the membranes and (ii) the reaction proceed in homogeneous media.
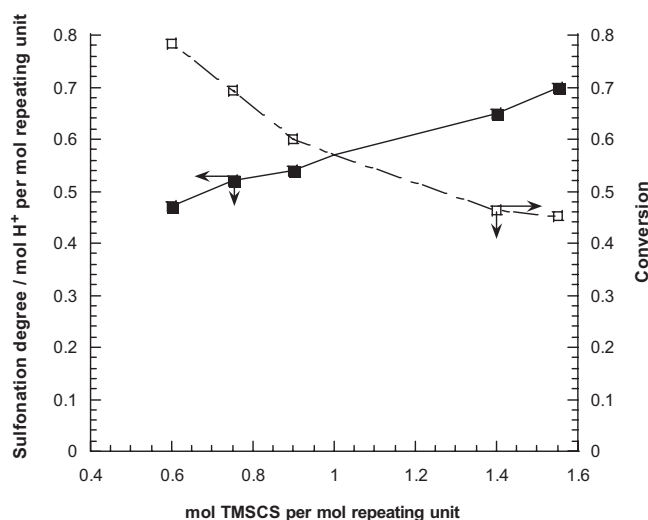
4.2 Sulfonation Through Metalation

Whatever the reagent and solvents used for the sulfonation, the reaction will take place on the aromatic carbons bearing a partial negative charge. This means that it will be impossible, by an electrophilic route, to get sulfonic groups onto the phenyl sulfone moiety. Now it is well known that substituents which exert an electron-withdrawing effect on an aromatic acid, e.g. benzoic or phenol, increase the acid strength, while those which exert an electron-donating effect decrease the acid strength. Therefore, sulfonation onto the phenylsulfone ring should lead to a more acidic ionomer than sulfonation onto the phenyl ether.

An alternative route involves three successive steps, namely metalation-sulfination-oxidation [32, 33, 67].

First, aryl lithium is prepared by treatment of the polymer with a strong base, such as butyl lithium. The base reacts with the most acidic hydrogen, i.e., due to its electron withdrawing effect in ortho position of the sulfone group. The aryl anion is then reacted with SO_2, providing an arylsulfinate whose oxidation leads to the sulfonate.

Generally, both metalation and sulfination steps occur with very good yields (> 90%). The efficiency of the oxidation step ranges between 45 and 100% and depends on the experimental conditions and on the oxidation reagent. A loss in sulfinate groups is observed. It may be related, at least partially, to a desulfination occurring during the oxidation process [32] and substitution of sulfinate groups by H. The loss in *IEC* can be greatly decreased by a good selection of oxidation conditions. Kerres et al. [32] have reported that ionic oxidants as $KMnO_4$ and $NaOCl$ are the most suitable for $IEC > 1.9$ mol H^+ kg^{-1} but that the higher oxidative [68] power of $NaOCl$, $E° = 0.90$ V *vs.* RHE for ClO^-/Cl^- as compared to 0.58 V *vs.* RHE for Mn^{7+}/Mn^{4+}, may lead to partial polymer degradations. For the polymeric sulfinates with a lower substitution degree, i.e. less hydrophilic, a non-ionic oxidant H_2O_2 (5 to 10 in excess) must be used. However, the standard reduction potential of H_2O_2 in alkaline conditions $E° = 0.87$ V *vs.* RHE for HO_2^-/OH^- may also favour a polymer degradation.

The authors reported an increased hydrolytic stability of their sulfonated polymers as compared to that obtained by electrophilic substitution. One may also expect an increased acidity for these sulfonated polysulfones. However, Cerfontain [44] reported that the *pKa* of benzene sulfonic acid is not very sensitive to the nature and position of substituents on the aromatic ring (see Section 3). As the scale-up of this synthesis seems difficult because it requires perfectly anhydrous conditions but also inert atmosphere, low temperatures, and involves the use of highly concentrated solutions of butyl lithium, the global interest of this innovative synthesis must be appreciated compared to the expected improvement in membrane performances.

