



HAL
open science

Synthesis of polymers containing perfluoroalkyl sulfonated side chains for proton conductivity membranes

Joanna Swiecicka Fichou Swiecicka

► **To cite this version:**

Joanna Swiecicka Fichou Swiecicka. Synthesis of polymers containing perfluoroalkyl sulfonated side chains for proton conductivity membranes. Materials. Université de Lyon, 2016. English. NNT : 2016LYSEI116 . tel-01920774

HAL Id: tel-01920774

<https://theses.hal.science/tel-01920774>

Submitted on 13 Nov 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



N°d'ordre NNT : 2016LYSEI116

THESE de DOCTORAT DE L'UNIVERSITE DE LYON
opérée au sein de
INSA Lyon

Ecole Doctorale N° 34
Matériaux de Lyon

Spécialité/ discipline de doctorat :
Matériaux

Soutenue publiquement le 15/11/2016, par :

Joanna Swiecicka Fichou

**Synthèse de polymères aromatiques à
chaînes latérales perfluoroalkyles sulfonées
pour la conception de membranes
conductrices protoniques**

Devant le jury composé de :

Sanchez Jean-Yves	Professeur Université de Madrid	Président
Iojoiu Cristina	CR1 CNRS Université de Grenoble	Rapporteuse
Robin Jean-Jacques	Professeur Université de Montpellier	Rapporteur
Bounor Legaré Véronique	CR1 CNRS Université de Lyon	Examinatrice
Sanchez Jean-Yves	Professeur Université de Madrid	Examineur
Fleury Etienne	Professeur INSA Lyon	Directeur de thèse
Mercier Régis	CR1 CNRS Université de Lyon	Co-directeur de thèse

Département FEDORA – INSA Lyon - Ecoles Doctorales – Quinquennal 2016-2020

SIGLE	ECOLE DOCTORALE	NOM ET COORDONNEES DU RESPONSABLE
CHIMIE	CHIMIE DE LYON http://www.edchimie-lyon.fr Sec : Renée EL MELHEM Bat Blaise Pascal 3 ^e étage secretariat@edchimie-lyon.fr Insa : R. GOURDON	M. Stéphane DANIELE Institut de Recherches sur la Catalyse et l'Environnement de Lyon IRCELYON-UMR 5256 Équipe CDFA 2 avenue Albert Einstein 69626 Villeurbanne cedex directeur@edchimie-lyon.fr
E.E.A.	ELECTRONIQUE, ELECTROTECHNIQUE, AUTOMATIQUE http://edeea.ec-lyon.fr Sec : M.C. HAVGOUDOUKIAN Ecole-Doctorale.eea@ec-lyon.fr	M. Gérard SCORLETTI Ecole Centrale de Lyon 36 avenue Guy de Collongue 69134 ECULLY Tél : 04.72.18 60.97 Fax : 04 78 43 37 17 Gerard.scorletti@ec-lyon.fr
E2M2	EVOLUTION, ECOSYSTEME, MICROBIOLOGIE, MODELISATION http://e2m2.universite-lyon.fr Sec : Safia AIT CHALAL Bat Darwin - UCB Lyon 1 04.72.43.28.91 Insa : H. CHARLES Safia.ait-chalal@univ-lyon1.fr	Mme Gudrun BORNETTE CNRS UMR 5023 LEHNA Université Claude Bernard Lyon 1 Bât Forel 43 bd du 11 novembre 1918 69622 VILLEURBANNE Cédex Tél : 06.07.53.89.13 e2m2@univ-lyon1.fr
EDISS	INTERDISCIPLINAIRE SCIENCES-SANTE http://www.ediss-lyon.fr Sec : Safia AIT CHALAL Hôpital Louis Pradel - Bron 04 72 68 49 09 Insa : M. LAGARDE Safia.ait-chalal@univ-lyon1.fr	Mme Emmanuelle CANET-SOULAS INSERM U1060, CarMeN lab, Univ. Lyon 1 Bâtiment IMBL 11 avenue Jean Capelle INSA de Lyon 696621 Villeurbanne Tél : 04.72.68.49.09 Fax :04 72 68 49 16 Emmanuelle.canet@univ-lyon1.fr
INFOMATHS	INFORMATIQUE ET MATHEMATIQUES http://infomaths.univ-lyon1.fr Sec : Renée EL MELHEM Bat Blaise Pascal 3 ^e étage infomaths@univ-lyon1.fr	Mme Sylvie CALABRETTO LIRIS – INSA de Lyon Bat Blaise Pascal 7 avenue Jean Capelle 69622 VILLEURBANNE Cedex Tél : 04.72. 43. 80. 46 Fax 04 72 43 16 87 Sylvie.calabretto@insa-lyon.fr
Matériaux	MATERIAUX DE LYON http://ed34.universite-lyon.fr Sec : M. LABOUNE PM : 71.70 –Fax : 87.12 Bat. Saint Exupéry Ed.materiaux@insa-lyon.fr	M. Jean-Yves BUFFIERE INSA de Lyon MATEIS Bâtiment Saint Exupéry 7 avenue Jean Capelle 69621 VILLEURBANNE Cedex Tél : 04.72.43 71.70 Fax 04 72 43 85 28 Ed.materiaux@insa-lyon.fr
MEGA	MECANIQUE, ENERGETIQUE, GENIE CIVIL, ACOUSTIQUE http://mega.universite-lyon.fr Sec : M. LABOUNE PM : 71.70 –Fax : 87.12 Bat. Saint Exupéry mega@insa-lyon.fr	M. Philippe BOISSE INSA de Lyon Laboratoire LAMCOS Bâtiment Jacquard 25 bis avenue Jean Capelle 69621 VILLEURBANNE Cedex Tél : 04.72 .43.71.70 Fax : 04 72 43 72 37 Philippe.boisse@insa-lyon.fr
ScSo	ScSo* http://recherche.univ-lyon2.fr/scso/ Sec : Viviane POLSINELLI Brigitte DUBOIS Insa : J.Y. TOUSSAINT viviane.polsinelli@univ-lyon2.fr	Mme Isabelle VON BUELTZINGLOEWEN Université Lyon 2 86 rue Pasteur 69365 LYON Cedex 07 Tél : 04.78.77.23.86 Fax : 04.37.28.04.48

*ScSo : Histoire, Géographie, Aménagement, Urbanisme, Archéologie, Science politique, Sociologie, Anthropologie

Acknowledgements

First and foremost, I would like to thank Dr. Régis Mercier for giving me the chance to do my PhD in France, for his support and for helping me to solve every problem over the last few years. I would like to thank Prof. Dr. Etienne Fleury for supervising my PhD. I would like to thank: Dr. Guillaume Sudre, Dr. Pierre Alcouffe, Dr. Sébastien Pruvost, Dr. Arnaud Morin for their help and all analysis.

I would like to thank my family my husband and all my friends for their support and help, especially: Wiola and Bruno. I would like to thank people who work with me and have helped me to solve a lot problems, especially: Dr. Katy Marestin, Dr. Romain Heck and Edouard Chauveau. Last but not least I would like thank for financial support the FUI NMHT project and Conseil General du Rhône.

CONTENTS

INTRODUCTION GENERALE	9
Fuel cell.....	10
Proton Exchange Membrane Fuel Cell (PEMFC)	11
The membrane	13
Nafion®	13
Chapter I. Introduction literature review	17
I.1. Sulfonated aromatic and heterocyclic polymers.....	17
I.1.1. Post-modification	17
I.1.2. Polymerization of sulfonated monomers.....	18
I.2. Sulfonated copolymers containing side chains-post modification	20
I.2.1. Sulfonated copolymers containing aromatic side chains.....	20
I.2.2. Sulfonated copolymers containing aliphatic side chains	22
I.2.3. Sulfonated copolymers containing perfluoroalkyl side chains.....	27
I.3. Synthesis of sulfonated copolymers from monomers containing side chains.....	29
I.3.1. Synthesis of sulfonated copolymers from monomers containing sulfonated aromatic side chains.....	30
I.3.2. Synthesis of sulfonated copolymers from monomers containing sulfonated aliphatic side chains.....	33
I.4. Sulfonated block polymers	35
I.4.1. Post modification of block copolymers	36
I.4.2. Synthesis of sulfonated block copolymers from sulfonated monomers.....	37
I.5. Synthesis of block copolymers containing sulfonated side chains.....	38
I.5.1. Block copolymers containing sulfonated aromatic side chains	38
I.5.2. Sulfonated block copolymers containing aliphatic side chains	43
I.6. Synthesis of sulfonated block copolymers from monomers containing side chains	45
I.6.1. From sulfonated aromatic side chains monomers.....	45
I.6.2. From monomers bearing sulfonated aliphatic side chains	46
I.7. Conclusion	47
Chapter II. Synthesis of sulfonated poly(arylene ether)s	49

II.1. Introduction.....	49
II.2. Synthesis of 1-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-2,4-difluorobenzene (FPSAB-K)	49
II.3. Synthesis of a model compound from FPSAB-K monomer	54
II.4. Synthesis and structural characterization of sulfonated poly(arylene ether)s copolymers (SPAЕ)57	
II.5. Solubility of SPAЕ polymers	60
II.6. SPAЕ membrane manufacturing	61
II.7. Determination of IEC by titration	61
II.8. Thermal properties of SPAЕ polymers.....	63
II.9. Water uptake properties of SPAЕ polymers.....	63
II.10. Ionic conductivity of SPAЕ polymers	65
II.11. Conclusion	66
Chapter III. Synthesis of sulfonated poly(arylene ether sulfone)s	67
III.1. Introduction.....	67
III.2. Synthesis of 4-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-3,4'-difluorodiphenyl sulfone (3,4'-FPSAPS-K)	67
III.3. Synthesis of a model compound from 3,4'-FPSAPS-K monomer	71
III.4. Synthesis and structural characterization of sulfonated poly(arylene ether sulfone)s (SPAESulfone)	73
III.5. Solubility of SPAESulfone polymers.....	75
III.6. SPAESulfone membrane manufacturing	75
III.7. Determination of IEC	76
III.7.1. Determination of IEC by ¹ H NMR analysis	76
III.7.2. Determination of IEC by titration	76
III.8. Thermal stability of SPAESulfone	77
III.9. Water uptake of SPAESulfone	78
III.10. Proton conductivity of the SPAESulfone	80
III.11. Conclusion	81
Chapter IV. Synthesis of sulfonated poly(arylene ether sulfide)s	82
IV.1. Introduction	82
IV.2. Synthesis of 2-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-4,4'-difluorodiphenylsulfide (FPSAPS-K).....	83
IV.3. Synthesis of a model compound based on FPSAPS-K	87
IV.4. Synthesis of the sulfonated poly(aryl ether sulfide)s copolymers (SPAES).....	89

IV.5. Solubility of SPAES.....	93
IV.6. SPAES membranes manufacturing.....	93
IV.7. Determination of IEC.....	93
IV.7.1 Determination of IEC by ¹ H NMR analysis.....	93
IV.7.2. Determination of IEC by titration.....	94
IV.8. Thermal properties of SPAES	95
IV.9. Water uptake properties of SPAES polymers.....	97
IV.10. Ionic conductivity of SPAES polymers	98
IV.11. Conclusion.....	99
Chapter V. Synthesis of sulfonated poly(arylene ether ketone sulfone)s and poly(arylene ether ketone benzonitrile)s.....	101
V.1. Introduction	101
V.2. Synthesis of 3-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2-(potassiumoxysulfonyl)ethoxy]ethyl]-4,4'-difluorobenzophenone (FPSABP-K).....	101
V.3. Synthesis of model compound from FPSABP-K monomer.....	105
V.4. Synthesis of the sulfonated poly(arylene ether ketone sulfone)s and poly(arylene ether ketone benzonitrile)s copolymers	108
V.4.1. Synthesis of copolymers with biphenol	108
V.4.2. Synthesis of copolymers with hydroquinone.....	111
V.5. Solubility of SPAEK polymers	114
V.6. SPAEK membranes manufacturing	114
V.7. Determination of IEC of membranes	114
V.7.1. Determination of IEC by ¹ H NMR	114
V.7.2. Determination of IEC by titration.....	116
V.8. Thermal properties of SPAEK polymers	116
V.8.1 SPAEK containing biphenol unit.....	116
V.8.2. SPAEK containing quinone unit.....	118
V.9. Water uptake of SPAEK polymers	119
V.9.1. Water uptake of biphenol containing SPAEK polymers	119
V.9.2. Water uptake of hydroquinone containing SPAEK polymers	120
V.10. Ionic conductivity of SPAEK polymers	121
V.10.1. Ionic conductivity of biphenol containing SPAEK polymers.....	121
V.10.2. Proton conductivity of quinone containing SPAEK polymers	122

V.11. Conclusion	124
Chapter VI. Synthesis poly(arylene ether)s block copolymers	125
VI.1. Introduction	125
VI.2. Highly fluorinated sulfonated block poly(arylene ether ketone)s (BSPA EK-F)	125
VI.3. Sulfonated block poly(arylene ether ketone sulfone)s (BSPA EK-S)	128
VI.4. Statistic sulfonated poly(arylene ether ketone sulfone)s copolymer (statSPA EK)	130
VI.5. Solubility of BSPA EK and statSPA ER	132
VI.6. BSPA EK and statSPA EK membranes manufacturing	132
VI.7. Morphological characterization	133
VI.7.1. Transmission electron microscopy (TEM)	133
VI.7.1.1. Microstructure of BSPA EK-F	134
VI.7.1.2. Microstructure of the BSPA EK	134
VI.7.1.3. Microstructure of statSPA EK	136
VI.7.1.4. Effect of film casting conditions on the microphase separation of BSPA EK membranes	137
VI.7.2. Atomic force microscopy (AFM)	138
VI.8. Determination of IEC by titration	139
VI.9. Thermal stability	140
VI.9.1. Thermal stability of BSPA EK	140
VI.9.2. Thermal stability of statSPA EK	142
VI.10. Water uptake	144
VI.10.1. Water uptake properties of BSPA EK polymers	144
VI.10.2. Effect of film casting conditions on the water uptake of BSPA EK membranes	145
VI.10.3. Water uptake of statSPA EK	147
VI.11. Ionic conductivity	147
VI.11.1. Ionic conductivity of BSPA EK	147
VI.11.2. Effect of film casting conditions on ionic conductivity of BSPA EK	149
VI.12. Conclusion	150
VII. Conclusion générale	151
References	154
EXPERIMENTAL SECTION	161
I. Monomer Synthesis	161
I.1. Synthesis of PSA-K	161
I.2. Synthesis of FPSAB-K	161

I.3. Synthesis of 3,4'-FPSAPS-K	163
I.3.1. Synthesis of FPSAB-K	163
I.3.2. Synthesis of 1-1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro- 2(potassiumoxysulfonyl)ethoxy]ethyl-3,4'-diphenylsulfid (3,4'-FPSADPS-K)	163
I.3.3. Synthesis of 3,4'-FPSAPS-K	164
I.4. Synthesis of FPSAPS-K	165
I.4.1. Synthesis of 4,4'-difluoro-2-nitrodiphenylsulfide.....	165
I.4.2. Synthesis of 2-amino-4,4'-difluorodiphenylsulfide	166
I.4.3. Synthesis of 2-diazonium tetrafluoroborate- 4,4'-difluorobiphenylsulfide	166
I.4.4. Synthesis of 4,4'-difluoro-2-iododiphenylsulfide	167
I.4.5. Synthesis of FPSAPS-K	167
I.5. Synthesis of FPSABP-K	168
I.5.1. Synthesis of 4-fluoro-3-iodobenzoic acid	168
I.5.2. Synthesis of 4,4'-difluoro-3-iodobenzophenone.....	169
I.5.3. Synthesis of FPSABP-K	169
II. Model compound synthesis	170
II.1. From FPSAB-K monomer	170
II.2. From 3,4'-FPSAPS-K monomer	171
II.3. From FPSAPS-K monomer	171
II.4. From FPSABP-K monomer	171
III. Polymer synthesis.....	172
III.1. Synthesis of sulfonated poly(arylene ether)s polymers (SPAЕ)	172
III.2. Synthesis of sulfonated poly(arylene ether sulfone)s (SPAESulfone)	173
III.2.1. Synthesis of SPAESulfone-N	173
III.2.2. Synthesis of SPAESulfone-S	174
III.3. Synthesis of sulfonated poly(arylene ether sulfide)s polymers (SPAES).....	174
III.3.1. Synthesis of SPAES-S.....	174
III.3.2. Synthesis of SPAES-N	175
III.4. Synthesis of sulfonated poly(arylene ether ketone)s (SPAЕК)	176
III.4.1. Synthesis of SPAЕК-N.....	176
III.4.2. Synthesis of s-PAЕК-NQ.....	177
III.4.3. Synthesis of SPAЕК-SQ.....	177
III.4.4. Synthesis of SPAЕК-S	178

III.5. Synthesis of multiblock sulfonated poly(arylene ether ketone)s.....	179
III.5.1. Synthesis of B-SPA EK-F	180
III.5.2. Synthesis of BSPAEK-S	181
III.6. Synthesis of statSPA EK	182
IV. Characterization Methods.....	182

INTRODUCTION GENERALE

Au cours de ces vingt dernières années, la demande en sources d'énergie propre et renouvelable n'a pas cessé de croître. Parmi les différentes technologies se présentant comme des alternatives aux sources d'énergies fossiles et susceptibles d'être plus respectueuses de l'environnement, les piles à combustibles et plus particulièrement les "Polyelectrolyte membrane fuel cell" (PEMFC) ont fait l'objet d'une attention toute particulière qui s'explique par le fait qu'elles peuvent délivrer une forte densité de puissance, fonctionner dans un domaine de température compatible avec des applications dans le domaine des véhicules, des téléphones portables, des ordinateurs etc... mais également offrir une grande autonomie de fonctionnement.

Parmi les différents composants d'une PEMFC, la membrane polyelectrolyte joue un rôle essentiel car elle doit permettre le transport des H^+ dans le cas d'une pile H_2/O_2 ou des OH^- pour la pile au méthanol directe et d'autre part assurer une fonction de séparation physique entre les compartiments anodique et cathodique de la pile. Cela signifie que cette membrane doit posséder un ensemble de propriétés comme une conductivité ionique, des bonnes propriétés mécaniques, thermique et chimique[1],[2],[3].

Dans les années 80 du siècle dernier, l'utilisation du Nafion, polymère perfluoré sulfoné pour la conception de membranes polyelectrolytes a suscité un engouement pour le développement de polymères moins coûteux, plus facile à recycler et plus performant que le Nafion dans un domaine de températures supérieur à $100^\circ C$. Parmi les différentes voies explorées, celle concernant les polymères aromatiques et ou hétérocycliques a fait l'objet d'une attention toute particulière du fait de leurs bonnes propriétés thermique (T_g supérieure à $180^\circ C$) et chimiques. Pour qu'ils possèdent des propriétés de conduction protonique, l'introduction de fonction acide sulfonique le long des chaînes macromoléculaires a été envisagée.

Dans le cadre de cette thèse, l'objectif visé a été de combiner les propriétés des polymères aromatiques avec les très bonnes propriétés de conduction protonique du Nafion induite par la présence des chaînes latérales perfluoroalkyles sulfonées. Pour cela, il a été envisagé d'introduire des séquences perfluoroalkyles sulfonées dans des polymères de type poly ether aromatiques en utilisant des monomères contenant dans leur structure ce type de séquence. Ainsi des polymères aromatiques de type phényle éther, éther sulfone, phényl sulfure et phényle éther cétone ont été synthétisés. Leur synthèse et la caractérisation de leurs propriétés sont décrits dans les chapitres II à VI.

Fuel cell

The first fuel cell was invented in 1839 by Sir William Grove[4]. At the beginning of the 20th century electrical energy conversion technologies became more important because electricity was more and more widely used. In 1933, Sir Francis Bacon exposed his hydrogen-oxygen cell with alkaline electrolyte (AFC). Then in 1955 William Grubb presented the first polymer electrolyte fuel cell (PEMFC). Fuel cells found their first major applications in NASA's Gemini and Apollo programs, for the production of electricity and water. Nevertheless, the fuel cells from 1960s suffered from disadvantages such as high cost and short lifetimes. Over the last decade the increase of the world's population had an important influence on the development of more powerful and finely distributed power generators. The oil crises and awareness of the environmental consequences of fossil fuel use in electricity production have been the major factors in the development of fuel cells.

A fuel cell is an electrochemical device, in which the free energy of a chemical reaction is converted into electrical energy. It produces electricity and heat from fuel (hydrogen or methanol) and oxygen. This system gives water as the byproduct, which makes the fuel cell an environmentally friendly energy source.

A separator or electrolyte, which allows the transport of ionic charges but prevents the transfer of chemical species is needed in electrochemical cells like fuel cells and batteries.

The type of conductive electrolyte used is what characterizes a fuel cell. The major types of fuel cells, along with the type of electrolyte, are summarized in Table 1.

Table 1. Types of fuel cells[5].

Type of Fuel Cell	Electrolyte	Operating Temperature	Efficiency	Electric Power	Possible Applications
Alkaline (AFC)	Potassium Hydroxide	60-90 °C	45-60%	Up to 20 kW	Submarines, Spacecraft
Molten Carbonate (MCFC)	Immobilized Liquid Molten Carbonate	650 °C	45-60%	> 1 MW	Power Stations
Solid Oxide (SOFC)	Ceramic	1000 °C	50-65%	> 200 kW	Power Stations
Phosphoric Acid (PAFC)	Immobilized Liquid Phosphoric Acid	200 °C	35-40%	> 50 kW	Power Stations
Proton Exchange Membrane (PEMFC)	Ion Exchange Membrane	60-130 °C	40-60%	Up to 250 kW	Vehicles, Stationary
Direct Methanol (DMFC)	Ion Exchange Membrane	60-130 °C	40%	< 10 kW	Portable Applications

Proton Exchange Membrane Fuel Cell (PEMFC)

In recent years, polymer electrolyte membrane (PEM) in polymer electrolyte fuel cells (PEFCs) have drawn attention as energy sources for transportation, stationary, electric devices. Proton exchange membranes or polymer electrolyte membrane fuel cells (PEMFCs) are the most promising candidates of all fuel cell systems in terms of mode of operation and applications. The PEMFC offers efficient, safe and clean energy, which makes it a potentially good way to obtain nonpolluting systems. Thanks to the proton conducting membrane it is possible to attain high power densities and work at low temperatures (30-150°C).

Figure 1 shows a schematic representation of a single cell. The center of the PEMFC is the membrane electrode assembly (MEA). Fuel cells consist of two electrodes: an anode, a cathode and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrodes are connected in an external circuit which causes the electricity generation.

Hydrogen is fed on the anode. There, it reacts on the platinum catalyst and oxidizes into protons and electrons (Equations 1). The proton, in an aqueous environment, is transported through the membrane to the cathode and the electrons are forced through an external circuit, where the electrical energy is supplied to a light bulb for instance. At the cathode, gaseous oxygen is reduced and combined with protons and electrons to form water (Equation 2). The overall cell reaction yields one mole of water per mole of hydrogen and half mole of oxygen (Equation 3).

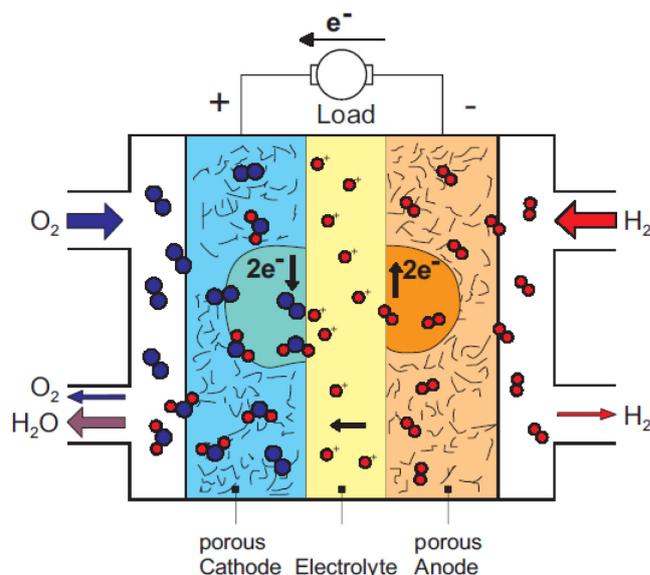
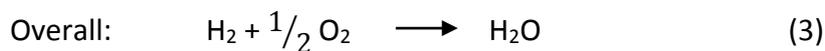
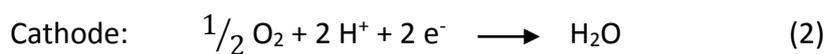
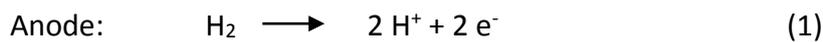


Figure 1. Schematic drawing of a hydrogen/oxygen fuel cell and its reactions based on the proton exchange membrane fuel cell (PEMFC).

Individual fuel cells produce about 0.7 volts, so to increase the voltage the single cells are incorporated into stacks of cells in series.

Recent investigations have shown that hydrogen energy is one of the ways to decrease pollution and dependence on fossil energy. Fuel cells are a new energy conversion technology which represents the latest development in the design and improvement of high performance proton conducting PEMs.

The membrane

The membrane is an essential element in the fuel cell system and hence it must display a combination of different properties:

- High proton transport.
- Barrier for gases. The membrane should be impermeable to prevent any contact between H₂ and O₂ which can lead to local burning.
- Selective and highly permeable to water.
- Resistant to chemical attack. The membrane must be resistant to redox attacks of the two gases, the chemical activation of the catalysts on the electrodes, the formation of active radicals at the electrodes and to hydrolysis.
- Excellent mechanical properties. It must be resistant to drastic conditions that can cause weakening of the membrane and its degradation.

Nafion®

Poly(perfluoroalkyl sulfonic acid)s such as Nafion® (DuPont) are known as the standard membrane materials for polymer electrolyte fuel cell (PEMFCs). Nafion® was developed by the E. I. DuPont Company in the 1960's.

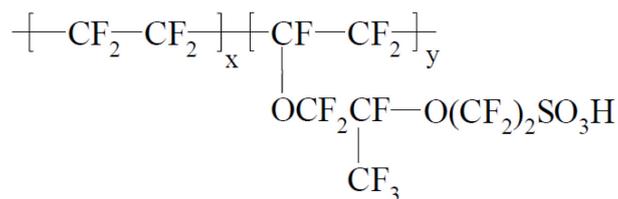
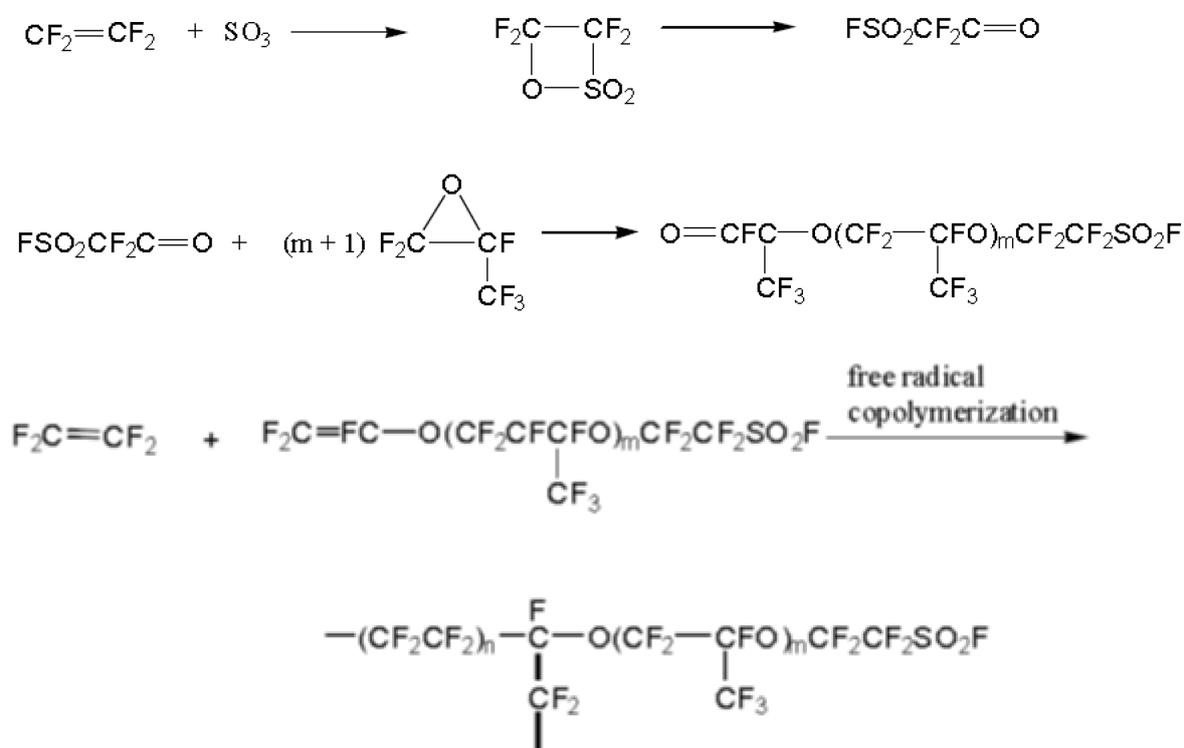


Figure 2. Structure of Nafion® ($x = 6-10$, $y = 1$).

Nafion® is a copolymer obtained by polymerization of tetrafluoroethylene and the perfluorovinyl ether, perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonic acid, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_3H$ (Fig. 2)[6].

The synthesis of sulfonated perfluorovinyl ether monomer used to prepare Nafion®, is based on a multi step process as illustrated Scheme 3. Tetrafluoroethylene is reacted with SO_3 to form a cyclic sulfone. Then the sulfone is reacted with hexafluoropropylene epoxide to produce sulfonyl fluoride adducts ($m > 1$). These adducts are heated with sodium carbonate to form sulfonyl fluoride vinyl ether[7].



Scheme 3. Multi step process to prepare Nafion®.

Among PEM fuel cell manufacturers, Nafion® ranks as the most widely used membrane material. The main reason of this great interest is due to its high conductivity and good chemical inertness. The specific morphology of Nafion® membrane can explain its good fuel cell performance. Nevertheless, disadvantages like high cost, high methanol permeability and restricted operation temperature (>80°C) limit their use and requires searching on new alternatives. For this reason interest in sulfonated aromatic polymers as an alternative for novel polymer electrolyte membranes has grown over the past 15 years.

Kreuer[8] has compared different properties of Nafion and sulfonated polyetherketones. Results showed that sulfonated aromatic polymers containing sulfonic acid groups directly in the main chain had a less pronounced microphase separation between hydrophobic-hydrophilic microstructure than Nafion. The model proposed by Kreuer (Figure 3) clearly explains the microstructure and helps understanding the different mechanical and transport properties of polyelectrolyte membranes.

As illustrated in Figure 3 water filled channels in Nafion are wider compared to PEEKK. Channels of sulfonated PEEKK are less separated, highly branched and with more dead-end channels than those of Nafion. However, sulfonated polyetherketones are interesting low-cost alternative membrane materials. They may also reduce swelling and help reduce problems with high methanol cross-over in direct methanol fuel cells (DMFC).

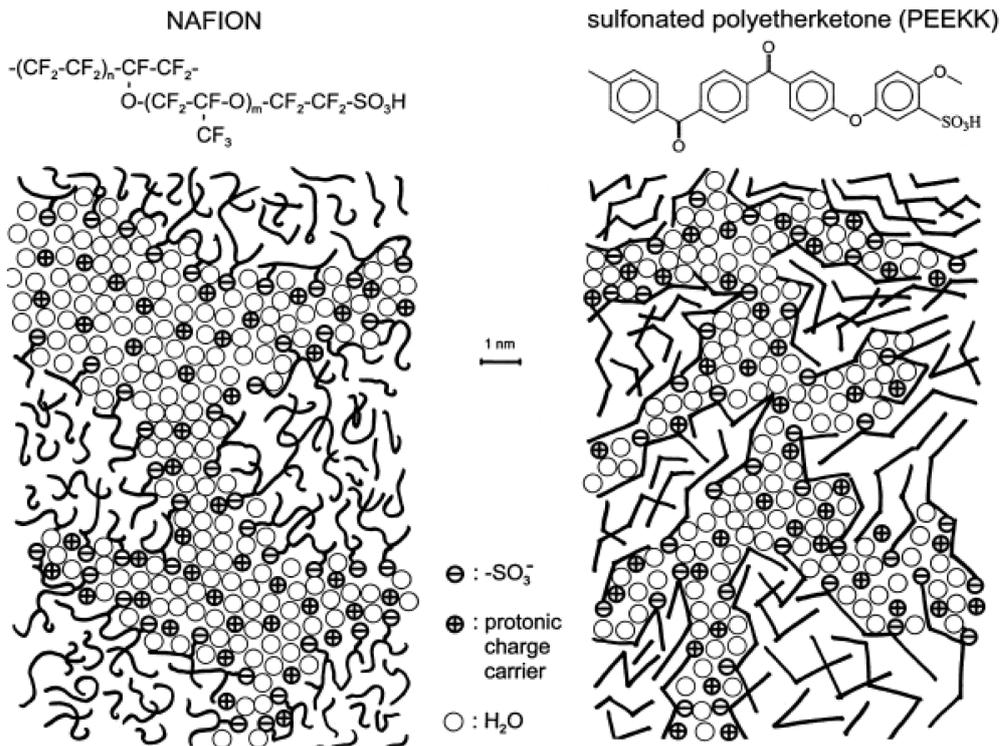


Figure 3. Microstructure of Nafion and sulfonated polyetherketone.

As illustrated in Figure 3 water filled channels in Nafion are wider compared to PEEKK. Channels of sulfonated PEEKK are less separated, highly branched and with more dead-end channels than those of Nafion. However, sulfonated polyetherketones are interesting low-cost alternative membrane materials. They may also reduce swelling and help reduce problems with high methanol cross-over in direct methanol fuel cells (DMFC).

Chapter I. Introduction literature review

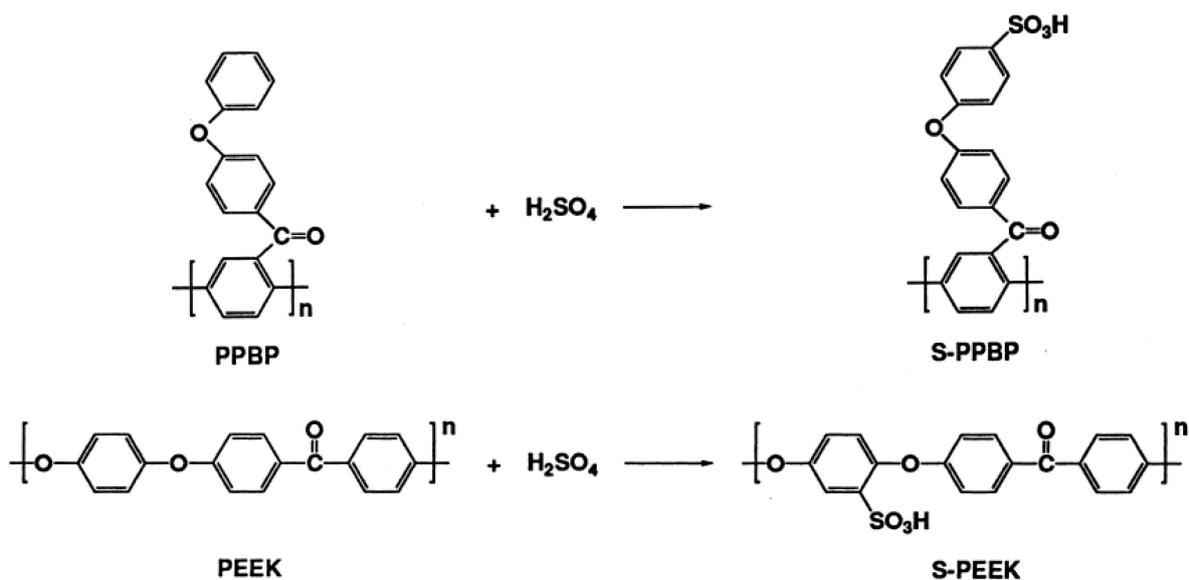
I.1. Sulfonated aromatic and heterocyclic polymers

Properties of aromatic and heterocyclic polymers allow their use as the alternative to perfluorinated PEMs. Sulfonated aromatic polymers include poly(arylene ether sulfone)s, poly(arylene ether)s, poly(arylene ether ether ketone)s, poly(phenylene)s, poly(phenylene sulfide)s, poly(phenylene sulfone)s, polyimides and polybenzimidazoles. They are expected to have low methanol crossover, high proton conductivity high glass-transition temperature (T_g). Other advantages include their chemical and thermal stability, good solubility in polar aprotic solvents such as dimethylsulfoxide (DMSO) or *N,N*-dimethylacetamide (DMAc). Furthermore, the design of a wide variety of aromatic polymer architectures can be achieved.

I.1.1. Post-modification

The most commonly used method to obtain sulfonated polymers is the post-sulfonation which consists in grafting sulfonic acid groups on the polymer chain using a sulfonating agent. Usually, sulfonation is carried out with concentrated sulfuric acid or chlorosulfonic acid. The main interest of this method is to perform the reaction directly from commercial parent polymers.

Rikukawa and coworkers[9] have reported the synthesis of different sulfonated polymers derived from poly(ether-etherketone) (PEEK) and poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP). Both polymers were sulfonated with sulfuric acid, which resulted in introducing sulfonic acid moieties in the main chain for PEEK and in the side chain for PPBP (Scheme I.1.1.1). The resulting sulfonated PPBP showed much higher proton conductivity which might be ascribed to the flexible pendant side chains of S-PPBP.



Scheme 1.1.1.1. Sulfonated route of PEEK and PPBP polymers.

An alternative method to sulfonate commercial poly(arylene ether sulfones), (Udel®) was described by Nolte et al.[10]. Udel® was sulfonated with trimethylsilyl chlorosulfonate in chlorinated solvent at room temperature.

The biggest problem of post-sulfonation is the lack of control over the degree of sulfonation of the polymer chain. Moreover, some sulfonating agents may cause degradation of the polymer chains, cross-linking or side reactions.

1.1.2. Polymerization of sulfonated monomers

Another approach is the preparation of sulfonated polymers from functionalized monomers. Polymerization of the sulfonated monomers is an attractive alternative for the synthesis of sulfonated polymers. This approach can allow overcoming some of the disadvantages occurring in the case of post-sulfonation. This method offers a better control of the sulfonic acid groups introduced in the polymer backbone and allows designing block copolymers. McGrath[11] prepared wholly aromatic, highly sulfonated poly(arylene ether sulfone)s containing up to two pendant sulfonated groups per repeat unit via direct polymerization of sulfonated monomer, 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone (Fig. 1.1.2.1). The resulting sulfonated membranes showed good results which confirms that the direct

polymerization of sulfonated monomers helps to control the degree of sulfonation (DS), improves proton conductivity, fuel cells performance and nanophase separation.

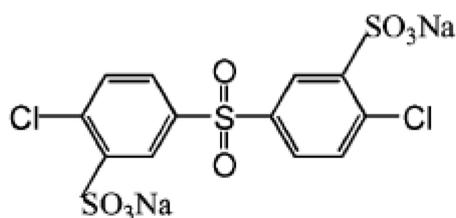


Figure I.1.2.1. 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone.

Mehdipour-Ataei and coworkers[12] presented series of novel sulfonated poly(arylene ether ketone)s prepared using direct copolymerization of sulfonated monomer 3,3'-disulfonated-4,4'-difluorobenzophenone (Fig. I.1.2.2). The ion exchange capacity of the corresponding membranes were between 0.76 and 1.46 meq/g. Membranes proton conductivities increased with increasing IEC and reached to 0.08 S/cm.

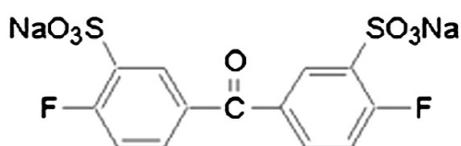


Figure I.1.2.2. 3,3'-disulfonated-4,4'-difluorobenzophenone.

Guiver et al.[13] reported the synthesis of sulfonated poly(aryl ether ether nitrile)s (SPAEEENs). SPAEEENs were prepared via direct polymerization of 2,6-difluorobenzonitrile, potassium 2,5-dihydroxybenzenesulfonate (Fig. I.1.2.3) and 4,4'-biphenol or hydroquinone. The proton conductivities of membranes at different sulfonic acid group content (SC) values were closed or higher than that of Nafion 117 and reached 10^{-1} S/cm.

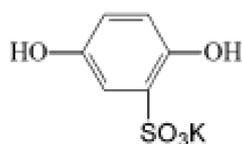


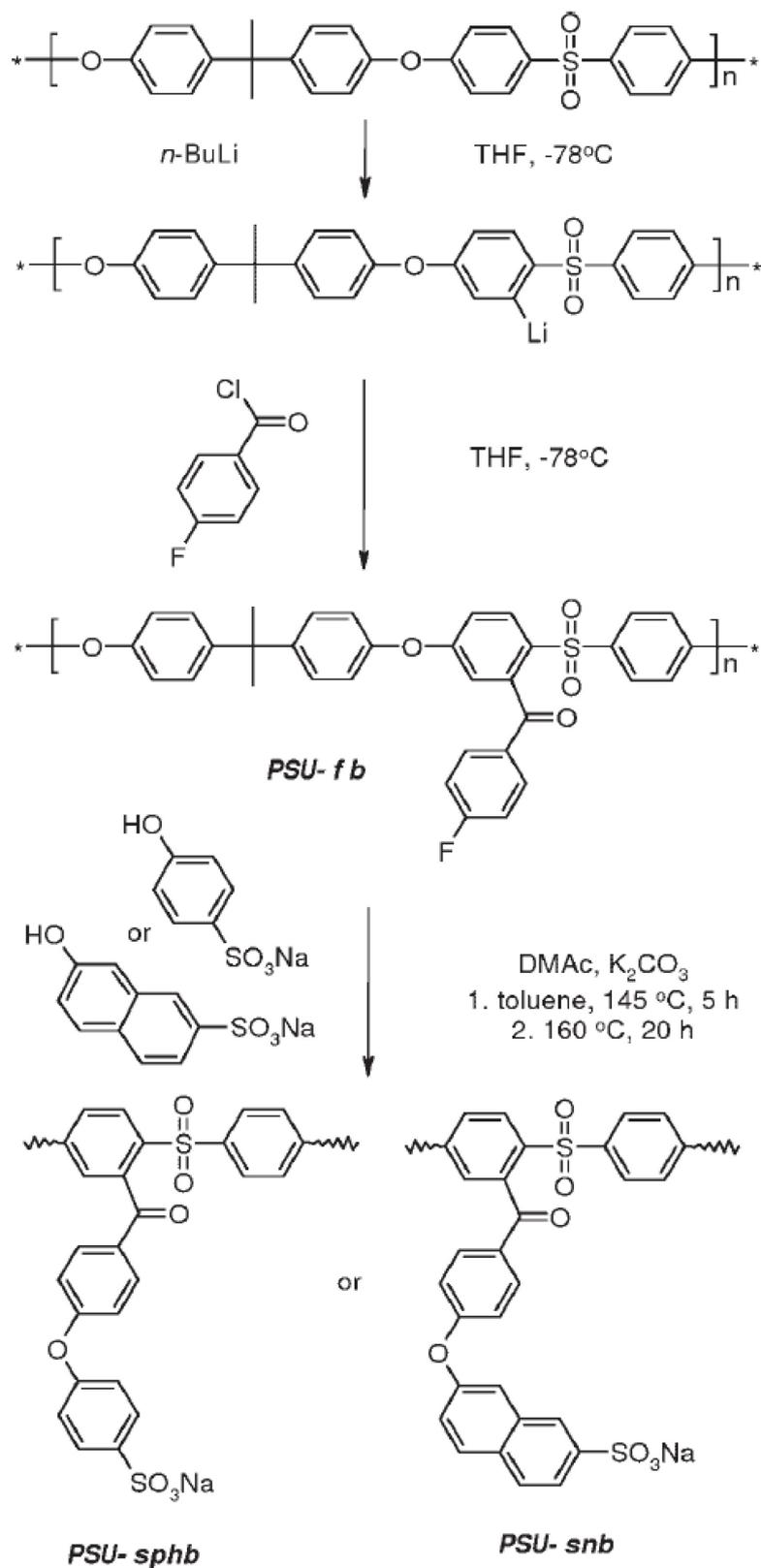
Figure I.1.2.3. Sulfonated hydroquinone.

I.2. Sulfonated copolymers containing side chains-post modification

A convenient route to split efficiently the hydrophilic and the hydrophobic structures is to locate the sulfonic acid groups in the pendant chain attached to the main polymer body. Recently, several researchers have worked on the synthesis of copolymers containing side chains[14, 15]. Studies have shown that membranes prepared from these polymers display nano phase separation morphology.

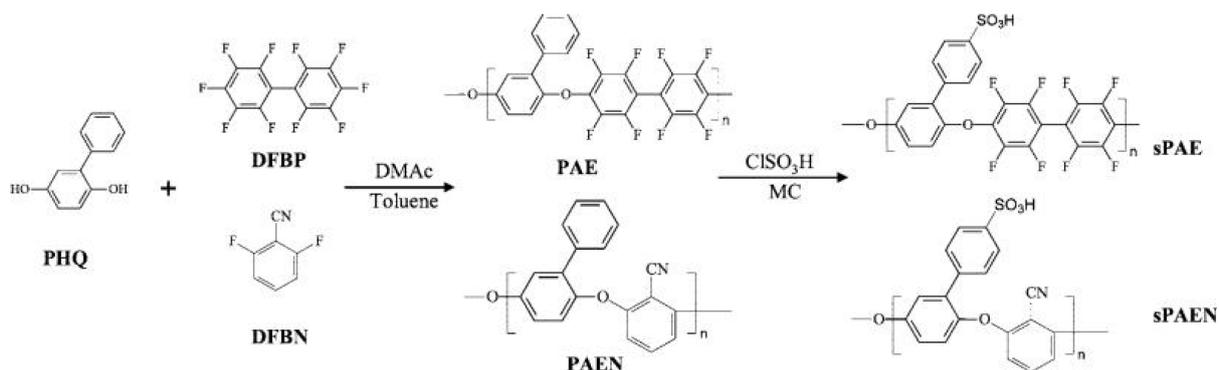
I.2.1. Sulfonated copolymers containing aromatic side chains

Jannasch and coworkers[16] have focused on the synthesis of polymers containing sulfonated aromatic pendant side chains. They reacted polysulfones with butyllithium at -78°C, then added 4-fluorobenzoic acid chloride to form PSU-fb. In the last stage they introduced sodium 4-sulfophenol or 2-naphtol-7-sulfonic acid by substituting the fluoride (Scheme I.2.1.1). The value of a degree of sulfonation (DS) can be controlled by the degree of lithiation. Synthesized polysulfone bearing naphthalene side chains gave very brittle membranes. For the second polymer the resultant membrane reached a proton conductivity of 32 mS/cm at 120°C.



Scheme 1.2.1.1. Synthesis way of sulfonated aromatic side chain containing polysulfone.

On the other hand, Guiver et al.[17] have synthesized two different polymers containing sulfonated pendant phenyl groups, highly fluorinated poly(arylene ether)s (sPAE) and poly(arylene ether nitrile)s (sPAEN) with high nitrile content (Scheme I.2.1.2). It has shown that the introduction of nitrile groups into sulfonated poly(arylene ether)s reduced their water uptake and dimensional swelling. The nitrile groups also presumably promote adhesion of the polymer matrix to the catalyst-electrode layer[18, 19]. A mild-post-sulfonation with chlorosulfonic acid was used to graft the sulfonic acid groups on the *para*-position of pendant phenyl rings. For the polymers sPAE and sPAEN with a degree of sulfonation of 100% an IEC of 1.77 and 2.55 mequiv/cm³ were measured. A proton conductivity of 135 mS/cm and a water uptake of 44.5 v% at 80°C were measured for the sPAE while for the sPAEN values of 140 mS/cm and 51.9 v% were obtained in the same conditions. It was also observed that the membranes based on these polymers were strong and flexible in both dry and wet states.

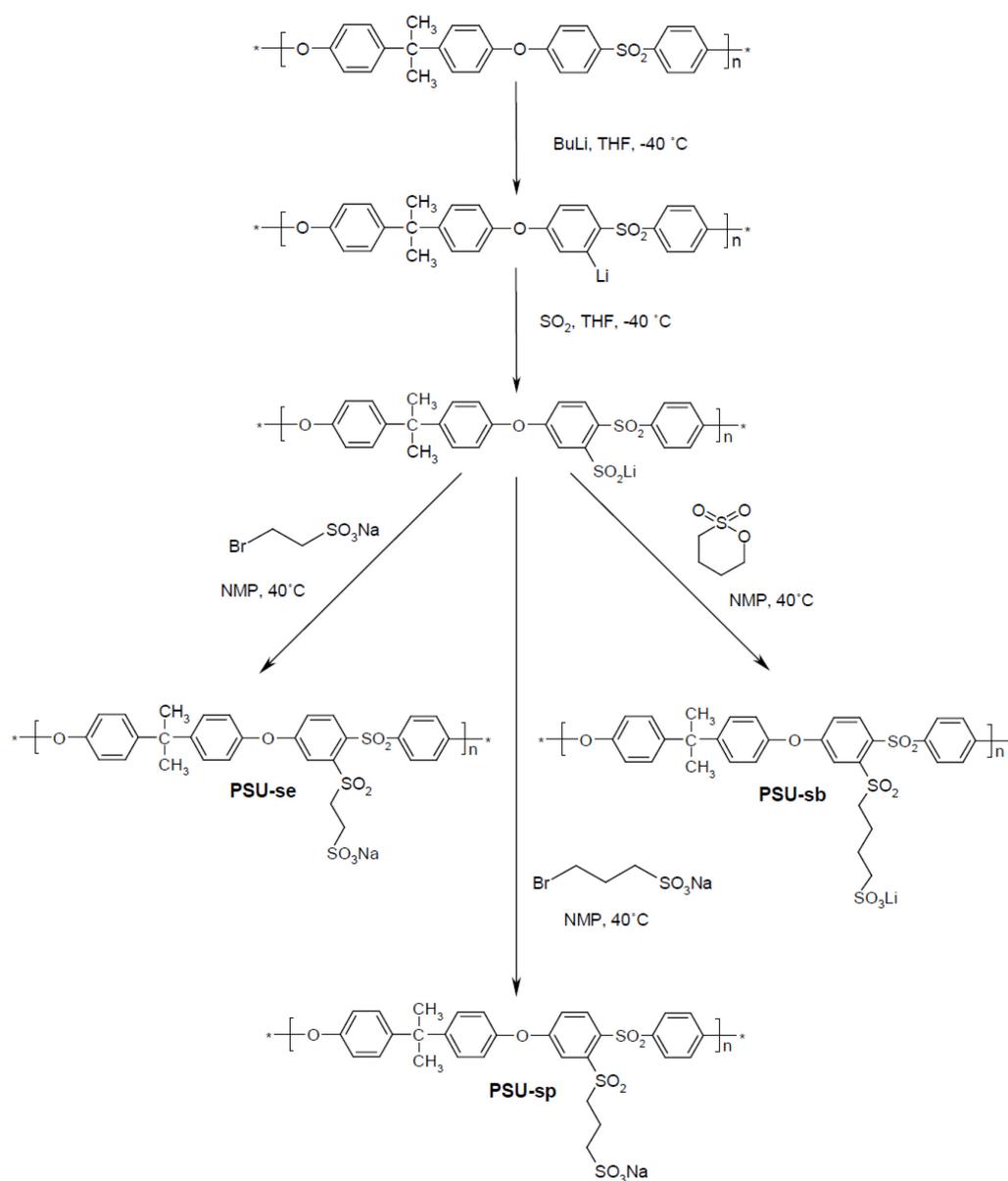


Scheme I.2.1.2. Synthesis of sulfonated poly(arylene ether) copolymers containing pendant sulfonic acid groups.

I.2.2. Sulfonated copolymers containing aliphatic side chains

Several research groups have been working on the introduction of sulfonic acid groups located on flexible aliphatic pendant side chains grafted onto the polymer main chain. In this way a good nano phase separation between hydrophilic and hydrophobic domains could be achieved. On these lines, Karlsson et al.[20] have worked on the post-modification of polysulfones (PSU). The main objective was to bound aliphatic pendant side-chains

containing sulfonic acid groups into polysulfone main chain. The modification involved different successive reactions. The first step was the functionalization of PSU by reaction with n-butyllithium at -40°C and then quenching the lithiated PSU with SO_2 gas. The last step was a sulfoalkylation, using three different compound: the sodium 2-bromoethanesulfonate, the sodium 3-bromopropanesulfonate, or the 1,4-butane sultone (Scheme I.2.2.1).