Fig. 2 Conversion plots of PSU sulfonation performed with TMSCS at 35 °C for 17 h.

5 How to Reconcile High Conductivity with Moderate Water Uptake

The water uptake of PEMFC membranes highly influences their physico-chemical properties i.e. conductivity, mechanical strength and gas permeability [69]. High water uptake increases the membrane conductivity but is detrimental to its mechanical strength. Whatever the sulfonation route selected, the sulfonated aromatic polysulfones dissolve in water, at room temperature, above 0.8 sulfonic acid groups per repeating monomer unit of the polymer [70]. In order to get high conductivities while limiting the water uptake several approaches were performed, such as:

(i)   crosslinking of highly sulfonated ionomers
(ii) ionomers consisting of hydrophobic and hydrophilic domains
(iii) composite membranes

5.1 Cross-Linking Approach

For example, Kerres et al. have investigated both covalently [71–74] and ionically crosslinked sulfonated polysulfone, that exhibit an increased dimensional stability compared with uncrosslinked membranes.

Kerres et al. have reported two types of covalent crosslinking [72]. In the first type (I) the polysulfone (UDEL) contains both sulfonate and sulfinate groups, the sulfinate groups have been alkylated by α,ω dihalogenoalkanes, resulting in a fully cross-linked ionomer. In the second type (II), the membrane contains a mixture of polysulfone–sulfinate and polysulfone-sulfonate resulting in a semi-interpenetrated network [73]. The main disadvantage of all these covalently crosslinked membranes, reported by Kerres [74] is their brittleness after drying.

The water uptake increases both with the temperature and the *IEC* and decreases with the crosslinking density [73]. Kerres et al. reported that for crosslinked membranes whose *IEC* range between 1 and 1.75 mol H^+ L^{-1} the water uptake at 75 °C ranges between 17 and 48%. It must be emphasized that an uncrosslinked S-PSU membrane, whose *IEC* reaches 1.75 mol H^+ L^{-1}, completely dissolves in water.

Blends of sulfonated polysulfone and N-containing polymers (aminated polysulfone, poly(4-Vinylpyridine) behave as acid base blends and lead to ionically crosslinked membranes [75, 76]. These membranes show a high flexibility, even in anhydrous state, but, unfortunately, the instability of the ionic crosslinks above 70 °C leads to a dramatic swelling (> 73% water uptake).

5.2 Ionomers with Hydrophobic and Hydrophilic Domains

5.2.1 Through Block Polycondensation

Adopting for sulfonated polysulfones an approach developed by Mercier et al. for sulfonated polyimides [19, 77], McGrath et al. prepared new polysulfone synthesised by co-polycondensation between sulfonated and non-sulfonated monomers [78] which should limit the swelling of the membrane. It was also shown that the location of sulfonic acid units on specific chain segments of the copolymer main chain resulted in the formation of well–separated hydrophilic and hydrophobic domains.

5.2.2 Through Spacing Sulfonic Group from the Polymer Backbone

Karlsson et al. [79] proposed an alternative way to separate the hydrophilic sulfonic acid units and the hydrophobic polysulfone main chain by spatial separation. Three different sulfoalkylated polymers with various alkyl side chain lengths were prepared using lithiation-sulfination-alkylation reaction. The spacing of the sulfonic acid groups from the polysulfone main chain seems to prevent the ionomer from too large a swelling as compared to polysulfone directly sulfonated on the aromatic rings of the backbone. The sulfoalkylated polymers keep their dimensional stability when equilibrated in water. The critical temperature of these ionomers ranges between 70 and 100 °C.

Laffite et al. [80] succeeded, too, in spacing aryl sulfonic acids from the polysulfone backbone by addition of a mixed acid aromatic anhydride, namely, 2-sulfobenzoic acid cyclic anhydride, on a lithiated polysulfone.

The acidity of alkyl sulfonic acids is probably lower than that of aryl ones. Besides, the comparison between the conductivities reported [79, 80] for these two polysulfone ionomers seems in agreement with this assumption as the aryl-sulfonic acid based ionomers are more conductive than those based on the alkylsulfonic acid ones. It seems, however, that the aromatic ketone spacing has a limited impact on the water uptake.

5.3 Composite Membranes

Good performances were reported with composite membranes [81], in particular sulfonated PSU associated with phosphatoantimonic acids, $H_3Sb_3P_2O_{14}$, xH_2O [58, 62, 81, 82] and PPSU associated with heteropolyacid $H_3PW_{12}O_{40}$ [83]. The main interest of the inorganic fillers is (i) to contribute to the overall conductivity, (ii) to keep a sufficient humidity inside the membrane and (iii) to enable the *IEC* of the ionomer to be maintained at levels that allow their mechanical properties to be retained. Baradie et al. reported that the water uptake is increased, with respect to sulfonated PSU, at low rate of phosphatoantimonic acid 3 to 7 wt.-% and decreases at 12% rate. Kim et al. [83] reported that blending sulfonated PPSU with heteropolyacid in the range 14 to 60 wt.-% results in a clear decrease of the water uptake. They assumed that this decrease is partly due to an interaction between sulfonic acid and heteropolyacid stronger than that between sulfonic acid and water.

Figure 3 shows an average evolution of conductivity data *vs.* temperature reported, at three relative humidities, for polysulfone ionomers blended or not with inorganic acid fil-
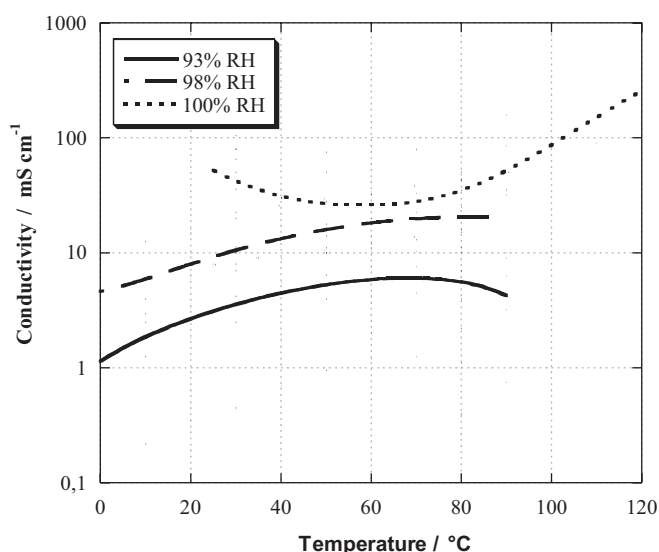
Fig. 3 Average conductivities of sulfonated polysulfones at 93, 98 and 100% of Relative Humidity through different references [58, 62–64, 78, 80, 81, 83].

lers. The comparison is obviously difficult as (i) the data originates from different research laboratories and (ii) it is difficult to get a high accuracy on the conductivity measurements. In the temperature range 25 to 100 °C the conductivities range between 20 to 80 mS cm^{-1}, with an advantage for the composite membranes.

6 Thermal Stability and Chemical Degradation

6.1 Thermal Stability

Sulfonation of thermostable polymers generally results in an increase of the glass transition temperature, T_g (Table 2).

An increase in T_g may be related to (i) the introduction of a rather bulky substituent on the aromatic rings, (ii) an increase of chain-chain interactions through hydrogen bonds and (iii) the ionic character of the substituent. When the ionomer is in its acidic form it may be assumed that hydrogen bonds between sulfonic groups and other sulfonic groups or diaryl ethers lead mainly to polymer stiffening. On the other hand, exchanging a proton by an alkaline cation, increases T_g dramatically (Table 2).

This increase, quite independent of the size of the alkaline cation (Li$^+$ or Na$^+$), is mainly related to chain-chain ionic in-

Table 2 Tgs of sulfonated polysulfones according to IEC and to cation nature (PPSU).