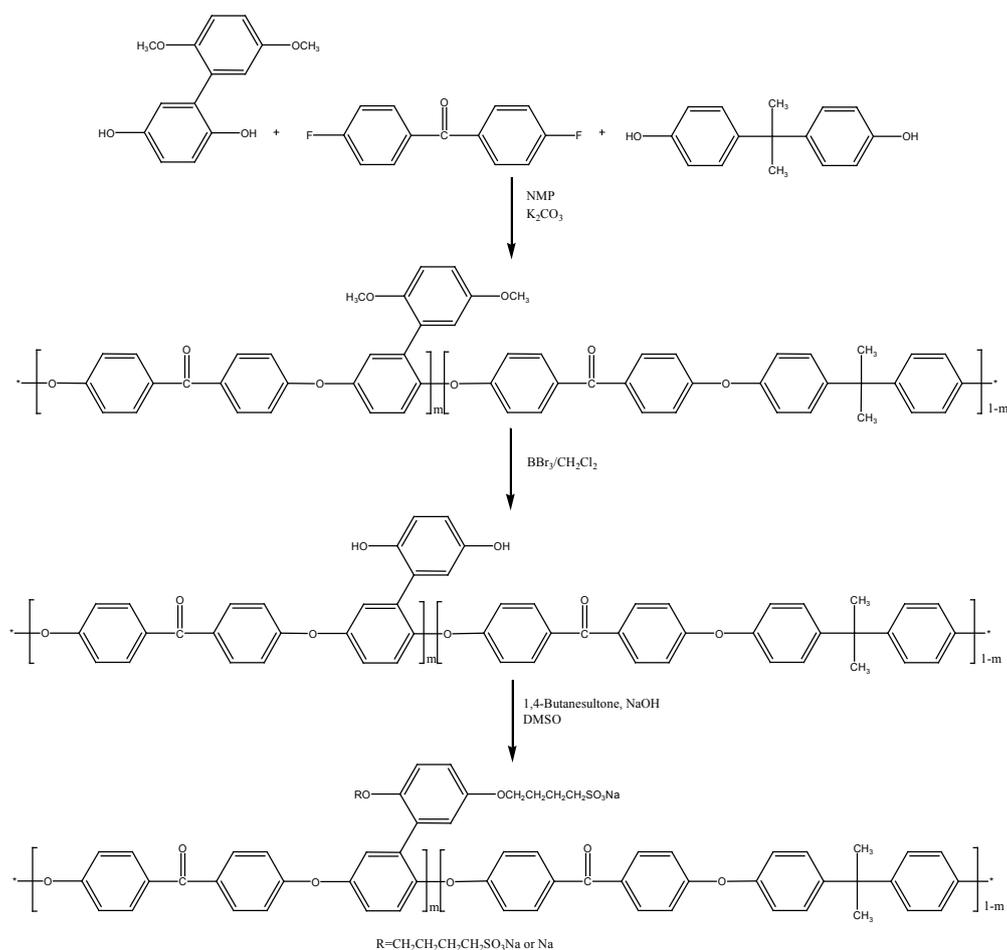


Scheme I.2.2.1. Sulfoalkylation of PSU.

Sulfoalkylated polysulfones kept their dimensional stability at high temperature (70-100°C) which probably depending on the DS. The measured proton conductivity of the membrane based on the polymer presenting 0.9 sulfopropyl pendant group per repeating unit, was 77 mS/cm at 70°C under humidifying conditions. The authors mentioned that the introduction of flexible, long sulfoalkyl side chains significantly improved the hydrophilic-hydrophobic domain separation, which enhanced proton conductivity. The effect of the length of the sulfoalkyl spacers has not been investigated.

Another way to attach sulfonated alkyl side groups onto a polymer chain was developed by Xing and coworkers[21]. They have synthesized novel naphthalene-based poly(arylene ether ketone)s copolymers containing methoxy groups. In a second step, the methoxy groups were converted to reactive hydroxy groups which were then reacted with 1,4-butane sultone, giving a copolymer bearing aliphatic sulfonic acid groups. The IEC (0.99-1.82 mequiv/g) of the SNPAEKs was readily controlled by using different -OH content in the copolymers. The proton conductivity for the IEC 1.82 meq H⁺/g was 179 mS/cm at 80°C. Resulting membranes displayed a methanol permeability in the range of 3.42×10^{-8} - 4.49×10^{-7} cm²/s, which is much lower than the Nafion membrane. The well controlled nanophase separated membrane morphology was confirmed by TEM analysis.

The same synthetic route was chosen by Na et al.[22, 23]. They worked on the post-sulfonation of polymers based on monomers bearing one[22] or two[23] methoxy groups (Scheme 1.2.2.2). For the polymer having the higher IEC=1.42 mequiv/g and prepared from the polymer with two hydroxy groups per repeat unit, an ionic conductivity of 123 mS/cm at 80°C was measured. It is worth to notice that a sulfonated polymer with an higher IEC of 1.54 mequiv/g prepared from the polymer having one hydroxyl group per repeat unit shows a lower ionic conductivity measured in the same conditions (83 mS/cm).



Scheme 1.2.2.2. Synthesis of side-chain-type SPAEK copolymer.

Novel main-chain-type and side-chain-type sulfonated poly(ether ether ketone)s (MS-SPEEKs) were synthesized by Lin et al.[24]. Their studies were focused on the post-aromatic substitution reaction of PEEK. The first reaction was a sulfonation with concentrated sulphuric acid of PEEK, followed by the reaction of the sulfonic acid groups with 1,1'-carbonyldiimidazole and then with the 2-aminoethane sulfonic acid (Fig. 1.2.2.3). Flexible and tough membranes with reasonable thermal properties were obtained. TEM analysis showed that introduction of side-chain-type sulphonic acid groups allowed for the formation of well-defined nanophase separated morphology. The single-cell performance results, obtained at 70°C showed a maximum power density and open-circuit voltage of 142 mW cm² and 0.79 V. Results were significantly better than values generated with Nafion 117. This result evidently indicates that the introduction of sulfonated pendant side chain considerably decreased the

rate of methanol crossover in DMFCs. However, the proton conductivity only reached 0.031-0.099 S/cm, which was lower than that of Nafion.

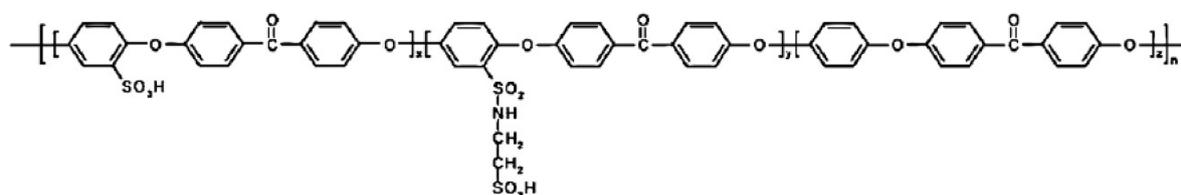


Figure 1.2.2.3. Sulfonated poly(ether ether ketone)s MS-SPEEK.

Another design of polymer based on the introduction of locally and densely sulfonated side chains into the aromatic polymer backbone was explored to enhance PEM performance. The idea is to improve the sulfonated and non sulfonated domain separation. From this concept, it was expected to get well-defined nano-phase-separated polymer structures and accordingly improve its proton conductivity. Hay and coworkers[25, 26] reported the synthesis of linear poly(sulfide ketone)s and branches poly(ether ketone)s containing clusters of six sulfonic acid moieties situated on the chain ends by regio selective postsulfonation. Polymers bearing clusters possessed good microphase-separated morphology. However, a drawback of this polymer architecture is the difficulty to increase the IEC of the polymers because the sulfonated groups are only located on chain ends. To overcome this problem many researches focused on copolymers bearing clusters in main chain. Guiver[27] proposed synthesis of a fluorene-based bisphenol monomer and of corresponding sulfonated poly(arylene ether sulfone) copolymers containing clusters of four butylsulfonic acid units per repeat unit along the main chain (Fig. 1.2.2.4). The poly(arylene ether sulfone)s copolymers containing methoxy groups were synthesized by polycondensation. The methoxy groups were then replaced by sulfonated chains using following procedure described by Xing[21]. These copolymers had a high proton conductivity ranging from 0.061 to 0.209 S/cm at 30°C and from 0.146 to 0.365 s/cm at 80°C, respectively. The methanol permabilities of these membranes were in the range of 3.22 to 13.1 x 10⁻⁷ cm²/s, which is lower than Nafion. The studies showed that the flexible nature of the hydrophilic sulfonated aliphatic side-chain had a helpful effect on the proton transport. The membranes exhibited high proton conductivity and very low water uptake. The

fluorene-based SPAES bearing clustered flexible pendant aliphatic sulfonic acid groups showed much better properties comparison with some reported sulfonated poly(arylene ether sulfone)s containing pendant sulfophenyl groups.

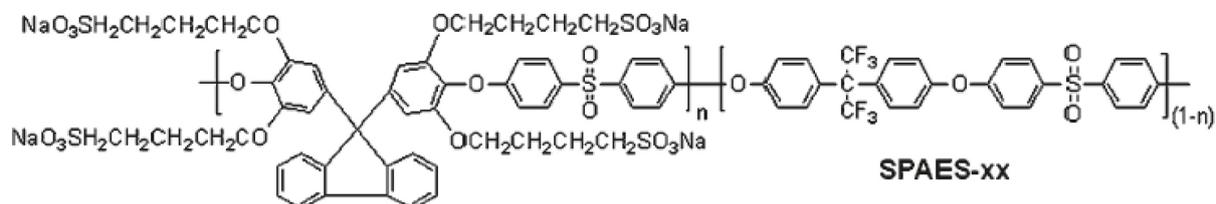


Figure 1.2.2.4. Fluorene-based poly(arylene ether sulfone)s containing clustered flexible pendant sulfonic acid.

1.2.3. Sulfonated copolymers containing perfluoroalkyl side chains

Another approach explored to improve the proton conductivity of aromatic PEMs is the introduction of perfluoroalkyl sulfonic acids into the main polymer chain. It is widely assumed that high conductivity results from perfluoroalkyl sulfonic acid acting as super acid. In this way, Ghassemi et al.[28] have shown that poly(arylene ether)s with pendant sulfonated perfluoroalkyl chains (Fig. 1.2.3.1) emphatically improve proton conductivity. To prepare these polymers they first lithiated a poly(arylene ether) and then reacted with the 4-(sulfonylfluoride)perfluorobutyryl fluoride. PSU-PSA with different IEC were obtained. A proton conductivity value of 0.091 S/cm was obtained for the of PSU-PSA with an IEC of 1.12 meq H⁺/g, at 80°C and under 100% relative humidity. On the other hand, it was observed that PSU-PSA membranes display relatively high water absorption. To account of this different behavior, it was suggested by the authors that the presence of perfluoroalkyl spacers in PPSU-PSA which provide higher mobility for acid sulfonic acid groups as well as more free volume between the packed polymer chains play a major role. A specific microphase separation in the PSU-PSA membranes was also considered to explain these results.

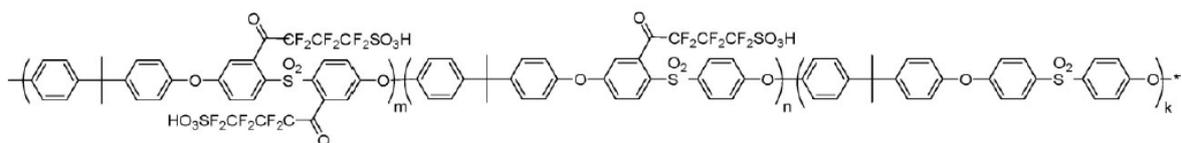
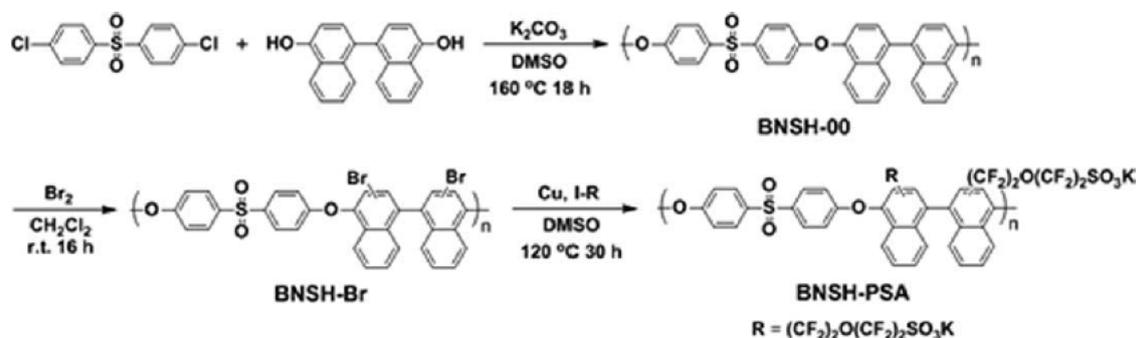


Figure I.2.3.1. Chemical structure of PSU-PSA polymers.

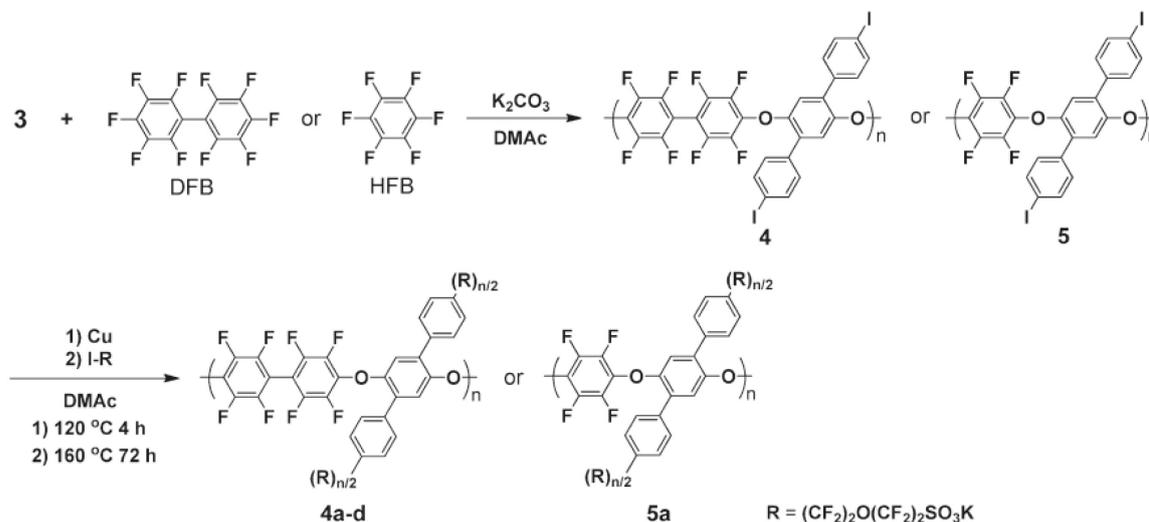
Recently, Ueda et al.[29] have also synthesized aromatic polymers bearing perfluoroalkyl sulfonic acid side chains. They also obtain much higher proton conductivity in comparison with the corresponding sulfonated aromatic polymers. Because of well-controlled morphology, their strong acidity contributes to the effective proton concentration and proton mobility, thus leading to high proton conductivity in sulfonated perfluoropolymers membrane[30]. Poly(arylene ether)s with pendant sulfonated perfluoroalkyl groups have been reported by Iwasaki[31] and Ueda[32] (Scheme I.2.3.1). They have worked on the post-modification of poly(arylene ether)s by halogenation with bromine and then Ullman coupling reaction with potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethanesulfonate. A proton conductivity of 0.12 S/cm at 80°C under 90% relative humidity was obtained with a membrane based on a PES-PSA with an IEC of 1.58 mequiv/g.



Scheme I.2.3.1. Synthesis of poly(ether sulfone) containing binaphthyl units with pendant perfluoroalkyl sulfonic acids (BNSH-PSA).

To gain better control of perfluoroalkyl sulfonic acid groups grafted on the polymer chain. Watanabe[33] and Ueda[29] have chosen a slightly different approach which consist first on the polymerization of halogenated monomer and then carried the Ullman coupling reaction. As a result Ueda have obtained perfluoropolymers with well-controlled substitution of

sulfonated perfluoroalkyl groups (Scheme 1.2.3.2). Resulting membranes displayed a low water uptake and a high proton conductivity of 3.3×10^{-3} S/cm, for IEC value (1.83 mequiv/g) at 30% RH. Watanabe showed that the degree of perfluorosulfonation was controlled up to 92%, which corresponds to an ion exchange capacity of 1.52 meq/g.



Scheme 1.2.3.2. Synthesis of poly(phenylene ether)s containing pendant perfluoroalkyl sulfonic acids.

Good fuel cell performance was obtained at high relative humidity (78 and 100% RH). The ionomer membranes exhibited a characteristic hydrophilic/hydrophobic phase separation morphology with small interconnected hydrophilic clusters.

I.3. Synthesis of sulfonated copolymers from monomers containing side chains

As before mentioned the second synthesis method of sulfonated copolymers bearing pendant side chains can be obtained by polymerization of monomers containing functional groups, (i.e. sulfonic acid groups). This approach gives a way to control the polymer structure and degree of sulfonation (DS) well as the cost of risking the occurrence of side reactions or degradations. In spite of the risk, many scientists still use this method.

I.3.1. Synthesis of sulfonated copolymers from monomers containing sulfonated aromatic side chains

Guiver and coworkers[34, 35] have worked on the synthesis poly(arylene ether) from benzophenone based monomers containing an aryl sulfonic acid pendant group as illustrated Figure I.3.1.1. By adjusting the feed ratios of sulfonated and nonsulfonated monomers, series of polymers were prepared which exhibit reduced dimensional swelling and good proton conductivities. For example, the polymer with an IEC of 1.52 meq/g has proton conductivity of 0.12 S/cm and a water swelling of only 26% at 100°C. It was suggested that the good proton transport ability of these polymers is related with a hydrophobic/hydrophilic phase separation morphology as evidenced by TEM.

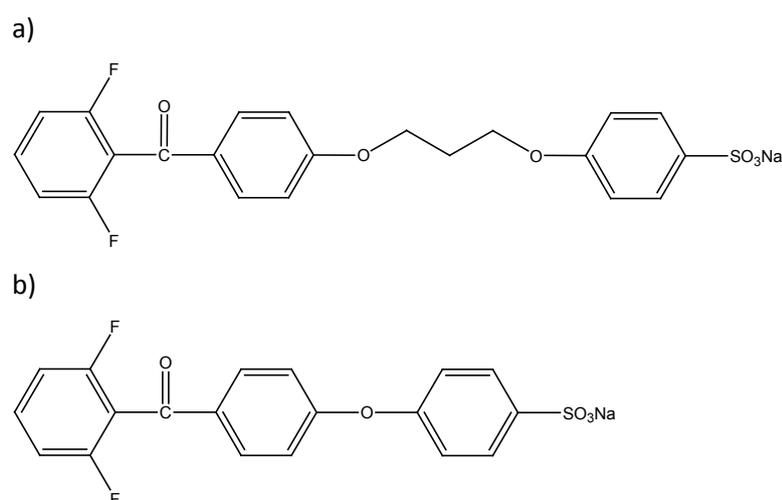
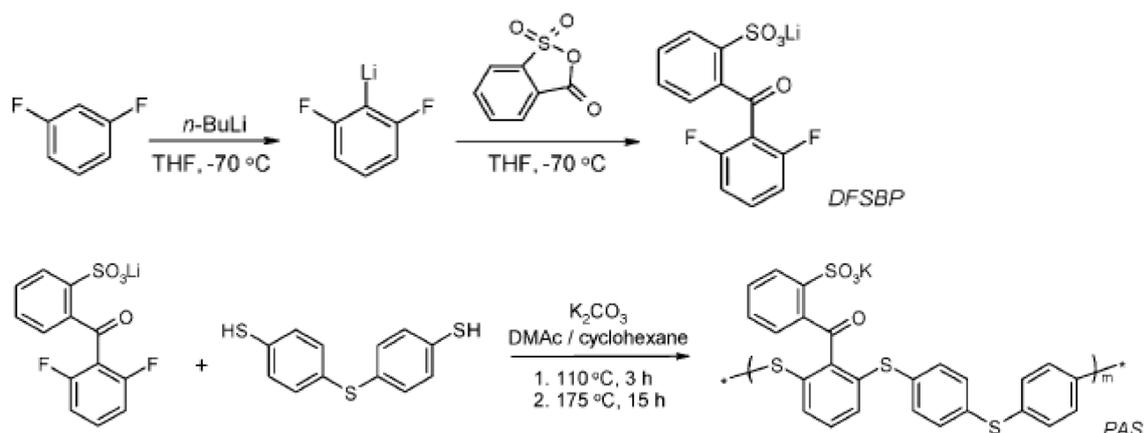


Figure I.3.1.1. Monomers containing aliphatic or aromatic side chains (a) sodium 4-(3-(4-(2,6-difluorobenzoyl)phenoxy)propoxy)benzenesulfonate, b) sodium 4-(4-(2,6-difluorobenzoyl)phenoxy)benzenesulfonate).

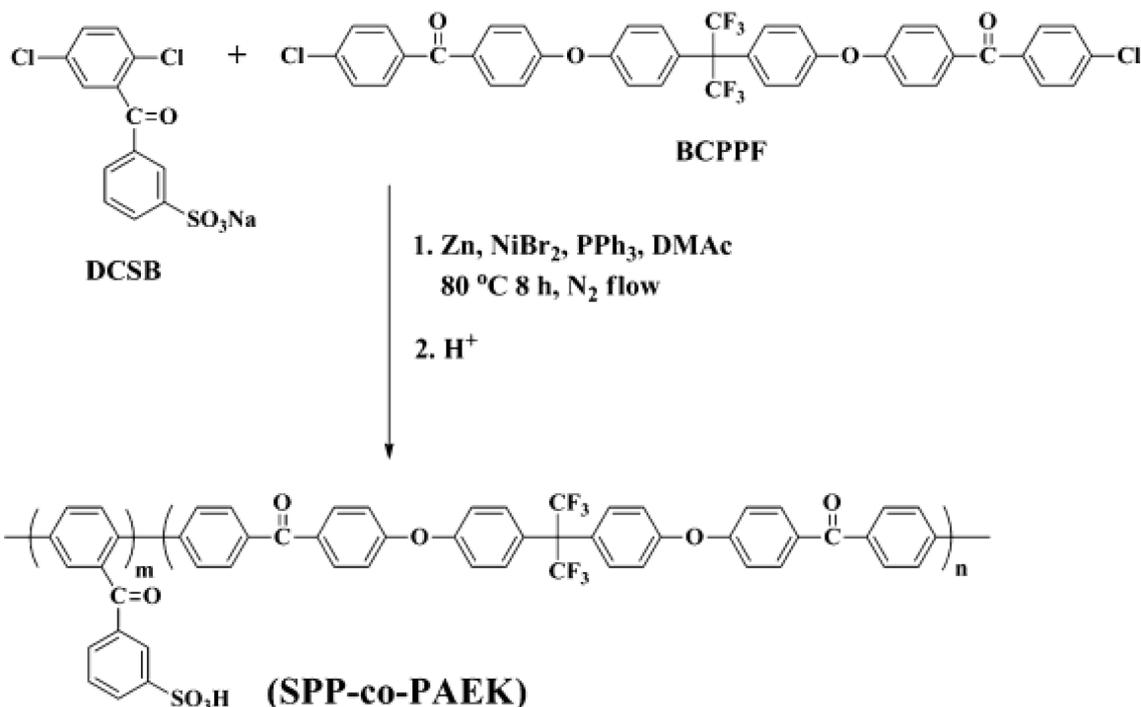
Jannasch et al.[36, 37] presented another synthesis of both high molecular weight poly(arylene ether) and poly(arylene sulfide) with sulfonobenzoyl side groups. A monomer, lithium salt of 2,6-difluoro-2'-sulfobenzophenone (DFSBP) was synthesized in one pot by reacting 2,6-difluorophenyllithium with 2-sulfobenzoyl cyclic anhydride (see Scheme I.3.1.1).



Scheme I.3.1.1. Synthesis way of DFSBP monomer and the subsequent polycondensation reaction to prepare the PAS.

Conductivities of poly(arylene sulfide) based membranes varied between 0.02 and 0.2 S/cm at 80°C exceeding the conductivities of Nafion measured in the same conditions.

Using Ni(0)-catalyzed coupling reaction rod-like polyparaphenylenes bearing sulfobenzoyl side groups[38] were prepared from 2,5-dichloro-3'-sulfobenzophenone monomer (Scheme I.3.1.2). The resulting membranes displayed comparable proton conductivities of Nafion 112. Fuel cell test involving the membrane based on SPP-co-PAEK(3/1) with IEC of 2.0 meq/g has given rather good results: an open circuit voltage (OCV) of 0.94 V, cell voltage at current density of 1.0 A cm² (V1.0) of 0.61 V, and output at 1.7 A cm² of 0.85 W cm² under 90°C, 82/68% RH condition (H₂/air).



Scheme I.3.1.2. Synthesis of SPP-co-PAEK copolymers via Ni mediated polycondensation reaction.

The synthesis of sulfonated aromatic side chain containing polyimides was also addressed using functionalized diamine monomer. Fan et al.[39] have designed a such diamine: 5-[1,1-bis(4-aminophenyl)-2,2,2-trifluoroethyl]-2-(4-sulfophenoxy)benzenesulfonic acid (BABSA) (Fig. I.3.1.2). This diamine was synthesized via a three-step reaction. Series of copolyimides with different extent of sulfonic acid groups were prepared by polycondensation of BABSA with different non sulfonated diamines and naphthalenic-type dianhydride monomers (NTDA or BNTDA). Tough and self supporting membranes were manufactured from these sulfonated polyimides. A good water stability of these membranes was observed in keeping them in boiling water for more than 100 hours. A fairly good oxydative stability of membranes was also observed in Featon test conditions. Proton conductivities of 0.18-0.22 S/cm at 80°C were obtained. All the synthesized SPIs showed good film forming properties. Hydrophobic/hydrophilic phase separation morphology of membranes was evidenced by TEM. In this connection, it was observed that the average size of hydrophilic domains was depending of the structure of the dianhydride monomer.

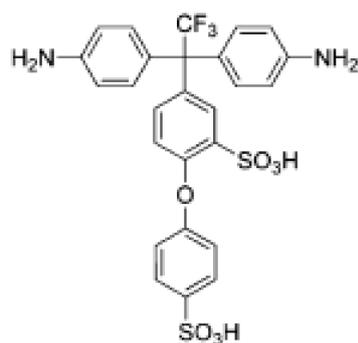


Figure I.3.1.2. Structure of sulfonated aromatic diamine BBSA.

I.3.2. Synthesis of sulfonated copolymers from monomers containing sulfonated aliphatic side chains

The incorporation of sulfonated alkyl side chains along a polymer chain from a functional monomer has been investigated. Jiang et al.[40-42] have succeeded in the preparation of different sulfonated poly(arylene ether)s from the sulfonated monomer, e.g. sodium 3-(4-(2,6-difluorobenzoyl)phenyl)propane-1-sulfonate. These copolymers display good thermal-oxidative and dimensional stability. Despite the presence of the flexible alkyl chains, the polymers have a high T_g up to 200°C. Moderate water absorption was observed even at temperature as high as 100°C. A water swelling of only 12.9% at 100°C for a polymer with an IEC 1.3 mequiv/g was determined. Low temperature dependence of ionic conductivities was established for these membranes, in the temperature range 30-100°C. Noteworthy the lower methanol permeability of these membranes compare to Nafion 117 that can be of interest for the direct methanol fuel cell. Nano phase separation morphology of membranes was evidenced by TEM and as expected higher the degree of sulfonation of polymers, larger are the ionic domains.

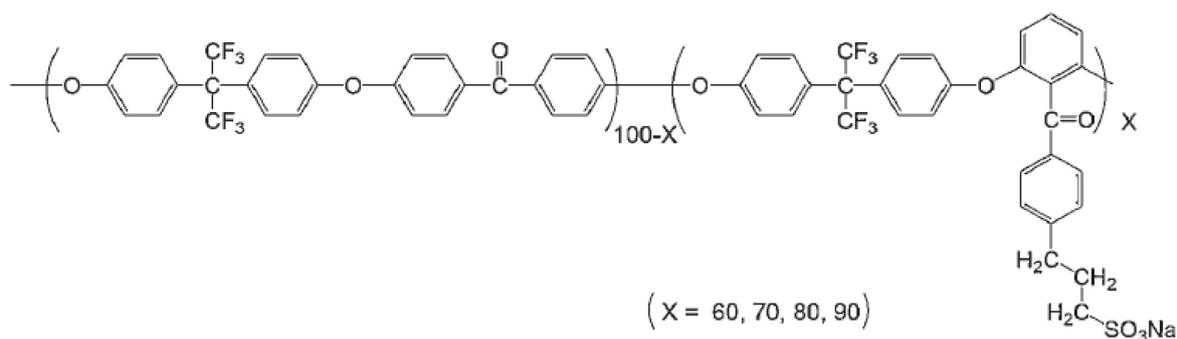


Figure I.3.2.1. Synthesis of poly(arylene ether)s with pendant sulfoalkyl groups.

To attach a sulfonated alkyl side group on the chemical structure of monomers, many researchers concentrated their work on the synthesis of novel monomers using 1,3-propane sultone (Fig. I.3.2.2).

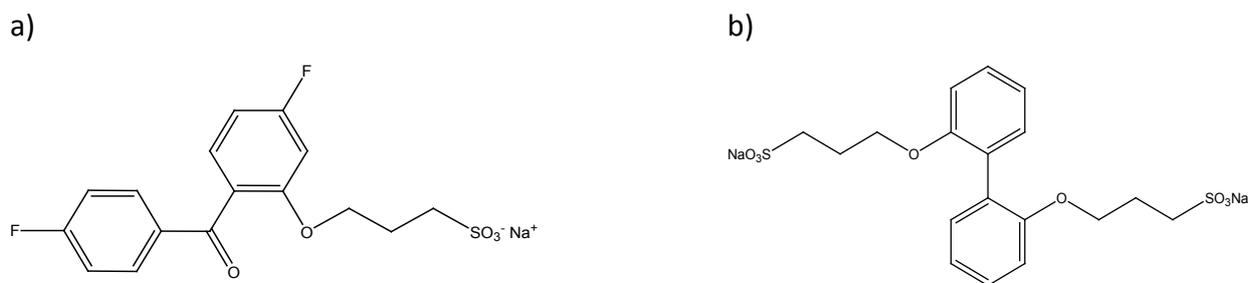


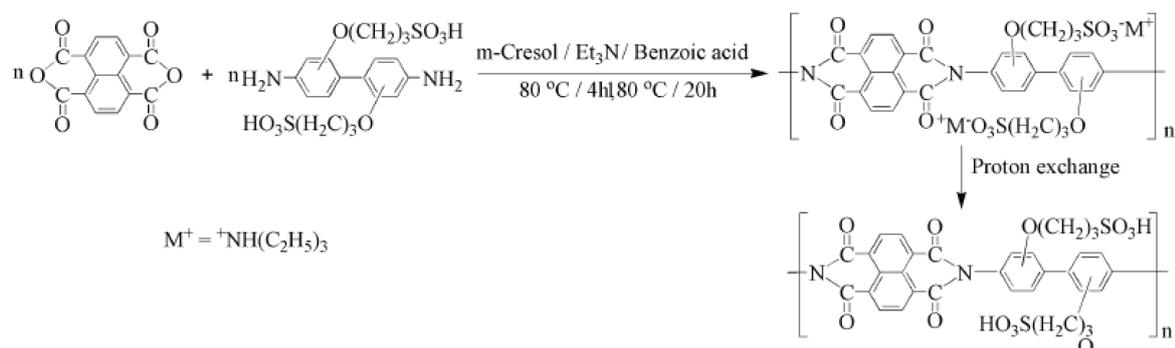
Figure I.3.2.2. Sulfonated monomers synthesized by grafting 1,3-propane sultone.

Prasad et al.[43] have successfully synthesized monomer with sulfonic acid groups in the alkyl pendant side chain (see Figure I.3.2.2 (a)) using propane sultone as sulfoalkylation reagent. This monomer along with the difluorobenzophenone were reacted with bisphenol A via a nucleophilic substitution reaction to obtain sulfonated poly(ether ether ketone)s. Unfortunately, any membranes characterizations were done due to their high brittleness which was accounted for by the too low molecular weights of polymers. All membranes prepared were brittle.

Xu et al.[44] have also prepared an original sulfonated monomer by reacting the monomer 2,2'-dihydroxybiphenyl with 1,3-propanesultone. Using the acid-catalyzed condensation of ketones with aromatic compounds (aromatic dicarboxylic acid precursors), known as hydroxyalkylation, they prepared high molecular weight poly(ether ketone)s with sulfonated

alkyl side chains. Membranes with good mechanical properties in hydrated state were obtained. Higher ionic conductivity than Nafion 115 was obtained at 25°C and 100% of RH for the membrane manufactured with the polymer having an IEC of 1.84 meqev/g. AFM characterization of membranes shown phase separation morphology with ionic cluster size about 5-15 nm.

The design of sulfonated polyimides from monomers bearing sulfonated alkyl side groups has been also addressed. For example, Okamoto et al.[45] have worked on the synthesis of polyimides (SPIs) containing pendant sulfoalkoxy groups (Scheme I.3.2.1). They found that this type of sulfonated PIs exhibited higher or similar-proton conductivities to those of Nafion 117 at RH up to 70%. These polymers display also a better water stability than the sulfonated polyimides with the sulfonic acid groups directly grafted on the polymer backbone. Based on TEM analysis showing a microphase-separated structure, it was suggested that the hydrophilic domains contain the sulfo alkoxy side chains while the hydrophobic domains contains mainly the polyimide chains.



Scheme I.3.2.1. Synthesis of highly sulfonated polyimides from bis(3-sulfopropoxy)benzidine diamines.

I.4. Sulfonated block polymers

Over the past decade, many effort have been done to improve the mechanical stability of membranes at the hydrated state as well as their proton conductivity at high temperature

($T > 100^\circ\text{C}$) and low relative humidity ($\text{RH} < 50\%$). In this connection, the concept of ion-containing block has attracted great attention[46-49], because these polymers can lead to well-defined nanostructures where the morphology and domain size are tunable on the nanoscopic length scale. These copolymers and specially those having one of the blocks sulfonated can display a highly ordered morphology where one of the domains contains the sulfonated blocks and facilitates proton transport while the other containing the non-sulfonated blocks contributes to the mechanical strength of the membrane. A number of recent studies have demonstrated significant enhancement in proton conductivity by sulfonated block copolymers compared to sulfonated random copolymers analogues. They have shown higher conductivities than Nafion across a wide range of temperatures and relative humidity[50, 51].

I.4.1. Post modification of block copolymers

Research efforts were devoted to the synthesis of sulfonated block copolymers using post-sulfonation method[52]. In general, the synthetic strategy consists on the synthesis of an oligomer which is subsequently sulfonated and then reacted with a non sulfonated oligomer. For example, Yoo[53] and coworkers using this synthetic scheme have obtained highly sulfonated poly(arylene biphenylsulfone ketone) block copolymers (Fig. I.4.1.1).

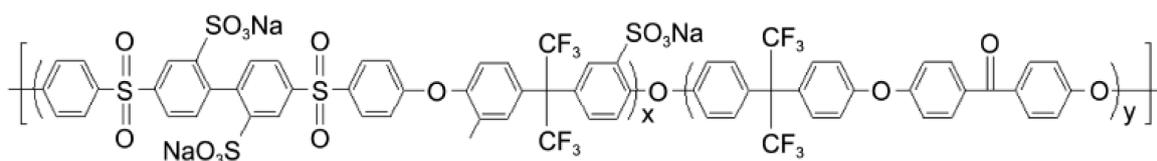


Figure I.4.1.1. Synthesis of sulfonated block copolymers via post-sulfonation by Yoo.

The resulting block copolymers showed good thermal stability and high oxidative stability. The ionic conductivities measured of these block copolymers were in the range of 15 to 80 mS/cm at 20°C and 100 % RH. The conductivities as a function of temperature (20°C to 60°C)

for the block copolymer with an IEC of 1.05 meq/g are similar and even better at 60°C than Nafion 115.

I.4.2. Synthesis of sulfonated block copolymers from sulfonated monomers

McGrath et al.[54, 55] have developed number aromatic block copolymers using the sulfonated diphenyl sulfone monomer with relevant structure (Fig. I.4.2.1). As illustrated in the Scheme I.4.2.1 these block-copolymers were synthesized by a coupling reaction involving two different telechelic oligomers one sulfonated and the other one non-sulfonated which were synthesized separately via nucleophilic aromatic substitution.

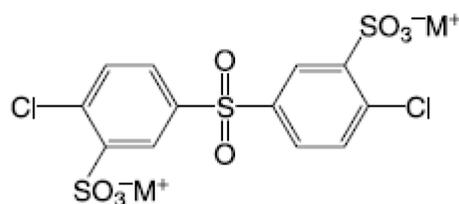
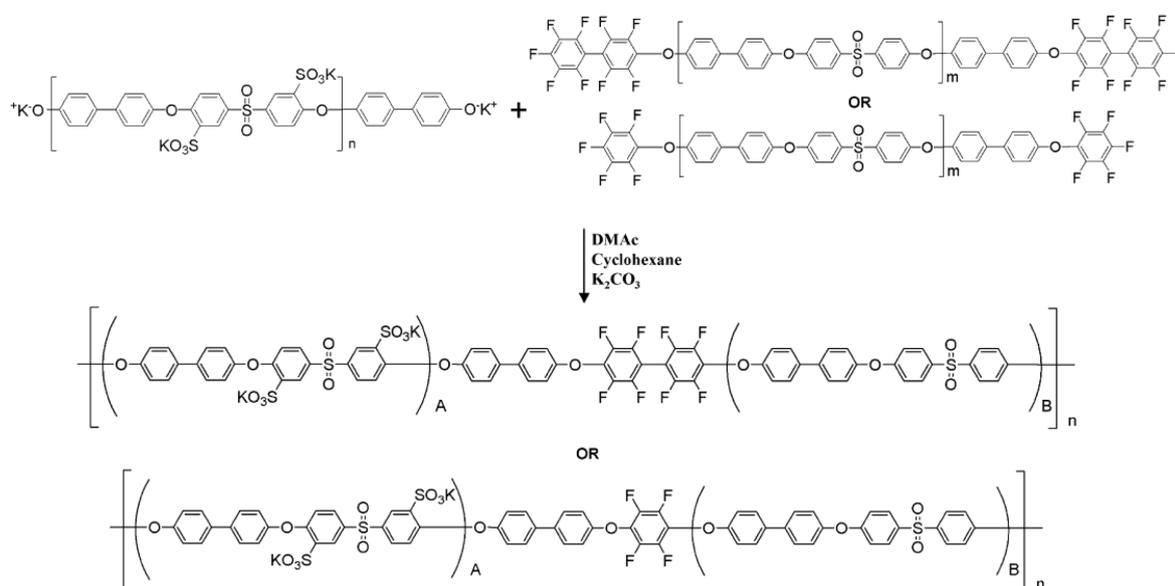


Figure I.4.2.1. Structure of 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS).



Scheme I.4.2.1. Synthesis of sulfonated poly(arylene ether) multi-block copolymers (BPSH-BPS).

The proton conductivities and water uptake of these block-copolymers were found to be highly dependent on the block length. Results were comparable or even higher than that of random copolymers with similar IECs. The multiblock copolymer membranes exhibited unique phase separated morphologies and permitted to significantly enhanced proton conductivities under partially hydrated state. Higher values of conductivity than Nafion 112 were obtained for the membranes prepared from the block-copolymers with IEC=1.83 meq/g and reached 0.160 S/cm at 30°C.

I.5. Synthesis of block copolymers containing sulfonated side chains

I.5.1. Block copolymers containing sulfonated aromatic side chains

Liu and coworkers[56] have worked on the synthesis of block copolymers bearing sulfonated methoxyphenyl side groups illustrated figure I.5.1.1. Initially, non-sulfonated block copolymers were prepared and then selectively sulfonated on the methoxyphenyl side groups. The membranes made from these copolymers exhibited good thermal and dimensional stability. The proton conductivities of membranes based on *S-m*-block1-50 (0.21 S/cm) and *S-m*-block2-50 (0.22 S/cm) were higher than Nafion up to 80°C. Comparing with Nafion 117, the block copolymers had much higher water uptake but a lower methanol permeability. The water uptake and proton transport of block copolymers increased with increasing sulfonated block length. It was also observed that the water uptake and the ionic conductivity of membranes based on the *m*-series polymers were higher than those based on *p*-series polymers.

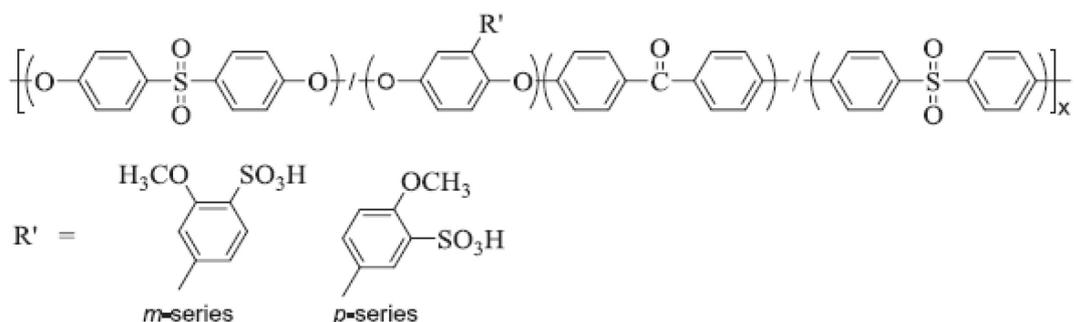


Figure I.5.1.1. Sulfonated poly(ether ether ketone)-block-poly(ether sulfone)s.

McGrath et al.[57] have work on the design of block copolymers of sulfonated poly(4'-phenyl-2,5-benzophenone) copoly(arylene ether sulfone). Difluoro end-capped poly(4'-phenyl-2,5-benzophenone)s oligomers were first synthesized from 2,5-dichloro-4'-phenylbenzophenone and 4-chloro-4'-fluorobenzophenone via Ni(0) mediated coupling reaction (Fig. I.5.1.2). Post sulfonation was then performed to selectively grafted sulfonic acid groups on the biphenyl side groups. On the other hand, dihydroxy telechelic polysulfone oligomers were prepared and then reacted with the sulfonated oligomers. Although self supporting and tough membranes were obtained, very limited data relative their properties were reported. Only ionic conductivity values at 30°C and 100% RH and lower than that of Nafion were mentioned.

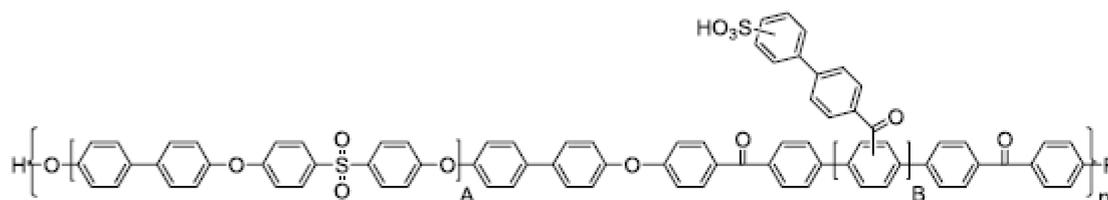


Figure I.5.1.2. Sulfonated multiblock copolymers.

More recently, Guiver et al.[58] have addressed the synthesis of densely sulfonated block copoly(arylene ether sulfone)s with pendant phenylsulfonic acid groups. The copolymers were prepared by the coupling reaction of corresponding hydroxyl-terminated pendent-phenyl oligomers with bis(4-hydroxyphenyl)sulfone (BHPS) and decafluorobiphenyl (DFBP),

followed by a selective sulfonation reaction of the pendant phenyl groups to yield highly sulfonated blocks (Fig. I.5.1.3). The resulting polymers gave membranes with good proton conductivities comparable to that of Nafion. For example the membrane with IEC=1.82 mequiv/g had a proton conductivity of 3.6×10^{-2} S/cm at 80°C and 50% RH. It was observed that the block copolymer showed higher tensile strength and lower elongation at break than Nafion. Some impacts of block length on the mechanical properties were established with the general trend of lower Young's modulus for polymers with longer sulfonated block length. Based on AFM investigation, it was considered that membranes displayed clear hydrophilic/hydrophobic phase separation morphology with interconnected hydrophilic clusters.



Figure I.5.1.3. Segment sulfonated copolymer.

Similarly to Guiver approach and afore mentioned, Miyatake et al.[59] reported the synthesis of sulfonated block poly(arylene ether)s (SPEs). The choice of the chemical composition of each block in the parent polymers was done to allow a selective sulfonation of the block containing fluorenyl groups. Sulfonation of polymers was performed using chlorosulfonic acid. Sulfonated polymers with a IEC ranging from 1.2 to 2.2 mequiv/g were prepared. As expected, membranes containing high IEC absorbed more water, have higher proton conductivity. As observed by many other research laboratories, these block copolymers showed much higher proton conductivity than the random one. Miyatake et al.[60-62] have also worked on the design of block sulfonated poly(arylene ether)s having a similar highly sulfonated block (Fig. I.5.1.4) with different hydrophobic blocks. It was shown that high local concentration of sulfonic acid groups within the hydrophilic blocks enhanced phase separation between the hydrophilic and hydrophobic blocks which resulted in high proton conductivity even at low RH. For the membrane with IEC=1.86 mequiv/g, high proton

conductivities in the range of 0.13 and 0.03 S/cm at 80% and 40% RH, respectively and at 80°C were obtained.

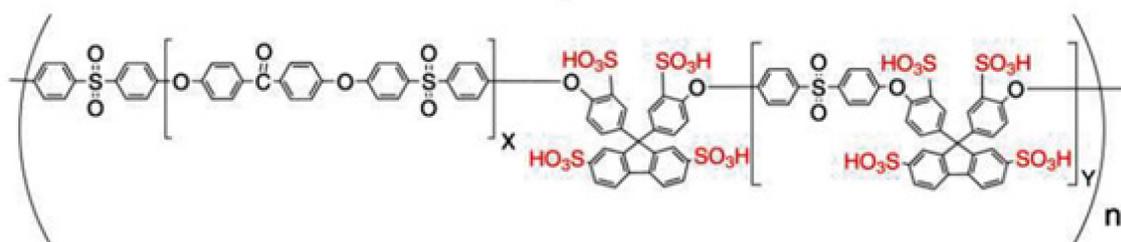


Figure I.5.1.4. Sulfonated poly(arylene ether sulfone ketone) multiblock copolymer having highly sulfonated hydrophilic block.

It was also observed that the incorporation of rigid naphthalene units into the hydrophobic poly(ether sulfone) blocks was effective in improving nano-phase separation and then the ionic conductivity of membranes. As it can be seen in Figure I.5.1.5, the block copolymer (5b X15Y4) with an IEC of 2.01 mequiv/g shows comparable ionic conductivity to Nafion in the range of 40 to 90 % of RH at 80°C.

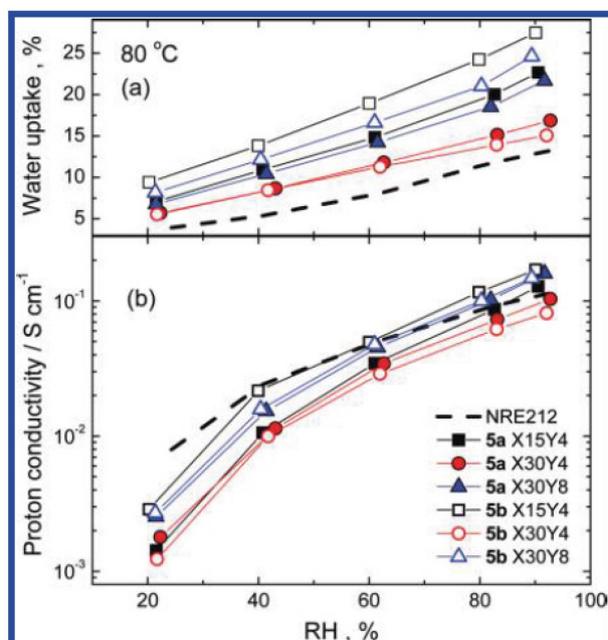


Figure I.5.1.5. a) Water uptake and b) in-plane proton conductivity of NRE 212 and 5a, sulfonated block copolymers with hydrophobic block containing biphenyl units, 5b sulfonated block copolymers with hydrophobic blocks containing naphthalene units.

Kim et al.[63] reported the synthesis of multi-sulfonated block copolymers (MSBPs) using the selective post sulfonation method. As illustrated in Figure I.5.1.6, the sulfonic acid groups were concerning only the multi phenyl substituted monomers. The resulting membranes showed IECs from 0.79 to 1.87 mmol/g, water uptake from 14.8 to 90.8%, and proton conductivity from 65.7 to 131.1 mS/cm.

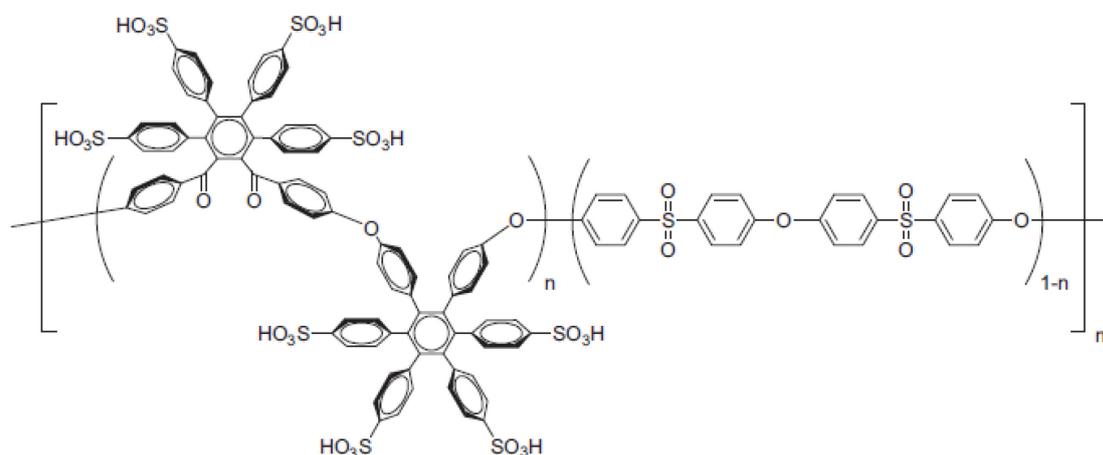


Figure I.5.1.6. Structure of MSBP copolymer.

Fuel cell tests were performed for different MSBP membranes (see Figure I.5.1.7). Similar power density to Nafion were obtained with the membranes based on MSBP 10 and MSBP-14 which have an IEC of 1.52 and 1.87 mequiv/g, respectively.