P(P)SU and sulfonated P(P)SU	IEC / mol H$^+$ kg^{-1}	T_g / °C
PPSU	0	220
S- PPSU H+1	1.05	243
S- PPSU H+2	1.3	248
S- PPSU H+3	1.5	247
S- PPSU H+4	1.65	250
S-PSUH+	1.35	196
S-PSULi+	1.3	248
S-PSUNa+	1.3	252

teractions as the ionic character always increases from proton to alkaline cation. The presence of the sulfonic acid groups destabilises the polymer chain of the S-PSU. While thermogravimetric analysis of PSU showed a modest amount of decomposition at 350 °C, S-PSU showed substantial decomposition at 300 °C and even from 250 °C. If some of this weight loss can be attributed to a loss in sulfonic acid groups, chain breakings also occur and lead to the formation of low molecular weight by-products of 344 and 402 g mol^{-1} (Table 3) [84].

Table 3 Degradation products of PSU submitted to superheated steam [84].
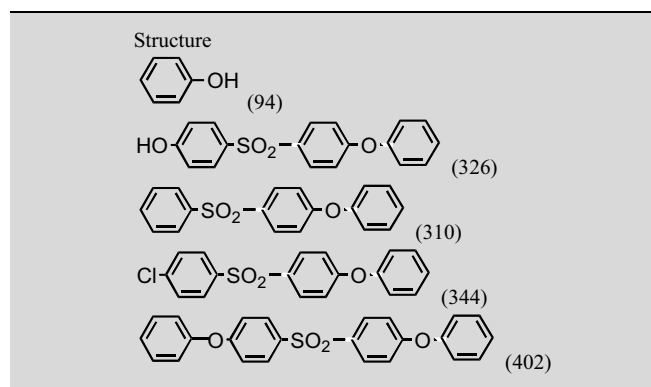
A preferential route for the polymer chain cleavage was not established for sulfonated PSU decomposition. Indeed, chain cleavages originate both from ether and sulfone linkages, the by-product molecular weights ranging between 94 and 402 g mol^{-1}.

Kopitzke et al. [84] demonstrated that neither acid nor steam is the crucial factor in the decomposition of these polymers. Heating of the PSU in the presence of steam generated from 6 mol L^{-1} HCl aqueous solution did not show any effect on its stability. The decomposition of the polymers appears to be thermally driven in a steam atmosphere.

6.2 Chemical Degradation in Relation to Sulfonation Scaling-up

Chemical degradations may occur when the membrane is operated in a fuel cell but chemical degradations may also occur during the polymer sulfonation and, therefore, shorten the membrane lifetime. In Section 4.1 of this paper we claim that the use of a sulfonation reagent, trimethylsilylchlorosulfonate, allows the chain breakings to be minimized, if not avoided. This is true at the laboratory scale. Thereafter, we have performed syntheses at the pilot scale and we have found that, even with this reagent, chain breakings may occur.

Thus, viscosimetric measurements performed in diluted solutions, using 0.1 mol L^{-1} NaI in DMF as a solvent, allowed a drop in intrinsic viscosity, and therefore in M_v (average viscosimetric molecular weight), to be characterized. The viscosity drop was found to be dependent on the experimental con-

Fuel Cells Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application
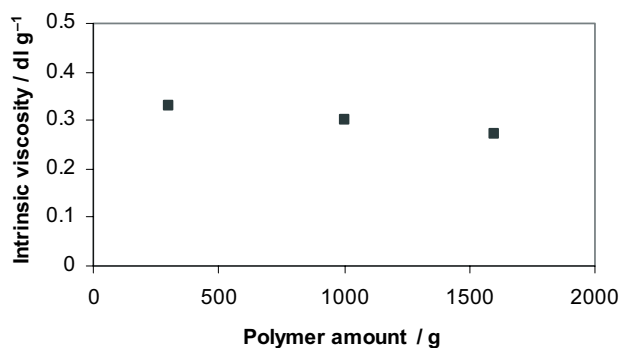
REVIEW

Fig. 4 Intrinsic viscosity dependence with polysulfone amount. Operating conditions: sulfonation of PSU with TMSCS, mol TMSCS per mol repeating unit = 0.9, low argon flux, θ = 45 °C.

ditions of the sulfonation, in particular on the amount of polymer to be sulfonated (Figure 4).