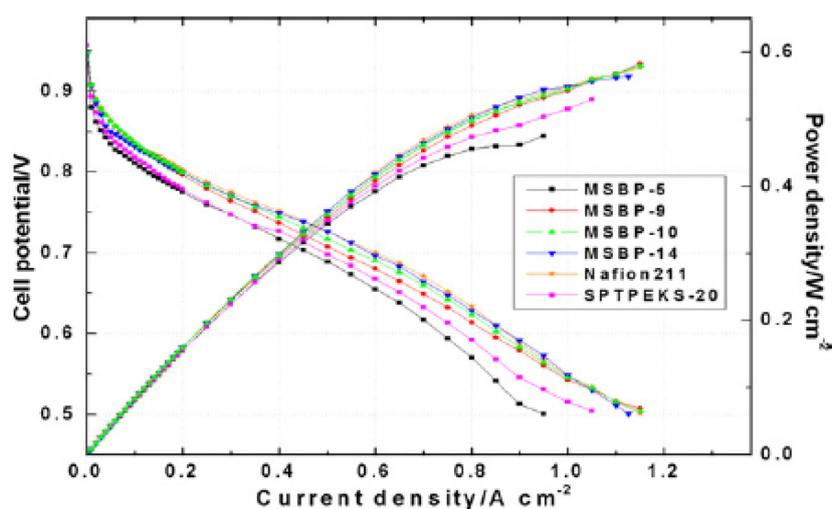
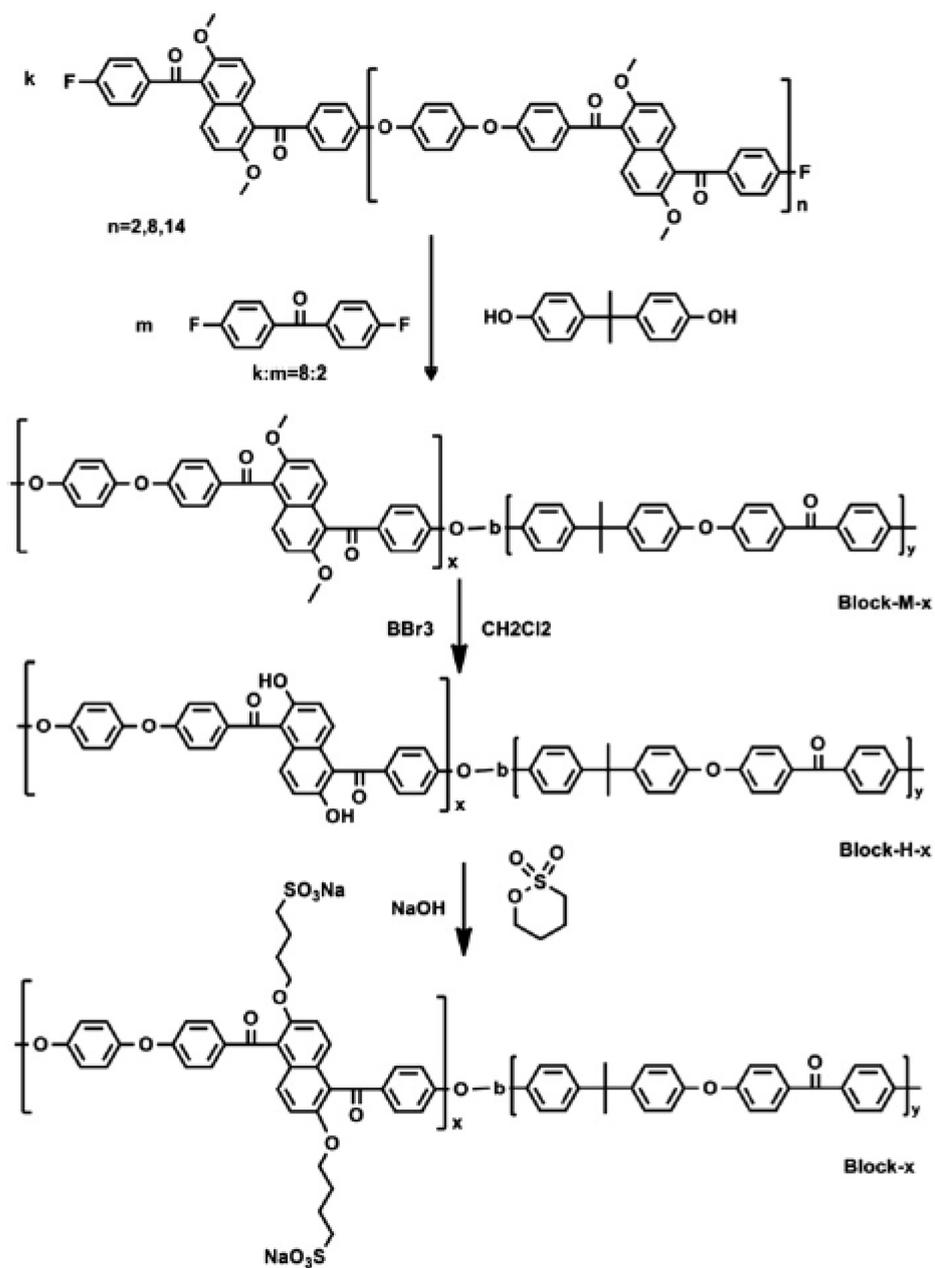


Figure I.5.1.7. Polarization curves of different MSBPs and Nafion 211 under fully humidified hydrogen and air condition at 70°C.

It was also observed that the fuel cell performance of MSBP membrane was better than that based on the random copolymer (SPTEKS-20) with the same IEC.

I.5.2. Sulfonated block copolymers containing aliphatic side chains

The design of sulfonated block aromatic polymers with sulfonated alkyl side chains was also addressed. For example, Zhang et al.[64] have developed block poly(arylene ether ketone)s containing sulfonated aliphatic side chain groups. To graft the sulfonated side chains, the synthetic route involves two successive post modifications of parent poly(arylene ether ketone)s (Scheme I.5.2.1). The first one was to cut the methoxy groups to generate phenol reactive groups which were further reacted with sulfone. A series of sulfonated polymers were prepared with an IEC up to 2.11 mequiv/g. Better mechanical properties as well as ionic conductivities than that of random copolymer were obtained.

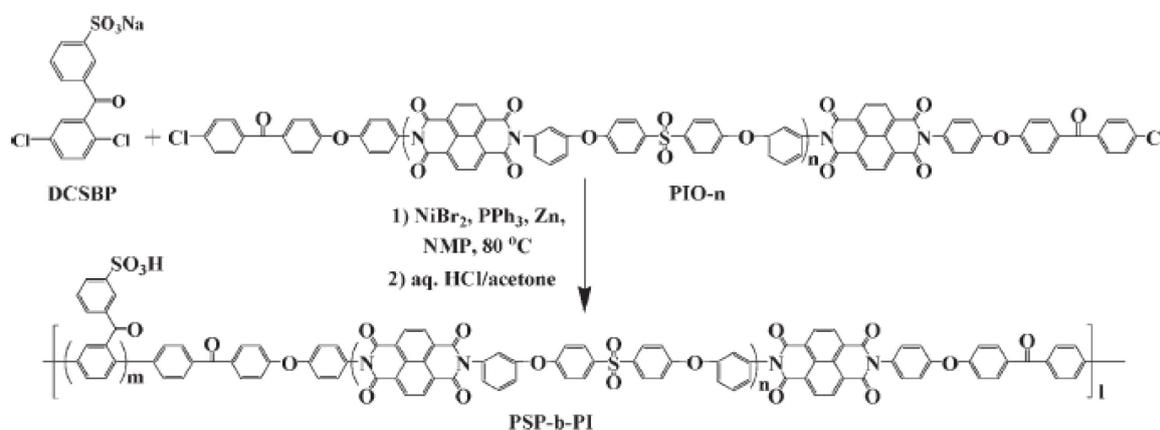


Scheme 1.5.2.1. Synthesis of block sulfonated poly(arylene ether ketone)s.

I.6. Synthesis of sulfonated block copolymers from monomers containing side chains

I.6.1. From sulfonated aromatic side chains monomers

One typical example of sulfonated block aromatic copolymer synthesized from sulfonated aromatic side chain monomer is the research work achieved by Okamoto et al.[65]. They prepared multi-block poly(sulfonated phenylene)-block-copolyimides obtained by Ni(0)-catalyzed copolymerization of 2,5-dichloro-3'-sulfo benzophenone and dichloro-terminated naphthalimide oligomers (see Scheme I.6.1.1). The membranes based on these polymers exhibited a well microphase separated structure a good hydrolytic stability even at 130°C. On the other hand, it was observed that the membranes had fairly good through plane conductivity in water and also at low RH. Fuel cell tests at 90°C gave good results with the membrane manufactured from the copolymer with an IEC of 1.5 mequiv/g and power density up to 0.8 Watt/cm². This performance was accounted by the high through plane conductivity.



Scheme I.6.1.1. Synthesis of PSP-b-PI copolymers.

By using the same synthetic approach Okamoto et al.[66] have synthesized poly(tri-sulfonated phenylene)-*block*-poly(arylene ether sulfone). In this case a tri-sulfonated benzophenone monomer namely the 2,5-dichloro-3'-sulfo-4'-((2,4-disulfo)phenoxy)-benzophenone was used. It was observed that the membranes based on these polymers

display a well defined microphase separated structure with hydrophilic domains well connected each other. Fuel cell tests have shown better performances of the membranes based on those sulfonated block copolymers than that of Nafion 112 specially at high current density and at low RH i.e. 30%.

I.6.2. From monomers bearing sulfonated aliphatic side chains

Watanabe et al.[67-69] worked on the synthesis of random copolymers containing aliphatic segments and aromatic ionomers containing sulfonated aliphatic side chain. They reported that incorporating aliphatic segments significantly improves the hydrolytic stability of polyimide ionomers without sacrificing other favorable properties. Therefore, they used the same principle to synthesize block copolymers containing sulfonated aliphatic segments[70]. Watanabe has compared the properties of random and block copolymers. Obtained block polymers have the structure illustrated in Figure I.6.2.1. The corresponding membranes showed higher proton conductivity ($2.0 \times 10^{-2} \text{Scm}^{-1}$ at 48 RH) which is comparable to that of a conventional perfluorinated ionomer membrane. In general the block copolymer containing aliphatic main chain does not practically affect the thermal, hydrolytic, and oxidative stability of the SPI membranes.

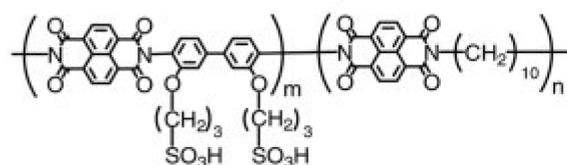


Figure I.6.2.1. Structure of the sulfonated polyimide block copolymer.

Kawakami et al.[71] have synthesized sulfonated block, graft, random-graft, and block-graft copolyimides from 1,4,5,8-naphthalene tetracarboxylic dianhydride, 3,5-diaminobenzoic acid and sulfonated monomer, 3,3'-bis(3-sulfo-propoxy)benzidine which was prepared using the same method reported by Watanabe et al.[68] (Fig. I.6.2.2). Block-graft copolyimide membranes has proton conductivity of 0.44 S cm^{-1} at 80°C and 98% RH which was 3 times

more than that of Nafion 117. It is well known that under low humidity conditions proton conductivity of sulfonated polyimide emphatically decreases. In this study the sulfonated polyimide membranes possess similar IEC values, although, the block-graft copolyimide showed much higher conductivity than those of other sulfonated copolyimides at low humidities. This means that polymer architecture has the main influence over its properties. The gas permeability of the sulfonated block polyimide was higher than that of Nafion, although, the oxygen permeability of the graft-type copolyimides membranes showed radically lower results ($3.2 \times 10^{-12} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ sec cmHg})$ at 35°C and 76 cmHg).

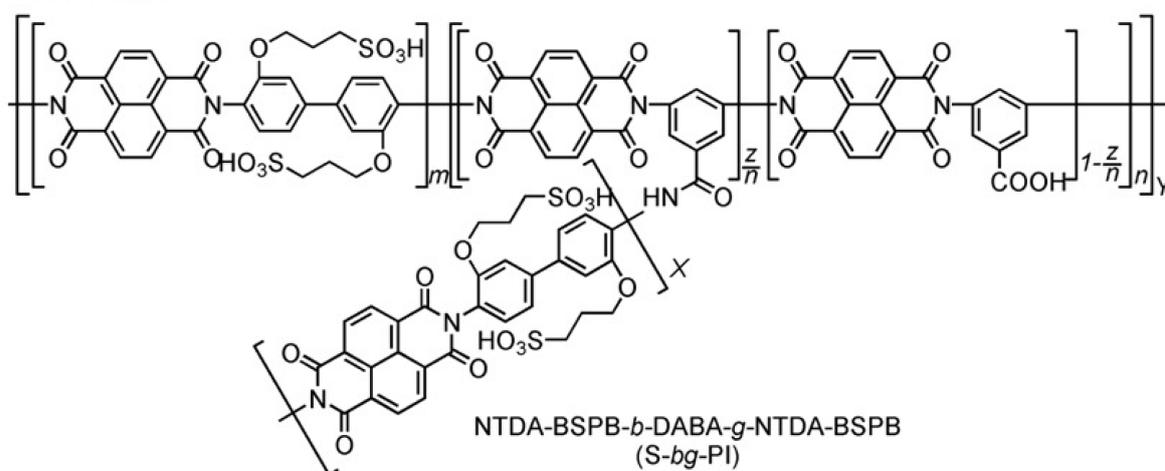


Figure I.6.2.2. Synthesis of the sulfonated block-graft copolyimide.

I.7. Conclusion

There is no doubt that extensive efforts have been made in recent years to develop less expensive and more efficient polymer electrolyte membranes for fuel cells. Sulfonated poly(arylene ether)s such as poly(sulfone) and PEEK have shown excellent chemical and thermal stability in fuel cell applications. However, aryl sulfonic acid groups usually cause lower proton conductivity than that of perfluorosulfonic acid membranes. The performance of ionomers membranes can be improved by introducing more sulfonic acid groups but it may cause large swelling. Study showed that introduction of perfluoroalkyl sulfonic acids in place of normal sulfonic acids highly improves the proton conductivity and the performance of PEMs.

However, postsulfonation of polymers can provide side reactions and does not allow control of the degree of sulfonation. Therefore, direct polymerization of sulfonated comonomers has drawn attention as a suitable method of controlling the chemical structure and content of functional groups.

Block copolymers showed that the morphology of polymers greatly affected membranes performance. Membranes with well-separated hydrophilic/hydrophobic phase are great materials for fuel cell applications. The blocky nature of the copolymer gives rise to improved proton conductivity without massive increase in water swelling. Block copolymers are promising materials which open the possibility to the synthesized polymers with excellent mechanical properties as well as thermal and chemical stability.

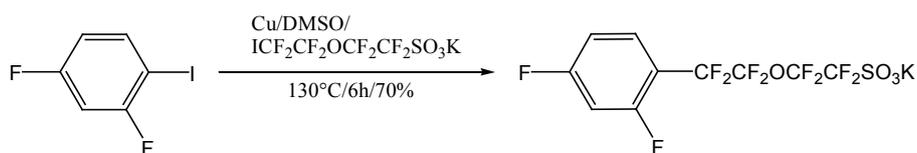
Chapter II. Synthesis of sulfonated poly(arylene ether)s

II.1. Introduction

La première approche qui a été envisagée pour obtenir des polymères aromatiques à chaînes latérales de type perfluoroalkyle sulfonée repose sur l'idée d'utiliser un monomère possédant un motif perfluoroalkyl sulfoné dont la position dans la structure du monomère favorise de par son caractère électro attracteur, la réaction de substitution nucléophile (S_NAr) classiquement utilisée pour la synthèse de poly aryl éthers. Le précurseur qui nous est apparu comme une solution allant dans le sens de cette idée, se présentait sous une forme structurale simple composée d'un noyau aromatique possédant deux atomes de fluor et une chaîne perfluoroalkyle sulfonée. A partir de ce précurseur dont la synthèse est décrite au paragraphe suivant, une étude modèle a été réalisée pour évaluer sa réactivité vis-à-vis d'agents nucléophiles de type phénolate. La synthèse de copolymères contenant différents taux de séquences perfluoroalkyl sulfonées a ensuite été abordée. La préparation de membranes auto portantes a pu être réalisée avec certains de ces polymères. La caractérisation des propriétés de ces membranes a ensuite été abordée comme le gonflement à l'eau et la conductivité ionique.

II.2. Synthesis of 1-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-2,4-difluorobenzene (FPSAB-K)

For the synthesis of this new sulfonated monomer, FPSAB-K a synthetic way was developed based on one step reaction as illustrated in Scheme II.2.1.



Scheme II.2.1. Synthesis of FPSAB-K.

The FPSAB-K was in fact prepared via an Ullmann type reaction involving the 2,4-difluoroiodobenzene (dFIB), a commercially available product and the potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (PSA-K). This later reagent was obtained by the hydrolysis of the purchased 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy) ethanesulfonate fluoride compound (PSA-F) in the presence of 2,4-lutidine and

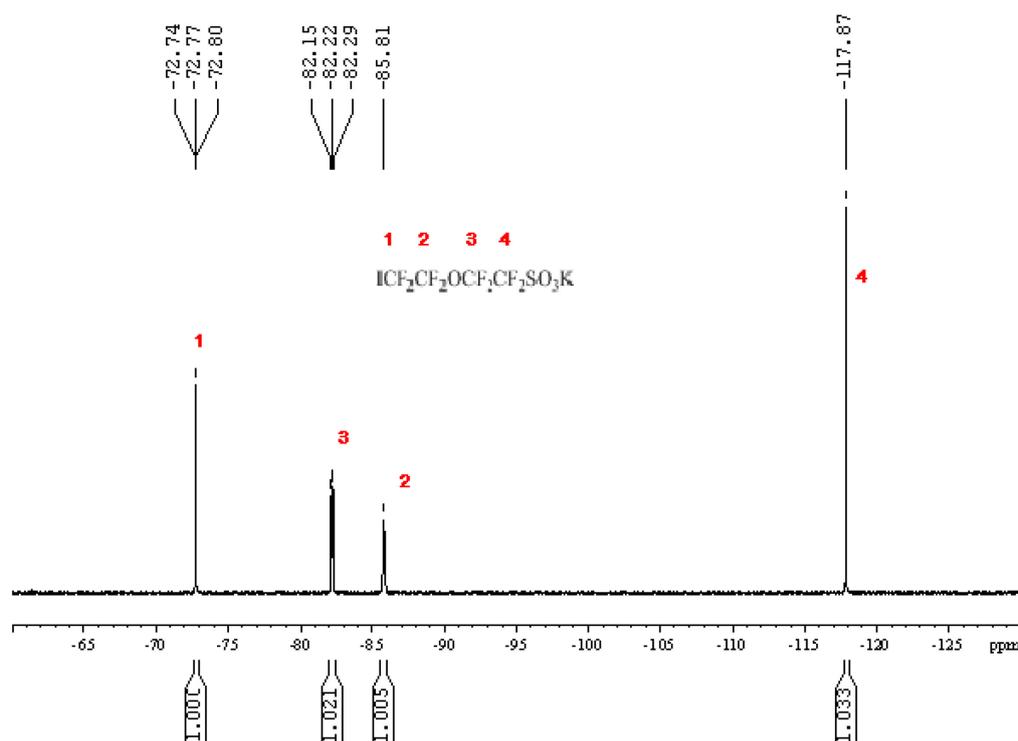
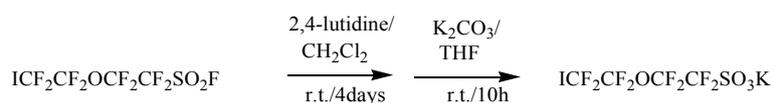


Figure II.2.1. ^{19}F NMR Spectrum of PSA-K in DMSO-d_6 .

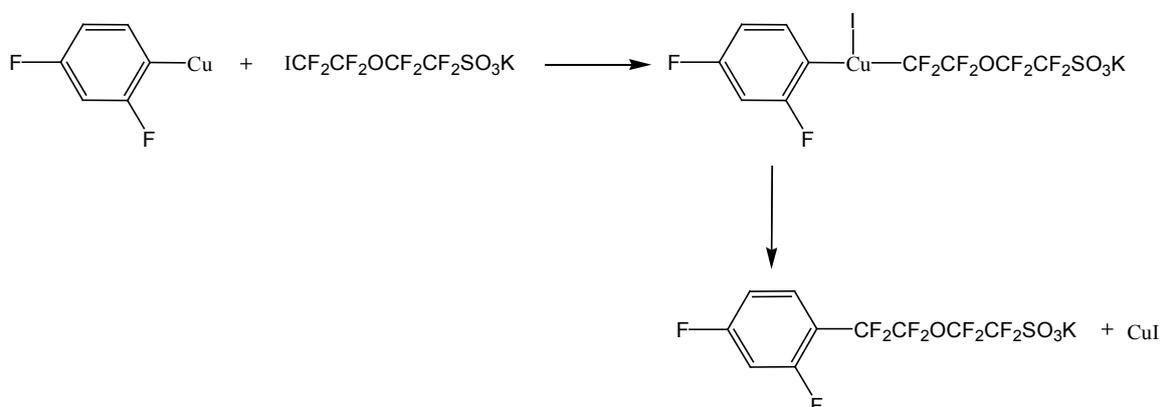
tetra-*n*-butylammonium fluoride (see Scheme II.2.2) and according to the procedure described by Iwasaki[31]. The PSA-K was isolated as a white solid product in 80-85% yield. Its purity was confirmed by ^{19}F NMR (Fig. II.2.1).



Scheme II.2.2 Formation of PSA-K.

This unsymmetrical Ullmann reaction was performed using copper bronze (mesh 200) as catalyst and 2,2'-bipyridine as ligand which is known to have a beneficial effect on the copper-assisted cross-coupling reaction[72]. However, a pretreatment[73] of copper bronze was achieved to improve its catalytic activity. As reported in literature[74], the polar aprotic solvents, like DMSO is suitable for this cross-coupling reaction. In this work, different experimental conditions were tested and we found that the following feed molar ratio PSA-K/dFIB/copper bronze/2,2'-bipyridine, 1.0/2.0/3.0/0.2 gave the best results.

In the early part of the reaction dFIB and copper bronze are put together in the DMSO at 80°C to form an organocopper intermediate compound which reacts further with PSA-K as illustrated in Scheme II.2.3. For this coupling reaction readily occurs but high temperature (130°C) was required.



Scheme II.2.3. Synthesis of FPSAB-K.

Taking advantage of the presence of fluorine atom in each reactant, ^{19}F NMR spectroscopy was used to monitor the reaction. As illustrated in Figure II.2.2, it was easy to observe the disappearance of the peak of the $-\text{CF}_2\text{I}$ group corresponding to the PSA-K reagent and on the other hand, the appearance of a peak at -112 ppm assigned to the CF_2 group grafted to the benzene ring. This powerful analysis method allowed also to reveal the presence of byproducts corresponding to the homo-coupling of dFIB and to the reaction of PSA-K with bipyridine-copper complex as well.

The structure of the expected product was confirmed by ^1H , ^{19}F NMR spectroscopy (see Figure II.2.3). One analysis was achieved by HPLC coupled with a mass spectrometer to control its purity. Only one peak was observed by UV detection with the correct mass, see Figure II.2.4.

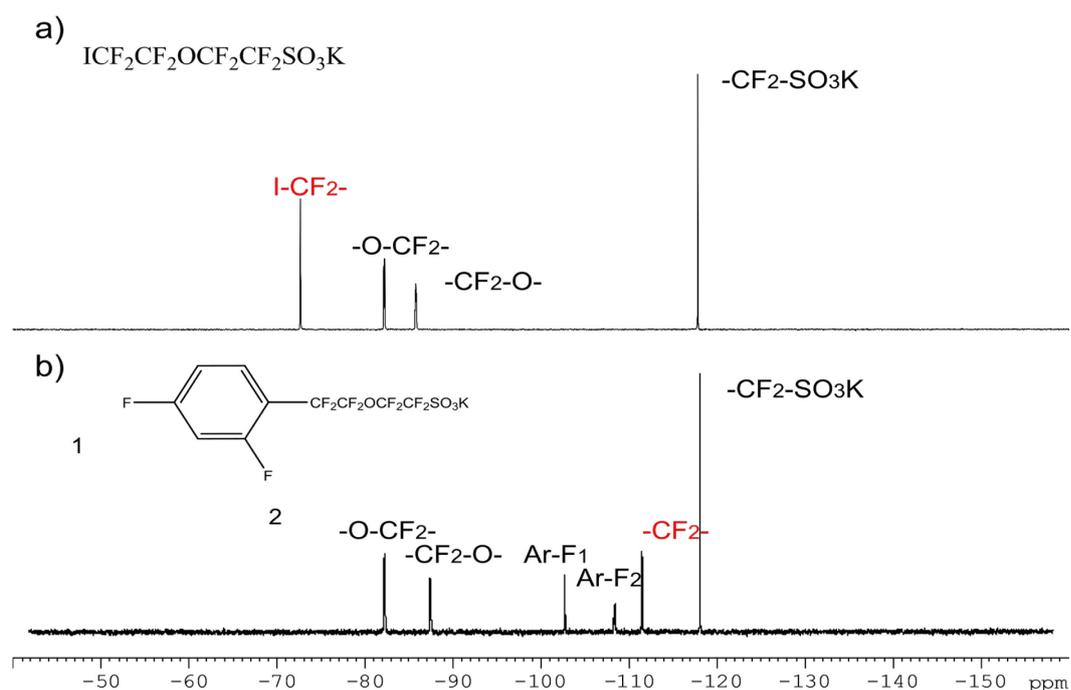


Figure II.2.2. ^{19}F NMR spectra in DMSO-d_6 . a) PSA-K reagent, b) FPSAB-K monomer.

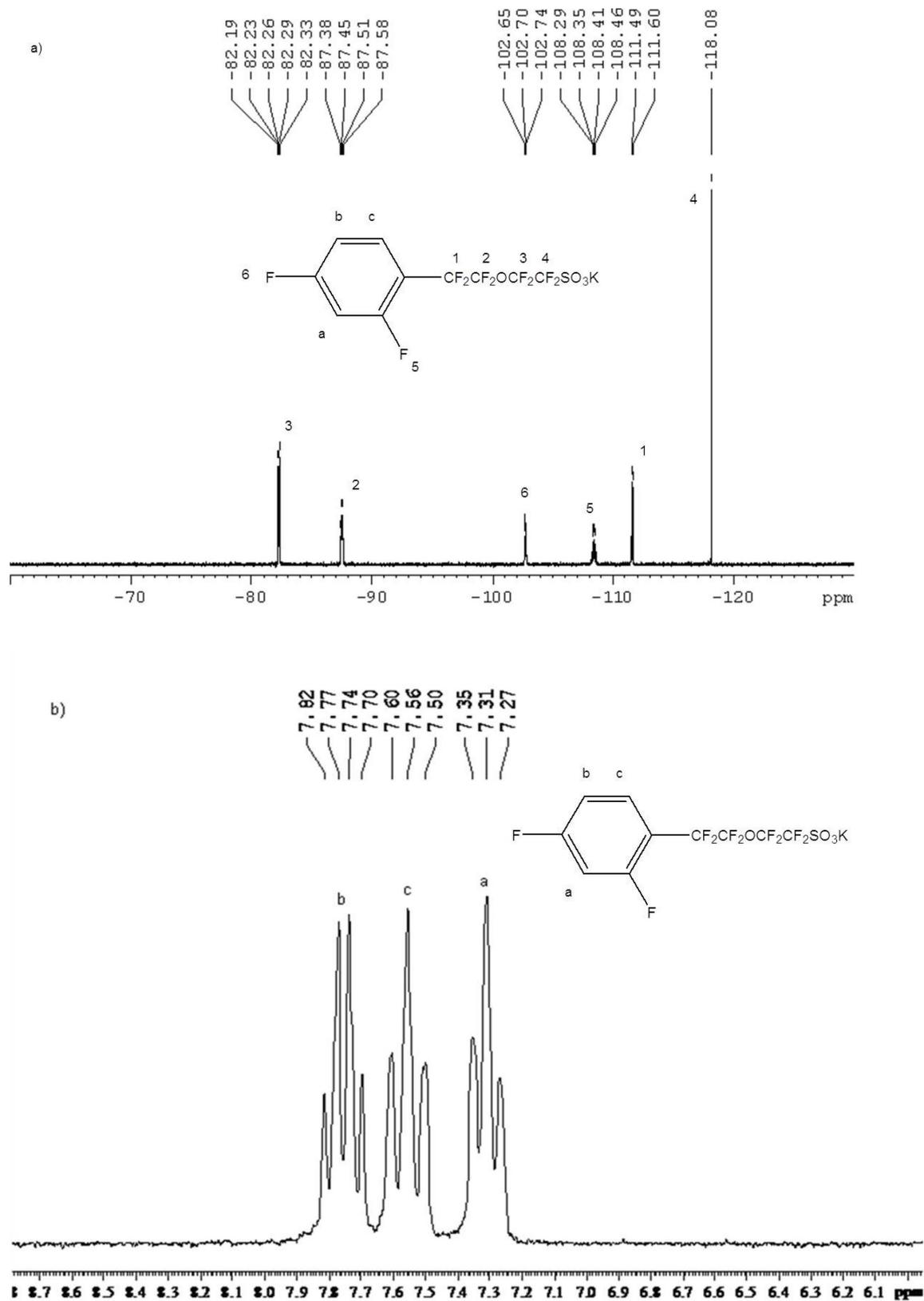


Figure II.2.3. a) ^{19}F NMR, b) ^1H NMR spectra of FPSAB-K in DMSO-d_6 .