Thus, using the same experimental conditions, a fall in viscosity was observed when increasing the amount of polymers to be sulfonated.

6.3 Degradation Mechanism

Due to the sulfonation experimental conditions, the degradation is obviously not thermally driven. We assume that chain scissions are induced by the HCl by-product of the electrophilic substitution. This is easily removed, under argon flux, when the reaction is carried out on small quantities, but much less easily when the polymer amount increases. We propose a mechanism based on a protonation of the ether lone pair in a rapid step followed by a nucleophilic attack of the chlorine anion in the alpha position during the rate-determining step (Scheme 2):
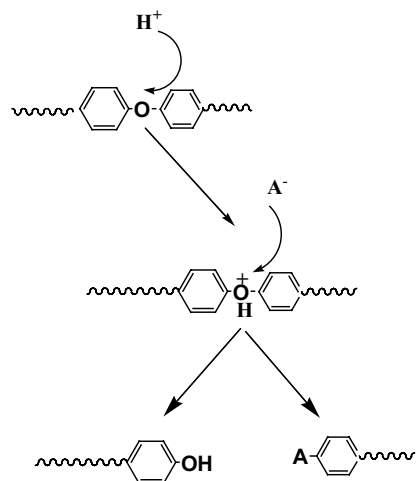
Scheme 2 Proposition of a mechanism of degradation occurring in the sulfonation of PSU by TMSCS in aprotic solvents.

These observations and assumptions clearly disagree with the previous report of Kopitzke et al. [84] which exposed polysulfone and sulfonated polysulfone to a steam of

6 mol L^{-1} HCl and concluded that for both polymers, degradation is thermally driven (Section 6.1). However the previous study did not pay attention to the average molecular weights of the polymer before and after the degradation experiments. Some chain scissions leading to high molecular fragments may, therefore, occur in these conditions without being detected. But, above all, the experimental conditions are clearly different. First, Kopitzke et al. did not use the polymers in solution, but as a powder exposed to steam. Then the polymers are in contact with a HCl steam i.e. Cl^- which is a hard base, is strongly solvated by water molecules [85] and in these conditions it is a poor nucleophilic reagent. On the other hand, comparison between the nucleophilic substitution rates in protic solvent (methanol) and aprotic one (DMSO) shows that a soft and large anion such as I^- is more reactive by one order of magnitude than Cl^- in methanol but that the situation is completely reversed in DMSO, Cl^- becoming ten times more reactive than I^- [86]. In the sulfonation experimental conditions, where a very poor solvating solvent is used, namely, dichloromethane, we may assume that Cl^- is probably a strong nucleophilic agent able to induce an aromatic nucleophilic substitution.

7 Conclusion

The majority of the alternate membranes to Nafion® are prepared starting from polymers with aromatic skeleton. This gives them a great thermal and mechanical stability and allows the ionic function to be introduced by electrophilic substitution. The industrial advantage is in modifying available polymers in a single chemical step. Thus the reaction of sulfonation has long been used to prepare detergents and ion-exchange resins. However, the schedule of conditions of PEMFC application imposes that the reaction does not involve any degradation by chain breaking and that the ionic groups are distributed in a statistical way on the whole polymer chains. We showed that the experimental procedures, i.e. solvents, temperature, sulfonation agent, conditions obtained sulfonated ionomers in a homogeneous way and the absence of chemical degradation. Consequently, it is difficult to compare publications dealing with the durability of the membranes, insofar as they are accompanied by no characterization related to possible chain breakings of the tested ionomers. This paper also shows that, in spite of an optimization of the conditions of reaction at the laboratory scale, the passage to an industrial scale can be accompanied by significant degradations of the ionomers.

Acknowlegments

Iojoiu et al.: Mastering Sulfonation of Aromatic Polysulfones: Crucial for Membranes for Fuel Cell Application **Fuel Cells**

REVIEW

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REVIEW

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