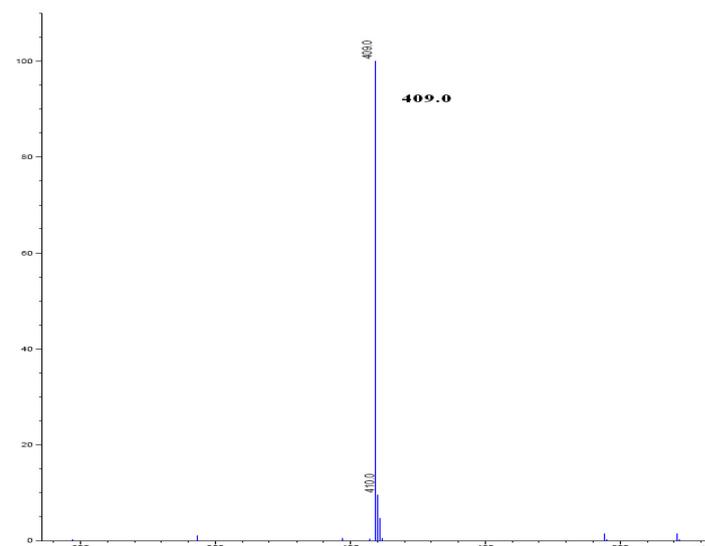
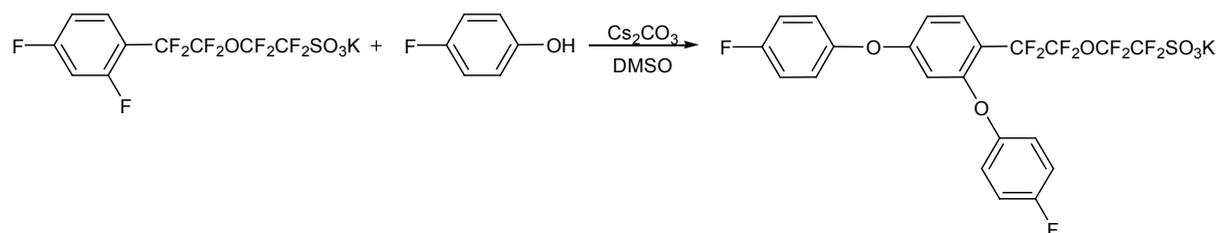


Figure II.2.4. Mass spectrum of FPSAB-K monomer.

II.3. Synthesis of a model compound from FPSAB-K monomer

To access to the target polymers in an efficient way, the synthesis pathway chosen consisted in a S_NAr reaction. In this connection, the reactivity of the two leaving fluorine of FPSAB-K monomer was evaluated toward a phenoxide nucleophilic reagent. The synthesis of a model compound was achieved as illustrated in Scheme II.3.1. To monitor this reaction, it was founded that ^{19}F NMR was the best analysis method. To this synthesis the 4-fluorophenol was chosen as a phenoxide precursor .



Scheme II.3.1. Model compound based on FPSAB-K and 4-fluorophenol.

Analysis of the spectra (Fig. II.3.1. b)) showed that, at 140°C reaction works very slowly. Initially, the temperature chosen was 140°C which is generally the polymerization temperature used for the synthesis of poly(arylene ether)s such as polysulfones. Because the reaction worked very slow, it was decided to increase temperature to 160°C. In these conditions, the reaction rate was much faster but it took about 24 h to go to completion. NMR analysis allowed us to establish a difference of reactivity of the two fluorine of the FPSAB-K reagent. Indeed, as illustrated in Figure II.3.1, the peak at -102,7 ppm corresponding to the fluorine in para position of the perfluoroalkyl chain and labelled Ar-F₂ (see spectrum a)) disappeared rapidly when temperature reach 160°C (see Figure b)). While in the same time only one part of the fluorine in ortho position reacted as evidenced by the appearance of the peak at -119 ppm assigned to the fluorine (Ar-F_{1'}) beard by the phenoxy group and the shift of the peak at -108,4 ppm assigned to the fluorine in ortho position of the perfluoroalkyl chain, to -110,5 ppm (see spectrum b)). It worth noting that in general in a S_nAr reaction, the reactivity of an halogene atom (fluorine or chlorine) in ortho position of an electron-withdrawing group is more reactive than that in para position (Scheme II.3.2). To account for the lower reactivity of fluoride F₁, a steric hindrance effect of the perfluoroalkyl chain could be considered.

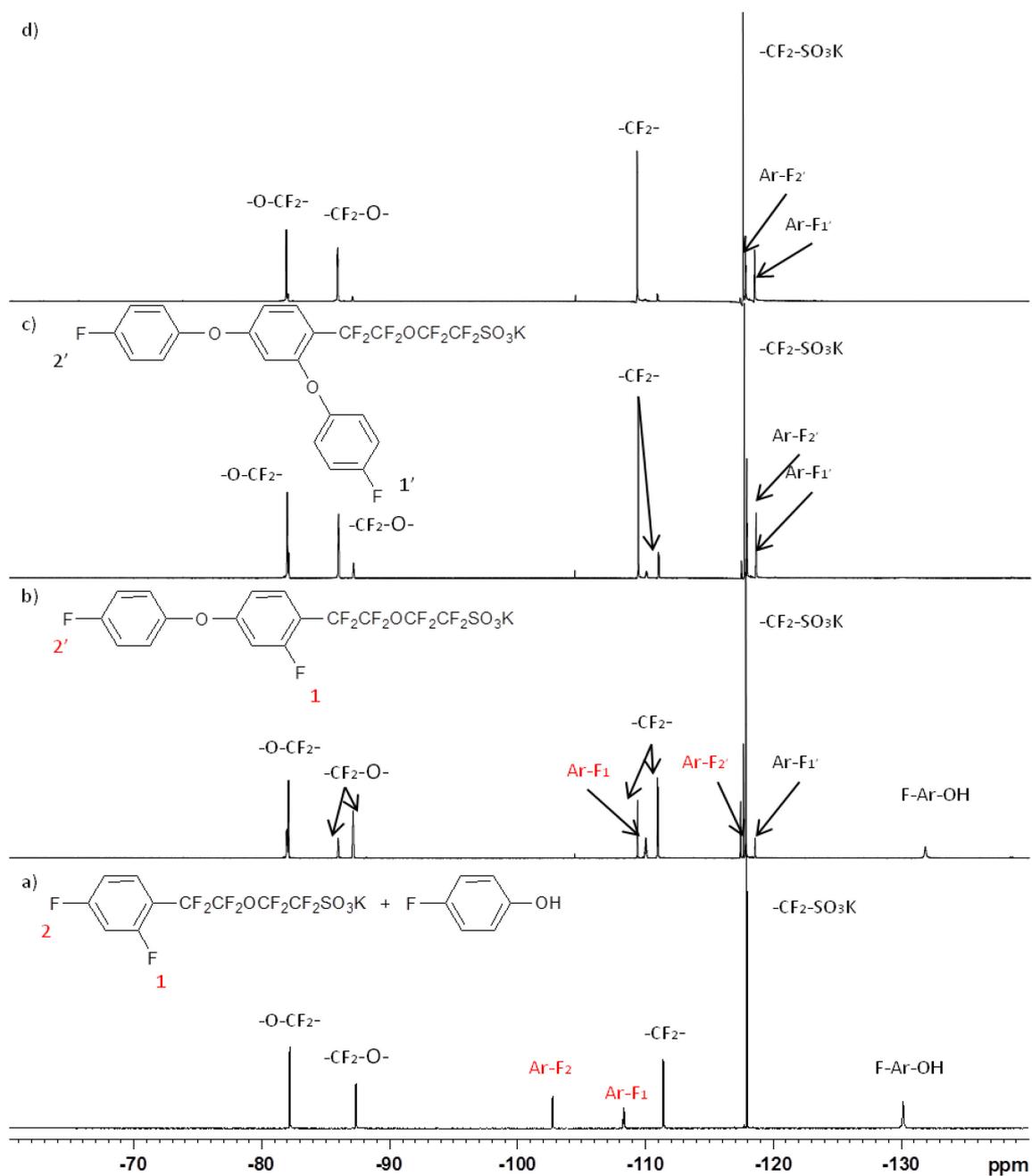
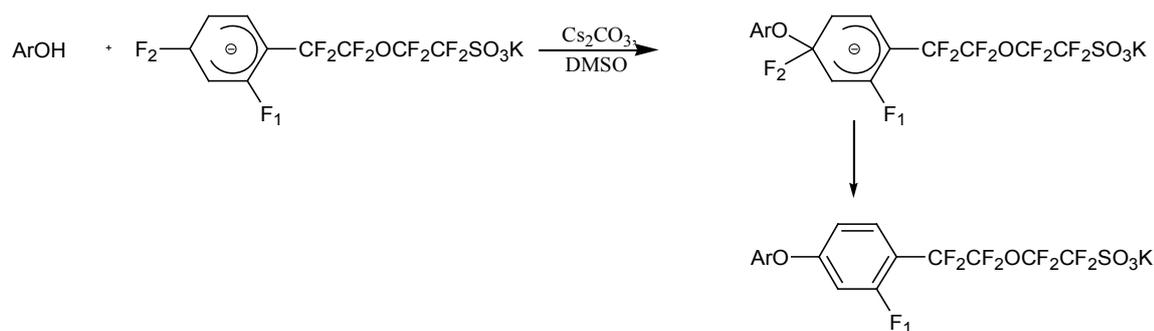


Figure II.3.1. ^{19}F NMR spectra of model reaction between FPSAB-K with 4-fluorophenol: a) at r.t., b) at 160°C after 10 min, c) at 160°C, after 5 h 20 min, d) at 160°C, after 24 h.

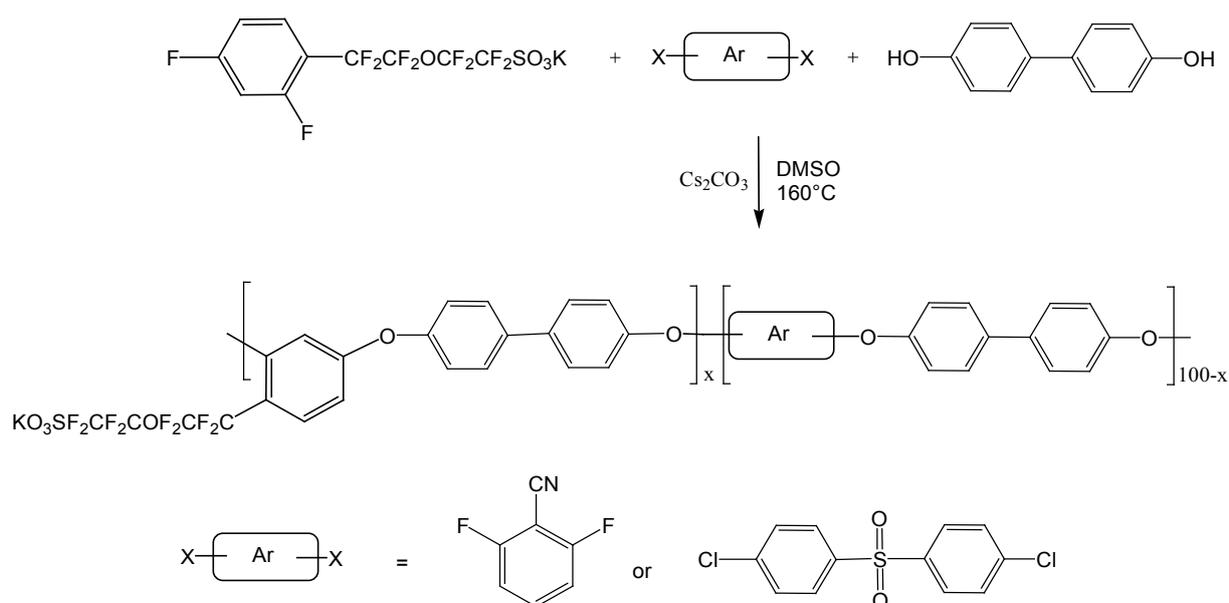


Scheme II.3.2. Activation effect of perfluoroalkyl group in FPSAB-K.

II.4. Synthesis and structural characterization of sulfonated poly(arylene ether)s copolymers (SPAEC)

From the sulfonated monomer FPSAB-K, the attempted preparation of SPAEC copolymers was looked on using different co-monomers such as the 4,4'-biphenol (BP), the 2,6-difluorobenzonitrile (FBN) or the 4,4'-dichlorodiphenyl sulfone (CIPS) (Scheme II.4.1). BP monomer was chosen in order to compensate for the possible plasticizing effect of perfluoroalkyl groups bonded along the polymer chains and then keep high the polymer T_g . To perform the polymerization reaction, the selected temperature 160°C was applied in order to get a complete conversion of the FPSAB-K monomer, as it was showed in studies of the synthesis of the model compound. However, when $\text{S}_\text{N}\text{Ar}$ polymerization reaction operates at this temperature with fluorinated monomers, a well known side reaction can occurs involving the formed side-product. The fluorine anion (CsF) can cleave the polymer chain by reacting with a phenyl ring of the phenyl ether linkages. Accordingly, CaCO_3 was added to the polymerization medium in order to trap the fluorine anion in the inert form (CaF_2 compound). The preparation of two series of sulfonated copolymers was considered: one involving FPSAB-K, FBN and BP monomers (polymers are denoted as SPAEC-N), and another one involving FPSAB-K, CIPS and BP monomers (polymers are denoted as SPAEC-S). For each series, the synthesis of different copolymers was attempted by varying the extent of FPSAB-K monomer with the purpose to obtain polymers with a IEC of 1.1, 1.3 and 1.6 meq/g. Only

the polymers with the targeted IEC of 1.1 meq./g were synthesized and membranes from these polymers were obtained. One hypothesis that can be put forth to explain the failures to obtain high molecular weight polymers with higher IEC, is the formation of too much cyclic oligomers. Indeed, the meta meta ether linkages resulting of the reaction of the FPSAB-K monomer are favorable to the cyclic structure formation. Accordingly, higher the feed ratio of FPSAB-K monomer for the synthesis of polymers, higher is the quantity of cyclic oligomers formed. Other processing conditions were tried to overcome this problem. One way to achieve the polymerization it was one pot two-step reaction. First, the sulfonated monomer was reacted with biphenol for 24 h at 160°C and then after cooling the reaction mixture, FBN or CIPS monomer was added. The mixture was then heated at 140°C for 24 h. The second approach was to allow to react all monomers at 180°C in NMP and CaCO₃. Whatever the alternative solutions, the polymerizations failed.



Scheme II.4.1. Synthesis of sulfonated poly(arylene ether)s copolymers.

The structure of the polymers was characterized by ¹H and ¹⁹F NMR. As it can be seen in Figure II.4.1, the peaks assigned to the fluorines F₅ and F₆ of FPSAB-K are not appearing on the spectrum of the SPAE polymer and the peak shifted from -111,5 ppm to -109,3 ppm attributed to F₁ confirms that the polymerization reaction was successfully achieved.

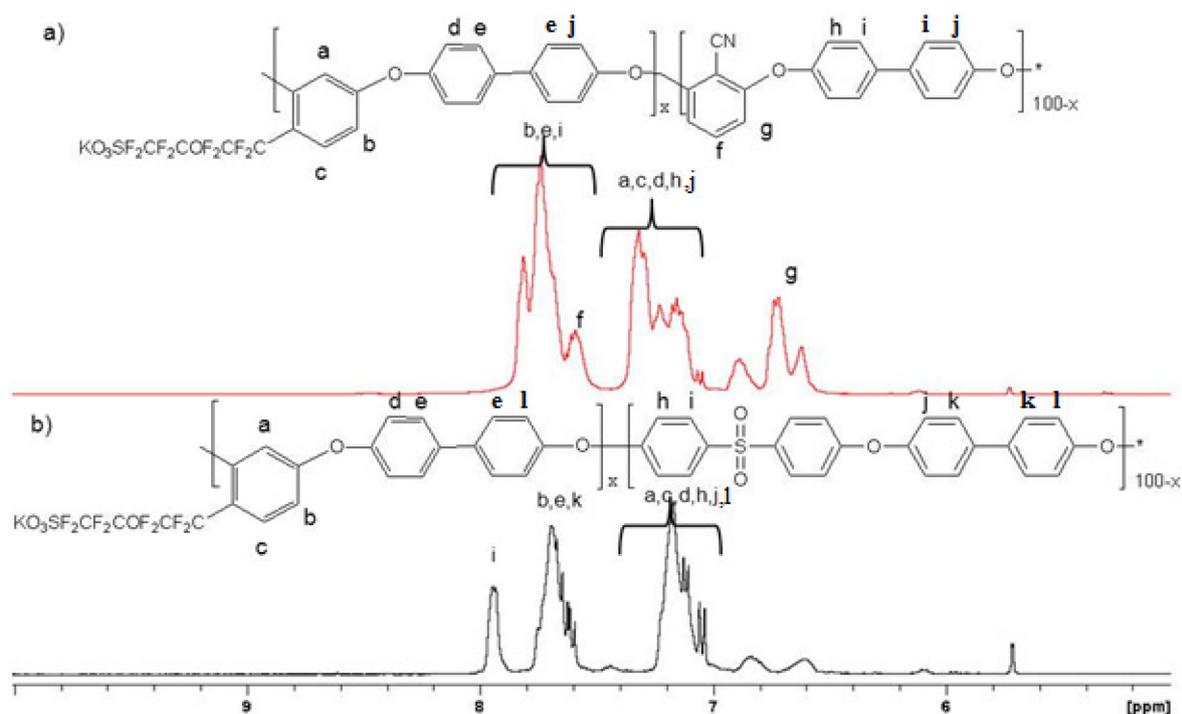


Figure II.4.2. ^1H NMR spectra of a) SPAE-N-1.1, b) SPAE-S-1.1 in DMSO-d_6 .

II.5. Solubility of SPAE polymers

The solubility of SPAE was determined in different usual solvents. The tests were performed at 10 wt./vol. %. Different polar and apolar, protic and aprotic solvents were used such as methanol, cyclohexane, toluene, THF, chloroform, water, DMSO, DMAc and NMP. Solubility was estimated by visual observation. It was observed that the SPAE polymers are not soluble in apolar solvents (Cyclohexane) and in protic solvents (methanol). The good solvents found are DMSO, DMAc and NMP. These results allowed us to consider the preparation of membranes using the solution casting method. They are insoluble in water.

II.6. SPAE membrane manufacturing

Sulfonated poly(arylene ether)s films were prepared by casting solution of polymer dissolved in NMP. Obtained membranes in K⁺ form gave tough, mechanical resistance material with yellow color. After acidification, membranes changed color from yellow to green.

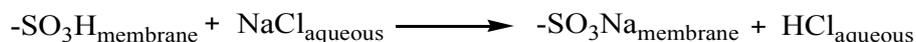
II.7. Determination of IEC by titration

The Ion Exchange Capacity of the SPAE polymers (IEC, mequiv/g, milliequivalent of -SO₃H functions per gram of polymer) were obtained from acid-base titration measurements. The titration analysis were performed in both aqueous solution and organic solvent solution. The IEC was calculated as:

$$IEC = (C_{NaOH} * V_{eq}) / m_s$$

where, V_{eq} and C_{NaOH} are the volume of NaOH required for the equivalence point (mL) and molar concentration (mol/L) of NaOH solution, respectively. m_s is the weight of the dried membrane sample.

The titration in aqueous solution was made according to the procedure reported elsewhere[33, 75, 76]: the dry free acid membranes were first immersed in water for 2 hours and then soaked in NaCl solution for 48 hours. In these conditions an exchange reaction occurs leading to the formation of HCl as illustrated hereinafter.



The titration of the resulting HCl solutions was made with a NaOH solution titrant. As it can be seen in Figure II.7.1, two very close equivalence points were observed. To explain this profil of the titration curve, different speculative explanations can be put forward. Probably, the first equivalence point corresponds to the reaction of NaOH with HCl in water while the

second one is related to the reaction of NaOH with HCl trapped into the membrane or it is due to the reaction of NaOH with the sulfonic acid groups unexchanged.

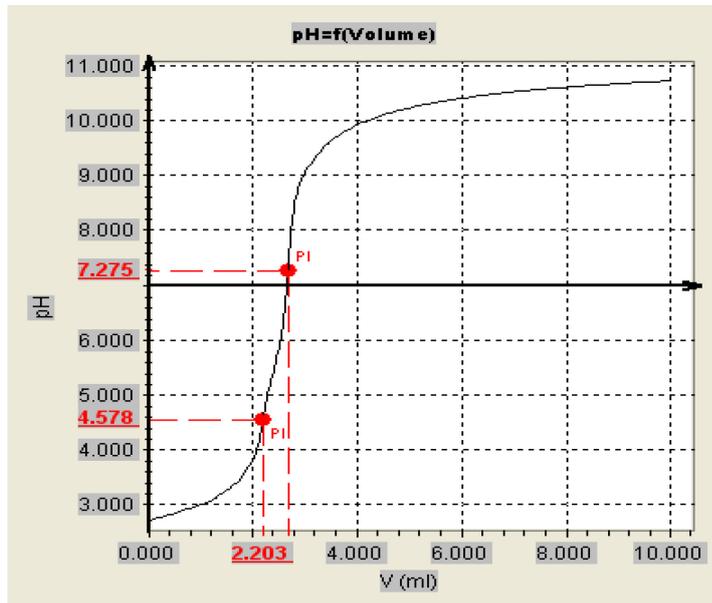


Figure II.7.1. Aqueous titration of sulfonated SPAE copolymer membrane. PH curve of HCl solution obtained after exchange reaction of sulfonated membrane with NaCl solution

Accordingly, the NaOH solution volume corresponding to the second equivalence point was taken in consideration to calculate the IEC (meq./g) of sulfonated poly(arylene ether)s membranes.

As to the titration in organic solvent solution, the method developed by Iojoiu et al.[77] was used. Dry free acid membrane samples were dissolved in diethylene glycol monomethyl ether (DGME) and then titrated with 0.05 N NaOH in DGME in the presence of bromothymol blue as pH indicator.

As reported in Table II.7.1 the experimental IEC values obtained from both titration methods are in good accordance with the theoretical values determined from feed molar ratio. Results contains an error of $\pm 5\%$.

Table II.7.1. IEC values of SPAE polymers.

copolymer	SPAE-N-1.1	SPAE-S-1.1
Theoretical IEC (meq/g)	1.1	1.1
Exper.IEC _{Aqu}	1.14±0.06	1.09±0.05
Exper.IEC _{Non-aqu}	1.13±0.06	1.2±0.06

II.8. Thermal properties of SPAE polymers

The thermal stabilities of the two sulfonated copolymers in both potassium and acid form were investigated by TGA. For the polymers in potassium form the onset weight loss was observed at 442°C and at 449°C for SPAE-N and SPAE-S, respectively which was assigned to the degradation of the polymer chain. For the polymers in acid form, after an isotherm at 150°C for 20 min to remove absorbed water, a weight loss was observed from 245 °C which can attributed to the sulfonic acid group degradation.

DSC analysis were performed for polymers in potassium form. The T_g values measured are 214°C and 219°C for SPAE-N and SPAE-S, respectively.

II.9. Water uptake properties of SPAE polymers

The water uptake of membranes is a critical property that, to a large degree, influences the proton conductivity of PEM materials. However, if water is required to facilitate proton transport, an excessive water absorption can dramatically increase the dimensional swelling leading to severe loss of mechanical strength. Therefore, the design of sulfonated polymers with appropriate water uptake is one of the critical requirements for their application as PEM. The water uptake of sulfonated polymers are mainly depending on the degree of sulfonation, temperature and to some extent of the chemical composition of the polymer chain. The water uptake was given by:

$$WU = \frac{(W_{wet} - W_{dry})}{W_{dry}} \times 100\%$$

where W_{wet} and W_{dry} are the wet and dry weight of the membrane .

Another manner commonly used to present the water sorption of sulfonated membranes is the hydration number (λ) which corresponds to the quantity of water molecules sulfonic acid site and is expressed as:

$$\lambda = \frac{(W_{wet} - W_{dry})}{MW_{H_2O}} \times \frac{1000}{(IEC \times W_{dry})}$$

where MW_{H_2O} is the molar mass of water (18.01 g/mol) and W_{wet} and W_{dry} are the wet and dry weight of the membrane.

The water swelling of membranes in acid form was determined at different temperatures. Initially, the membranes were kept in water for 4 hours at a chosen temperature. As it can be seen in Table II.9.1, the water uptake of the two membranes increases as expected with temperature. It worth noting that the water uptake at 90°C is relatively low. Similar results have been observed by Iwasaki et al.[31] with sulfonated perfluoroalkyl group containing polysulfones with a similar IEC but at 80°C.

Table II.9.1. Water uptake of SPAE membranes at different temperatures.

copolymer IEC(meq/g)	Water Uptake			
	30°C	50°C	70°C	90°C
SPAE-N-1.1	12	15	28	30
SPAE-S-1.1	12	16	21	23

As to the values of the hydration number listed in table II.9.2, they increase with temperature but they are lower than the reported values concerning the Nafion 117 membrane [78].

Table II.9.2. Hydratation number of SPAE membranes at different temperatures.

copolymer	λ (H ₂ O/SO ₃ H)			
	30°C	50°C	70°C	90°C
SPAE-N-1.1	6	8	14	15
SPAE-S-1.1	6	8	11	12

II.10. Ionic conductivity of SPAE polymers

The proton mobility in the sulfonated polymer membranes under hydrated conditions can be described by two principal mechanisms: the Grotthuss and vehicle mechanisms[79]. In the Grotthuss mechanism it is admitted that protons tunnel from one water molecule to the next via hydrogen bonding. As to the vehicle-type mechanism, it is assumed that protons diffuse through the medium together with a “vehicule”, H_3O^+ in case of water. The proton conductivity depends on the IEC of the membrane but is also strongly dependent on the level of hydration. Proton conductivity (δ) of membranes in sulfonic acid form was calculated according to the following equation:

$$\delta = \frac{d}{(L_s \times w_s \times R)}$$

where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane, and R is the resistance value measured.

The temperature dependence of proton conductivity of membranes was determined at 50, 70 and 95 % of relative humidity. In Table II.10.1 all results are presented. It appears clearly that their conductivity is not significantly depended on the relative humidity at least in the range of RH studied (Fig. II.10.1). On the other hand, the ionic conductivity of the SPAE-N-1.1 membrane are similar to that of the SPAE-S-1.1 membrane but much lower compared to that of Nafion membrane (see Figure II.10.1).

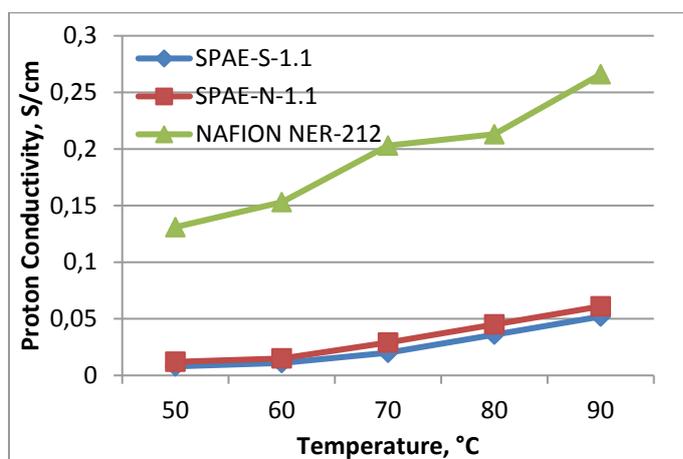


Figure II.10.1. Proton conductivity as a function of temperature of SPAE membranes and Nafion NRE-212 under 95% of relative humidity.

Table II.10.1. Proton conductivities of SPAE membranes.

T (°C)	Copolymer					
	SPA-E-N-1.1			SPA-E-S-1.1		
	Proton conductivity (mS/cm)					
	Relative Humidity					
	50%	70%	95%	50%	70%	95%
50	10	11	12	6	7	8
60	11	14	15	8	10	11
70	21	26	29	16	19	20
80	38	43	45	32	35	36
90	53	59	61	43	49	52

II.11. Conclusion

A simple synthetic way based on one step reaction was developed to prepare a difluorinated monomer bearing sulfonated perfluoroalkyl group which can be polymerized via a S_NAr reaction. However, it was observed that its reactivity was low and hence high temperature and long time reaction were necessary to obtain sulfonated poly(arylene ether)s. Only the co-polymers with an IEC= 1.1 mequiv./g were obtained with molecular weights high enough to prepare self supporting membranes. These polymers display high T_g and a good thermal stability. A low water uptake of SPAE membranes was brought out even at 90°C. But, a much lower ionic conductivity was obtained for these membranes in comparison with the Nafion NRE-212 membrane. So in order to prepare sulfonated polymers with higher IEC for the purpose of improving the ionic conductivity, the synthesis of a new monomer deriving from the FPSAB-K compound has been considered.

Chapter III. Synthesis of sulfonated poly(arylene ether sulfone)s

III.1. Introduction

Dans le but d'obtenir un précurseur perfluoroalkyl sulfoné présentant une plus grande réactivité que le FPSAB-K monomère décrit dans le chapitre précédent et ce pour mieux contrôler le procédé de polymérisation, l'une des options qui est apparue intéressante est celle qui consiste à adjoindre le motif perfluoroalkyl sulfoné à une structure moléculaire de type diphenyle sulfone. En effet de nombreux polymères aromatiques ont été développés depuis des dizaines d'années et certains sont fabriqués à l'échelle industrielle en utilisant des composés diphenylsulfone dihalogénés comme le plus connu le 4,4'-dichloro diphenylsulfone. En utilisant le schéma de synthèse du précurseur FPSAB-K complété par deux étapes supplémentaires, nous avons donc synthétisé un nouveau monomère à partir duquel différents copolymères contenant des entités diphenyle sulfone porteur d'un motif perfluoro alkyle sulfoné ont été préparés. Ces copolymères ont été mis œuvre sous la forme de membranes puis caractérisés.

III.2. Synthesis of 4-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-3,4'-difluorodiphenyl sulfone (3,4'-FPSAPS-K)

In this section is described the synthesis of the new monomer 3,4'-FPSAPS-K (Fig. III.2.1). This monomer requires a three-step reaction (the sequence shown in Scheme III.2.1). The monomer was prepared by modification of FPSAB-K product synthesized previously (Chapter II).

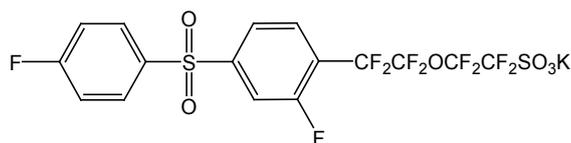
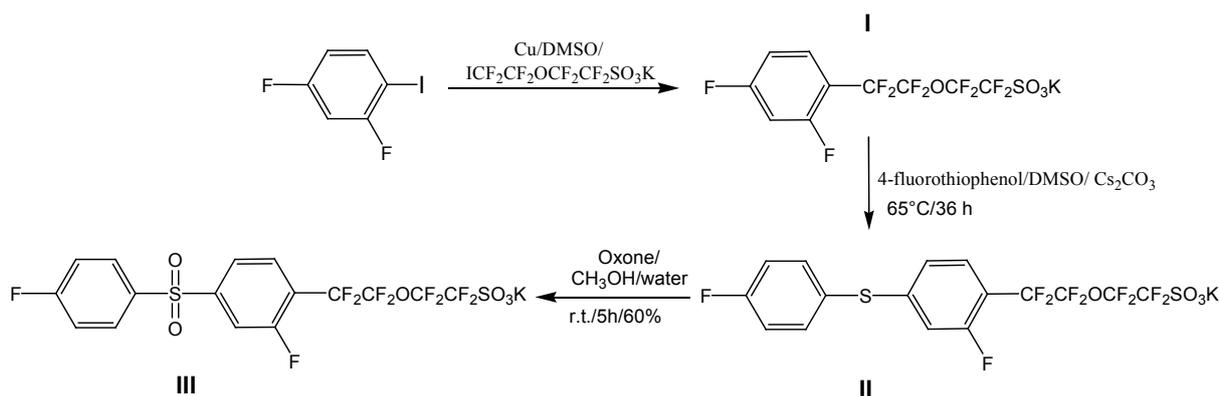


Figure III.2.1. Structure of 3,4'-FPSAPS-K monomer.



Scheme III.2.1. Synthesis of 3,4'-FPSAPS-K.

The first step, a Ullmann coupling reaction was performed between 2,4-difluoroiodobenzene and PSA-K in the conditions studied in Section II.2.

The second step was the preparation of the diphenylsulfide intermediate compound (II) via an aromatic nucleophilic substitution reaction involving the 4-fluorothiophenol and the FPSAB-K compound. The reaction was conducted at 65°C to limit the undesired reaction, i.e. the reaction of 4-fluorothiophenol with the F₁ in ortho position of the sulfonated perfluoroalkyl chain. The pure product was obtained with a yield of 65%. The purity of the product was confirmed by ¹⁹F NMR analysis (Fig. III.2.2 b).

For the last step different oxidizing agents were tested and it was found that Oxone in aqueous methanol was the best chemoselective oxidizing agent for the conversion of sulfide intermediate product to the final sulfone compound III.

The structure of the desired compound was confirmed by ¹⁹F and ¹H NMR (see Fig. III.2.3). The HPLC analysis of 3,4'-FPSAPS-K showed a single peak and therefore this product can be

considered as relatively pure. The mass spectrum (Fig. III.2.4) confirmed the oxidation of sulfide to sulfone product.

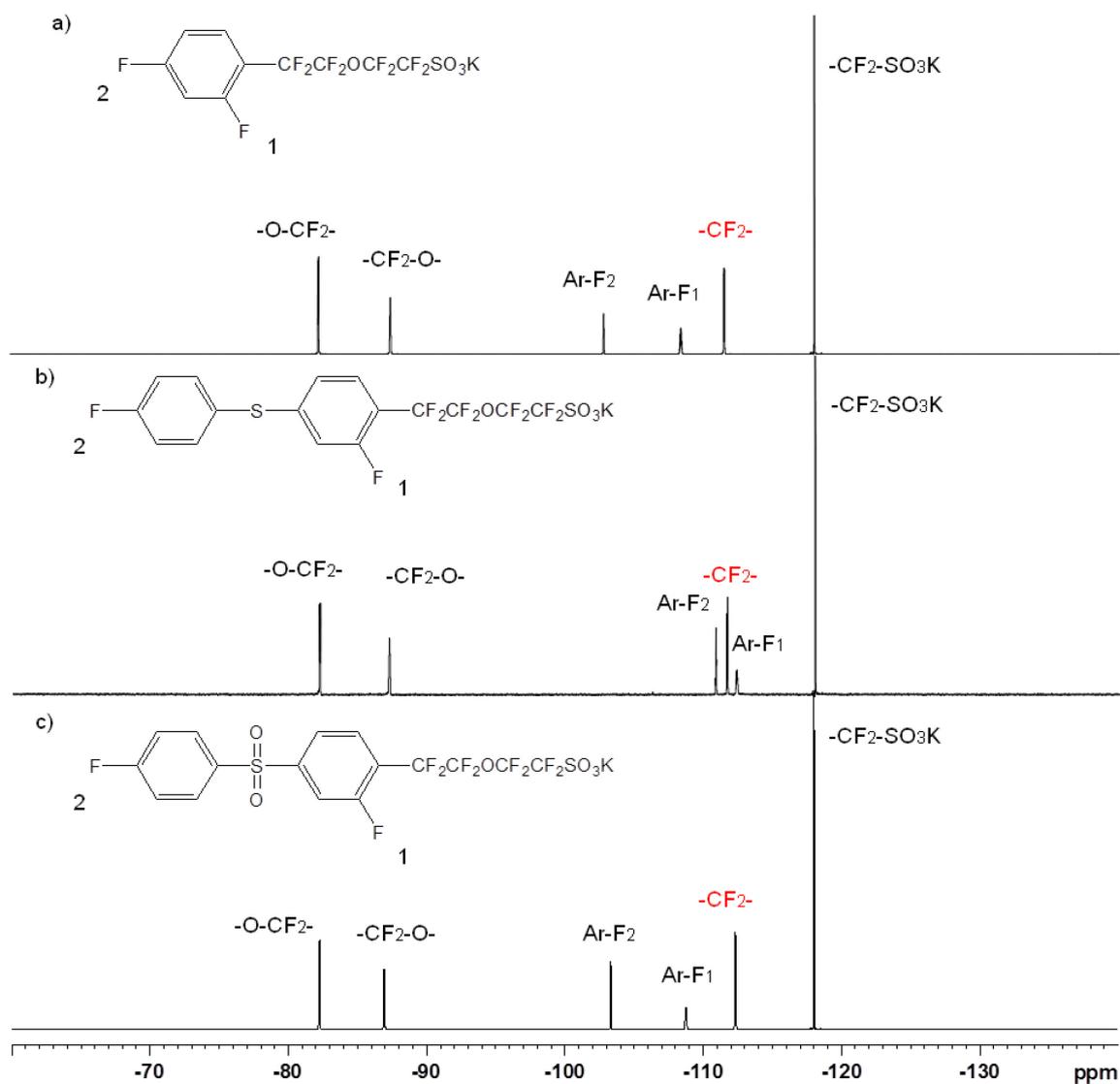


Figure III.2.2. ^{19}F NMR spectra in DMSO-d_6 of a) FPSAB-K, b) 3,4'-FPSAPSulfide-K, c) 3,4'-FPSAPS-K.

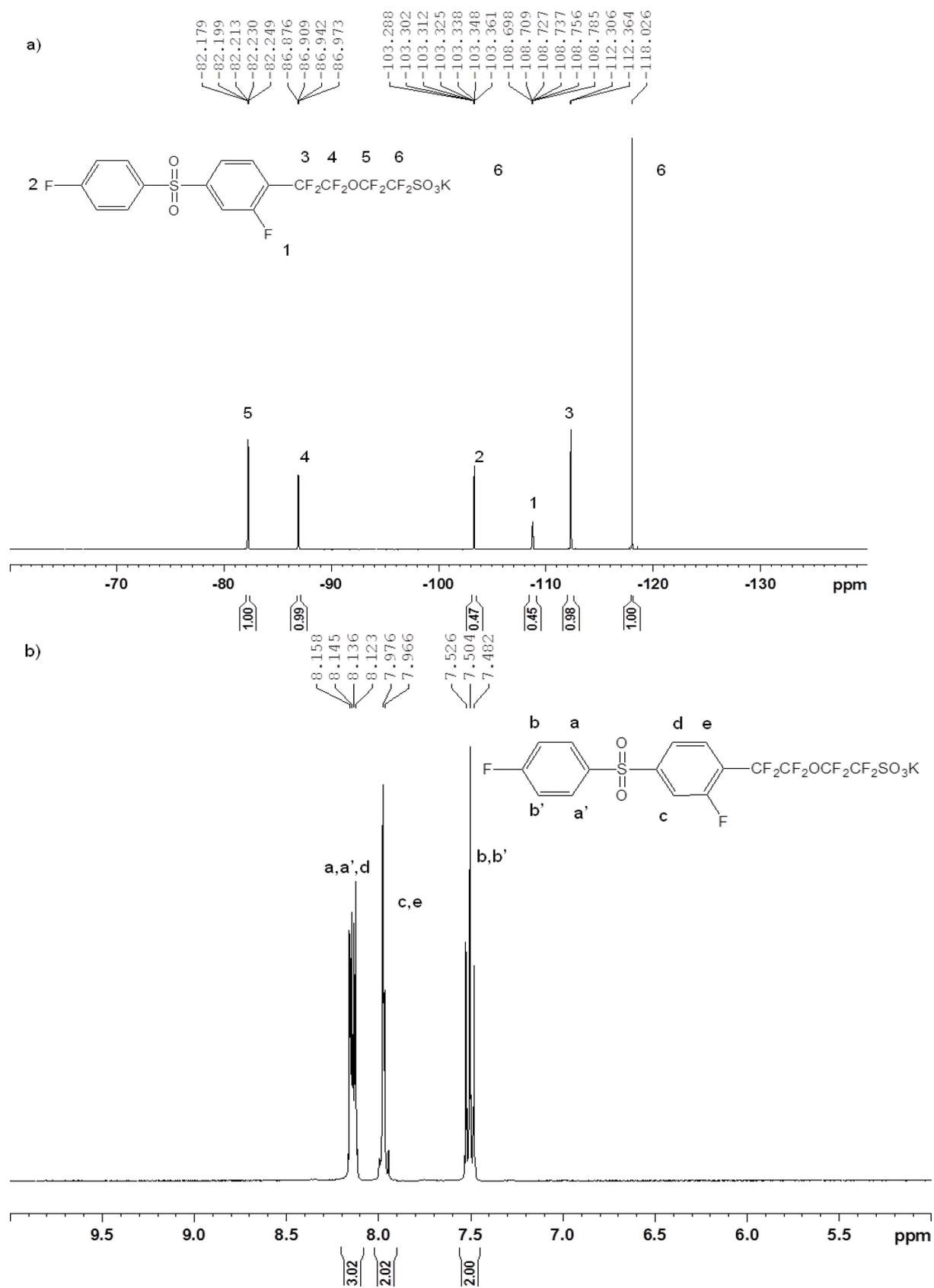


Figure III.2.3. ^{19}F (top) and ^1H NMR spectra (bottom) of 3,4'-FPSAPS-K in DMSO-d_6 .

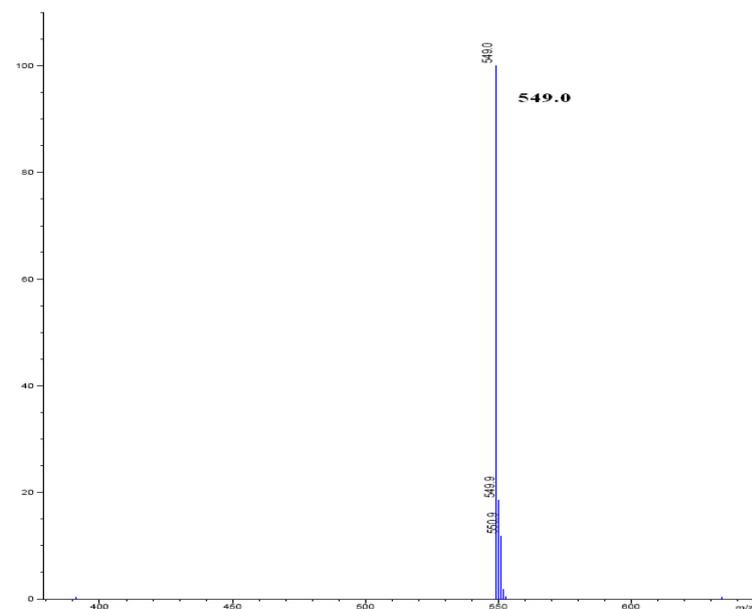
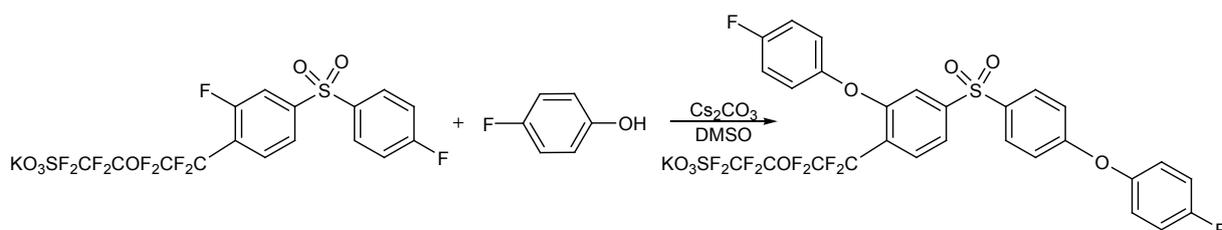


Figure III.2.4. Mass spectrum of the 3,4'-FPSAPS-K monomer.

III.3. Synthesis of a model compound from 3,4'-FPSAPS-K monomer



Scheme III.3.1. Model reaction between 3,4'-FPSAPS-K and 4-fluorophenol.

Knowing that the sulfone group has a beneficial effect on the aromatic nucleophilic substitution reaction due to its strong electron withdrawing character, the model reaction was carried out at 140°C. The progress of the reaction was monitored by ^{19}F NMR analysis. Surprisingly enough, the first NMR analysis corresponding to a sample of the reaction mixture taken off when the reaction was started (room temperature) showed that a small

fraction of fluorophenate reagent has already reacted with 3,4'-FPSAPS-K. Indeed, it can be seen in Figure III.3.1 (a) a peak at -117.5 ppm appearing which could be attributed to the fluorine labelled F2'. The intensity of this peak increasing as the reaction run. As it can be seen in Figure III.3.1,a), the peak at -103,3 ppm corresponding to the fluorine in para position of the sulfone group (Ar-F₂) and the peak at -109 ppm corresponding to the fluorine in ortho position of the perfluoroalkyl chain (Ar-F₁) disappeared quickly at 140°C (Figure III.3.1, c)). From this study, it can be considered that the reactivity of F₂ is higher than the F₁ which can be explained by the fact that the F₂ substitution is favored by the strong electron withdrawing effect of the SO₂ group in para position.

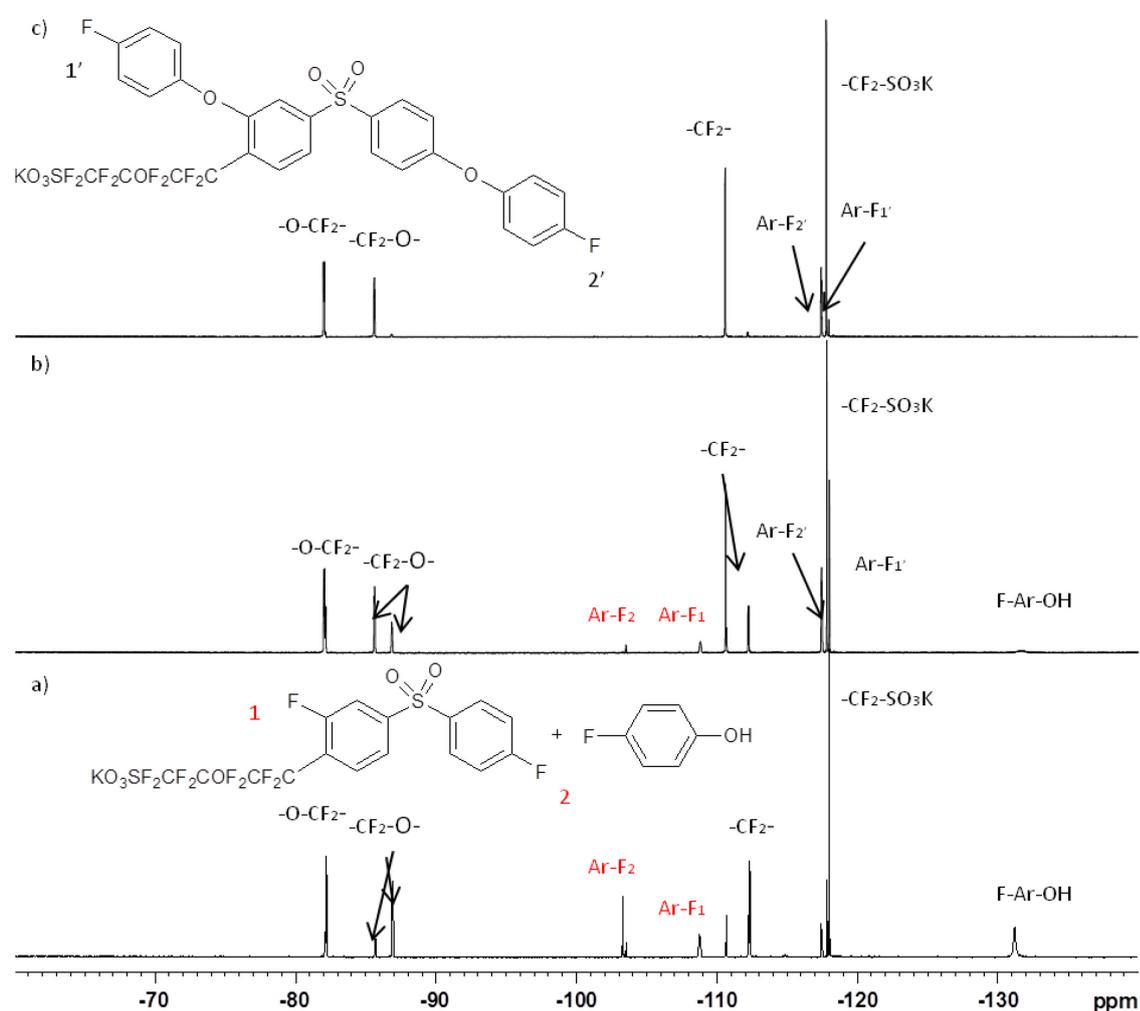
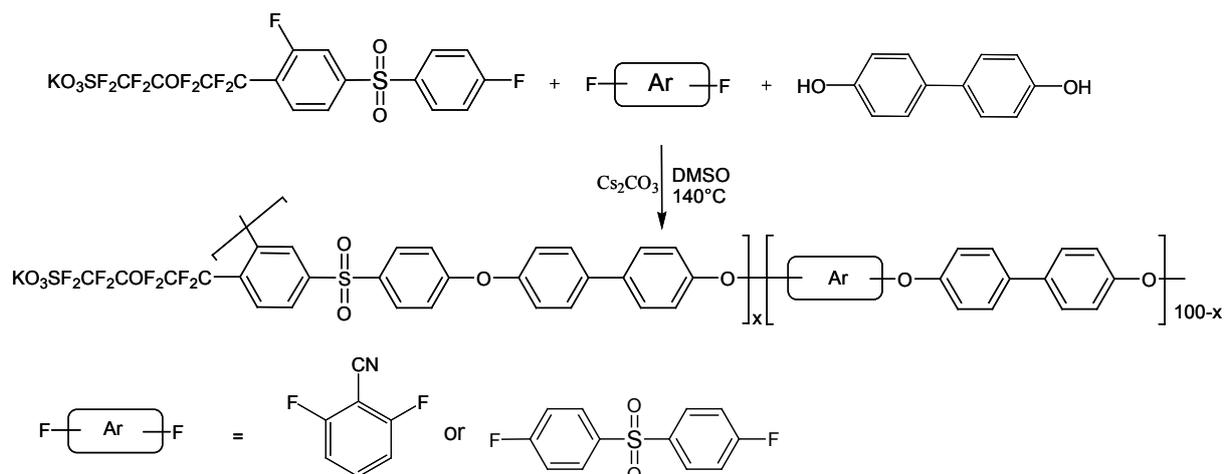


Figure III.3.1. ¹⁹F NMR spectra of model reaction between 3,4'-FPSAPS-K with 4-fluorophenol: a) r.t., b) 80°C, c) 140°C in DMSO-d₆.

The substitution of F₁ in meta position to the sulfone group is less reactive but thanks to the electron withdrawing effect of perfluoro alkyl group (less than SO₂ group) in ortho position to F₁ the reaction occurred quickly.

III.4. Synthesis and structural characterization of sulfonated poly(arylene ether sulfone)s (SPAESulfone)

For the synthesis of sulfonated copoly(arylene ether sulfone)s the 2,6-difluorobenzonitrile (FBN), the difluoro 4,4'-diphenylsulfone (FPS) and the dihydroxy 4,4'-biphenyl (BP) were chosen as comonomers. Copolymers with different IEC namely 1.1, 1.3 and 1.44 meq H⁺/g were successfully synthesized by nucleophilic aromatic substitution as illustrated in Scheme III.4.1. Accordingly to the synthesis of model compound (Section III.3) the polymerization was performed at 140°C.



Scheme VI.3.1. Synthesis of SPAESulfone copolymers

Based on ¹⁹F NMR spectra (see Fig. III.4.1) of monomer (a) and polymer (b), it can be considered that the polymerization reaction reached to a quasi completion based on the following observations. The peaks corresponding to F₅ and F₆ fluorine atoms of the 3,4'-FPSAPS-K monomer have completely disappeared and the peak labelled 1 attributed to the

fluorine nuclei of the CF₂ group directly bonded to the phenyl ring is shifted from -112 ppm to -108.5 ppm.

From the ¹H NMR spectra (Figure III.4.2) it was confirmed that benzonitrile monomer was well incorporated in the polymer chains as evidenced by the peak at 6.75 ppm corresponding to the protons h. As expected, the intensity of this peak decreases when the targeted IEC of polymer increases.

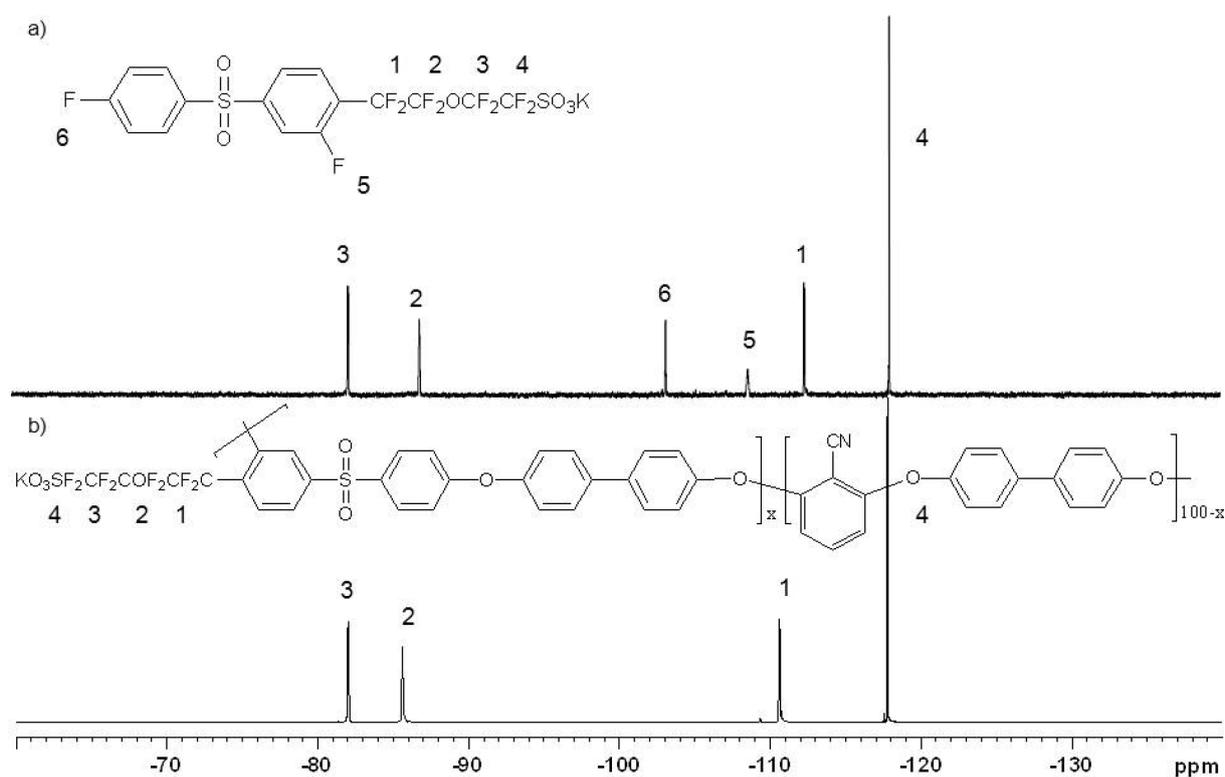


Figure III.4.1. Spectra ¹⁹F NMR: a) monomer 3,4'-FPSAPS-K, b) SPAESulfone-N-1.1 copolymer in DMSO-d₆.

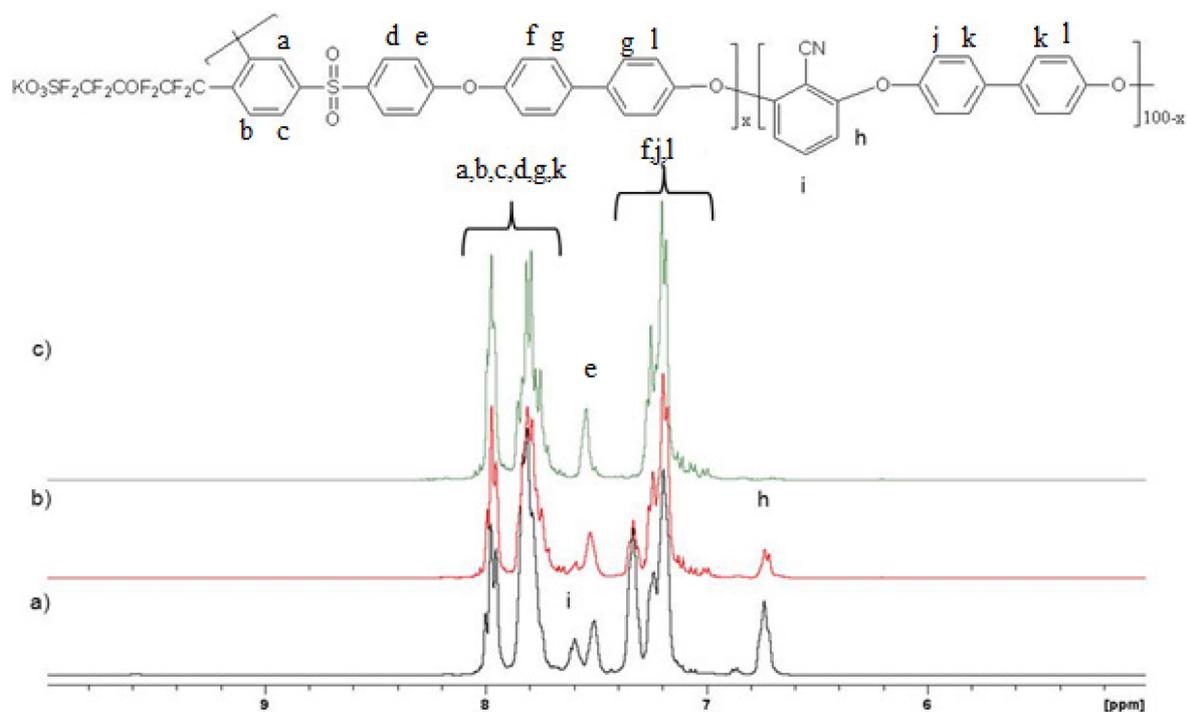


Figure III.4.2. ^1H NMR spectra: a) SPAESulfone-N-1.1, b) SPAESulfone-N-1.3, c) SPAESulfone-N-1.44 copolymers in DMSO-d_6 .

III.5. Solubility of SPAESulfone polymers

Sulfonated poly(arylene ether sulfone)s were found well soluble in DMSO, NMP and DMAc.

III.6. SPAESulfone membrane manufacturing

All SPAESulfone membranes were prepared via the casting solution method. The NMP was used as solvent. The membranes obtained as salt form were transparent and tough. After acidification they color was slightly yellow.

III.7. Determination of IEC

III.7.1. Determination of IEC by ¹H NMR analysis

¹H NMR spectra (Fig. III.4.2) were used to estimate the DS by taking in consideration the intensity of specific peaks and using the following formula:

$$DS \% = \frac{(Area\ abcdgk) \div 13}{[(Area\ abcdgk) \div 13 + (Area\ hi) \div 3]} \times 100$$

Area abcdgk – integration area of seven protons from sulfonated unit

Area hi – integration area of three protons from unsulfonated unit

The calculated values for the degree of sulfonation of SPAESulfone-N are reported in Table III.7.1.1 For SPAESulfone-S-1.1 it was not possible to determine DS by ¹H NMR spectrum because of overlapping of peaks.

Table III.7.1.1. IEC determination by ¹H NMR spectra.

Copolymer	DS Theoretical (mol%)	IEC theoretical (meq/g)	DS RMN (mol%)	IEC RMN (meq/g)
SPAESulfone-N-1.1	57%	1.1	67%	1.2
SPAESulfone-N-1.3	80%	1.3	81%	1.3
SPAESulfone-S-1.44	100%	1.44	-	-

III.7.2. Determination of IEC by titration

The same methods were used as mentioned in chapter II. Table III.7.2.1 shows results that confirm good relation between experimental and theoretical IEC values.

Table III.7.2.1. Theoretical and experimental IEC values of SPAESulfone.

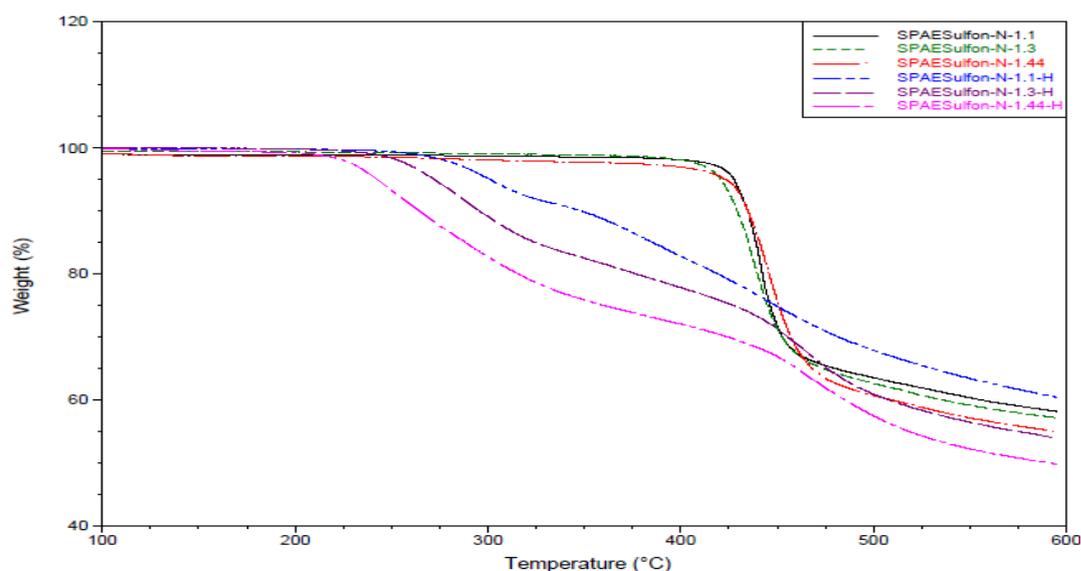
copolymer	SPAESulfone N-1.1	SPAESulfone N-1.3	SPAESulfone N-1.44	SPAESulfone S-1.1
IEC theoretical (meq/g)	1.10	1.30	1.44	1.10
Exper.IEC _{Aqu}	1.17±0.06	1.08±0.05	1.37±0.07	1.25±0.06
Exper.IEC _{Non-aqu}	1.12±0.05	1.22±0.06	1.44±0.07	1.10±0.06

± 5% of error

III.8. Thermal stability of SPAESulfone

Figure III.8.1, a) shows the TGA curves of copolymers. One step weight loss platforms were observed for all of the copolymers in potassium form. In particular SPAESulfone-N-1.1, SPAESulfone-N-1.3 and SPAESulfone-N-1.44 presented T_d values of 428°C, 420°C and 423°C, respectively. The weight loss was due to the degradation of the polymer main chain. Figure III.8.1, a) also shows TGA curves of polymers in acid form (ex: SPAESulfone-1.1-H). The polymers in acid form displayed two weight loss steps. The first one was assigned to the elimination of $-SO_3H$ groups. The second step was attributed to the degradation of the main chain polymer (Table III.8.1). The value of T_d decreases with an increase in the number of pendant sulfonated side-chain groups.

a)



b)

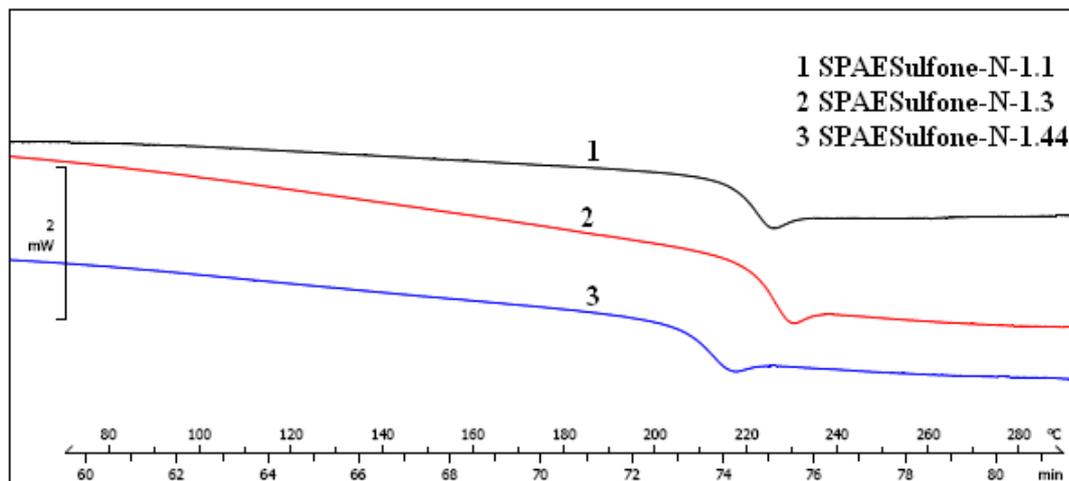


Figure III.8.1. a) TGA thermograms, b) DSC heating traces of the sulfonated poly(arylene ether sulfone)s copolymers.

Figure III.8.1.b shows the DSC thermogram of sulfonated poly(arylene ether sulfone)s. As for the polymers described in the precedent chapter, T_g of these polymers in salt form was higher than 200°C (Table III.8.1).

Table III.8.1. Thermal property data of SPAESulfone-N.

copolymer	SPAESulfone N-1.1	SPAESulfone N-1.3	SPAESulfone N-1.44	SAPESulfone S-1.1
IEC(meq/g)	1.1	1.3	1.44	1.1
T_d (°C)*	428	420	423	419
T_d (°C)**	301	273	243	258
T_g (°C)	220	224	211	232

* - Measured by TGA in the K^+ form, ** - Measured by TGA in the H^+ form

III.9. Water uptake of SPAESulfone

It was observed that the water uptake of SPAESulfone membranes highly depends on IEC and temperature.

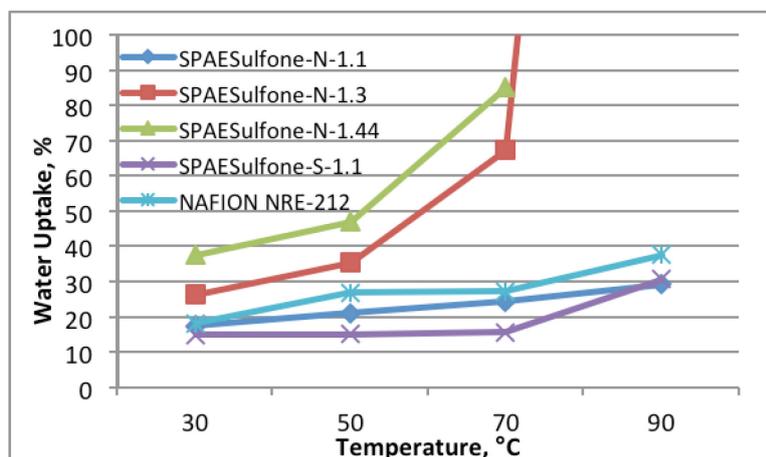


Figure III.9.1. Temperature dependence of water uptake of SPAESulfone-N and SPAESulfone-S membranes.

The membranes with IEC=1.1 meq/g for both polymers showed lower water uptake than that of Nafion. As it is shown in Figure III.9.1, the SPAESulfone-N membranes with high IEC (IEC=1.3 meq/g and 1.44 meq/g) presented a water uptake of 26% and 37% at 30°C, respectively. However, SPAESulfone films start to excessively swell in water at 70°C and 90°C causing its dimensional changes or even dissolution.

Table III.9.1. Hydration number of SPAESulfone membranes at different temperatures.

copolymer	λ (H ₂ O/SO ₃ H)			
	30°C	50°C	70°C	90°C
SPAESulfone-N-1.1	8	11	12	15
SPAESulfone-N-1.3	11	15	29	211
SPAESulfone-N-1.44	14	18	33	-
SPAESulfone-S-1.1	7	8	8	15

SPAESulfone with high IEC showed hydration numbers similar to Nafion at 30°C and 50°C ($\lambda=11$ and $\lambda=16$, respectively). Copolymer with sulfone moieties in the structure showed very similar absorption of water molecules than that of polymer with the same IEC but with nitrile groups in the polymer.

III.10. Proton conductivity of the SPAESulfone

The proton conductivity for SPAESulfone membranes was measured at different temperatures. With increasing temperature and RH the proton conductivity increased. This phenomenon was more significant at higher temperature (Table III.10.1).

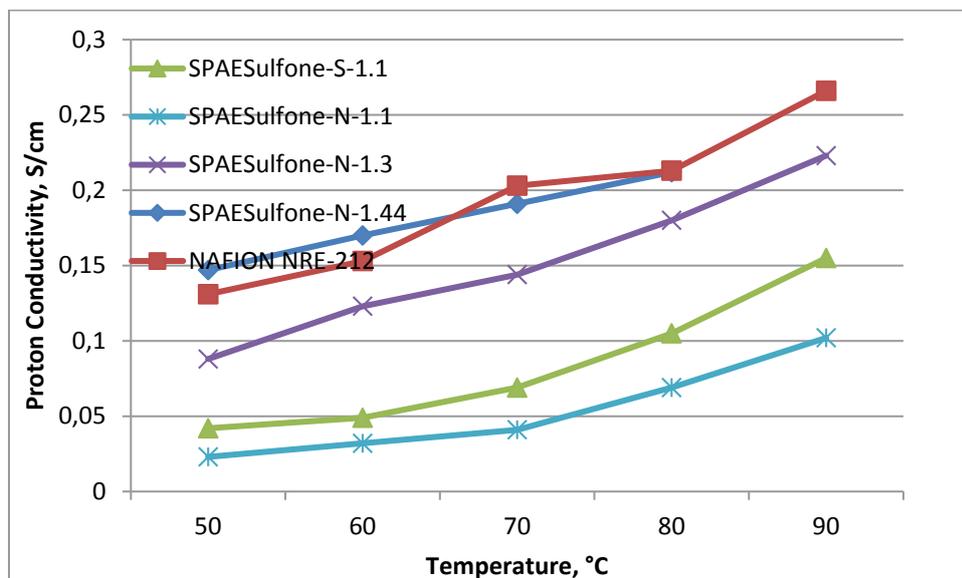


Figure III.10.1. Proton conductivity as a function of temperature of the SPAESulfone membranes and Nafion NRE-212 at different temperature under 95% relative humidity.

As it can be seen in Figure III.10.1, the membranes SPAESulfone-S-1.1 show higher proton conductivity than that of SPAESulfone-N-1.1. Proton conductivity of the sulfonated membranes seems to depend on the chemical polymer structure. SPAESulfone-N-1.44 membrane showed very similar proton conductivity to the Nafion NRE-212. Unfortunately, because of high water uptake of SPAESulfone-1.44 membrane during the measurement at 90°C under 95% RH was decomposed. To high swelling influences lower proton conductivities at higher temperatures.

Table III.10.1. Proton conductivities of sulfonated SPAESulfone copolymers.

Temp.	Copolymer											
	SPAESulfone-N-1.1			SPAESulfone-N-1.3			SPAESulfon-N-1.44			SPAESulfon-S-1.1		
	Proton conductivity (mS/cm)											
	Relative Humidity											
	50%	70%	95%	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	12	20	23	61	79	88	128	134	147	38	40	42
60°C	26	30	32	89	115	123	162	169	170	36	46	49
70°C	34	38	41	122	139	144	152	190	191	56	64	69
80°C	53	65	69	135	176	180	190	207	212	89	101	105
90°C	89	98	102	232	234	223	160	190	-	136	149	155

III.11. Conclusion

A new monomer deriving from the FPSAB-K compound was obtained from three steps synthesis scheme. A model compound study showed that the 3,4'-FPSAPS-K has higher reactivity than the sulfonated monomer described in chapter II. For this reason polymerisation was carried out at 140°C which allowed to obtain polymers with high T_g and good thermal stability. From all polymers, we were able to prepared tough membranes meaning that these polymers have relatively high molecular weight. Based on the water uptake and ionic conductivity investigation the membranes with the IEC of 1.3 meq H^+ /g offer the better compromise.

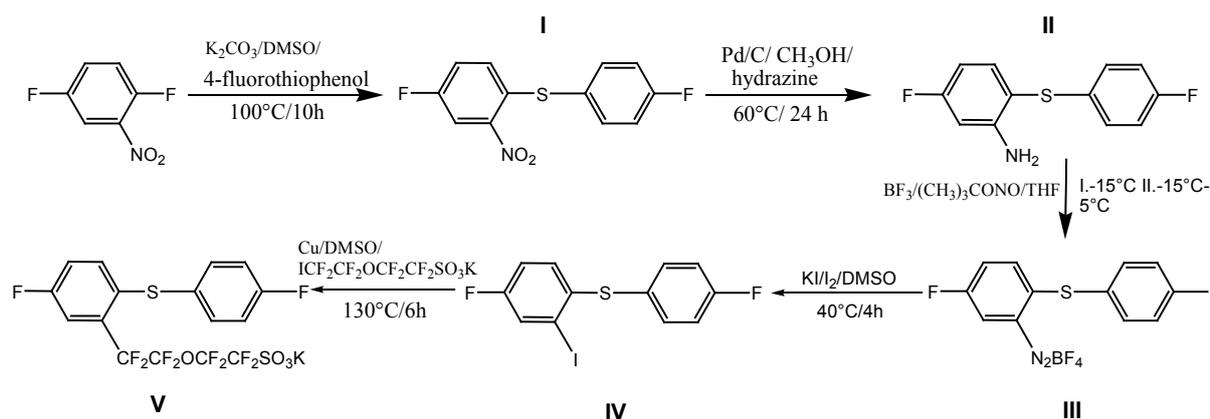
Chapter IV. Synthesis of sulfonated poly(arylene ether sulfide)s

IV.1. Introduction

Parmi les nombreux travaux publiés, consacrés aux polymères aromatiques sulfonés et développés pour l'application membrane de piles à combustible, certains d'entre eux[80] font état de l'intérêt d'incorporer dans la chaîne des motifs diphenylsulfure pour piéger les radicaux susceptibles de se former durant le fonctionnement d'une pile. En effet, l'interaction avec les radicaux qui se présenteraient sous la forme HO \cdot se traduirait par une oxydation de la fonction sulfure en sulfoxyde voire sulfone. Dans ce cas, les radicaux, espèces très réactives ne provoqueraient pas la coupure de chaînes qui se traduit par une fragilisation prématurée des membranes. L'idée de concevoir des polymères aromatiques contenant des motifs diphenyl sulfure et avec des chaînes latérales perfluoroalkyle sulfonées, nous est donc apparue intéressante et potentiellement réalisable à partir d'un composé intermédiaire utilisé pour la synthèse du monomère 3,4'-FPSAPS-K décrit dans le chapitre précédent (II.2.1). Pour cela nous nous sommes inspirés des travaux de Knauss[81]. Après plusieurs tentatives de polymérisation, malheureusement, tous les essais de polymérisation tentés se sont soldés par un échec. Nous avons supposé que les difficultés pour polymériser ce précurseur étaient peut être dû au fait d'avoir un des groupements partant fluor en méta du pont disulfure. En conséquence, nous avons envisagé la synthèse d'un précurseur présentant cette fois les deux groupements partant fluor en para de ce pont sulfure. Dans ce chapitre est donc discuté la synthèse en plusieurs étapes d'un nouveau monomère porteur d'un motif perfluoroalkyl sulfoné ainsi que la préparation de poly(arylene sulfure)sulfonés à partir de ce monomère et différents co-monomères. La caractérisation des propriétés de ces polymères dont notamment le gonflement à l'eau et la conductivité ionique est également discutée.

IV.2. Synthesis of 2-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-4,4'-difluorodiphenylsulfide (FPSAPS-K)

However, based on the Knauss's work[[81] the synthesis of this new monomer FPSAPS-K was performed in five steps as illustrated in Scheme IV.2.1.



Scheme IV.2.1. Synthesis of FPSAPS-K.

First 4,4'-difluoro-2-nitrodiphenylsulfide **I** (FNPS) was synthesized via an aromatic nucleophilic reaction involving 1,4-difluoro-2-nitrobenzene and 4-fluorothiophenol as nucleophiles in the presence of potassium carbonate (Scheme IV.2.1). The pure product was obtained in 95% yield. This nitro compound **I** was then reduced to the amine using hydrazine in the presence of the Pd/C as catalyst. The product, FNPS (**II**) was used in the next step which corresponds to the diazotization of amine function. Usually sodium nitrite with mineral acid is used to form diazonium salt in aqueous or organic solution. Because of the unstable character of these diazonium compounds, they are often not isolated and are reacted immediately in further reactions. In the present work, we preferred to use the *t*-butyl nitrite in presence of boron trifluoride etherate as the diazotizing agent. The main interest of the resulting diazonium tetrafluoroborate is its better stability which makes it

possible to carry out transformation reactions in different organic solvents such as DMSO and temperature conditions. Different methods[82, 83] have been reported about the preparation of such diazonium compounds. The product **III** was synthesized according to a previously published methods[84, 85]. However, in our case, the diazotization reaction was performed with an excess of boron trifluoride diethyle etherate. Using the Sandmeyer reaction, the Iodination of compound **III** was achieved in DMSO in presence of Iodine. The general reaction conditions for iodination of diazonium salt were described by Arnoldy[86]. The arenodiazonium product **III** was added drop wise to mixture of KI and I₂ at low temperature to prevent any side reactions. The product 4,4'-difluoro-2-iododiphenylsulfide (FIPS) was used in the next step. This last step which corresponds to the grafting of the sulfonate perfluoroalkyl chain was run via the Ullmann reaction using copper bronze as catalyst as mentioned in chapter II. This reaction was monitored by ¹⁹F NMR. The disappearance of the peak corresponding to fluorin nuclei of I-CF₂-group determined the completion of the reaction (Fig. IV.2.1 a). The overall yield is 70%.

The chemical structure of the intermediate compounds (**I**), (**II**) and (**IV**) was confirmed by proton NMR while the chemical structure of the final product (**V**) was confirmed both by proton and fluorin NMR (see Figure IV.2.2). The FPSAPS-K (**V**) was also analyzed by HPLC coupled with a mass spectrometer. Only one peak was observed with the expected molecular mass as reported in Figure IV.2.3. Based on this result we obtained the FPSAPS-K with a high purity.

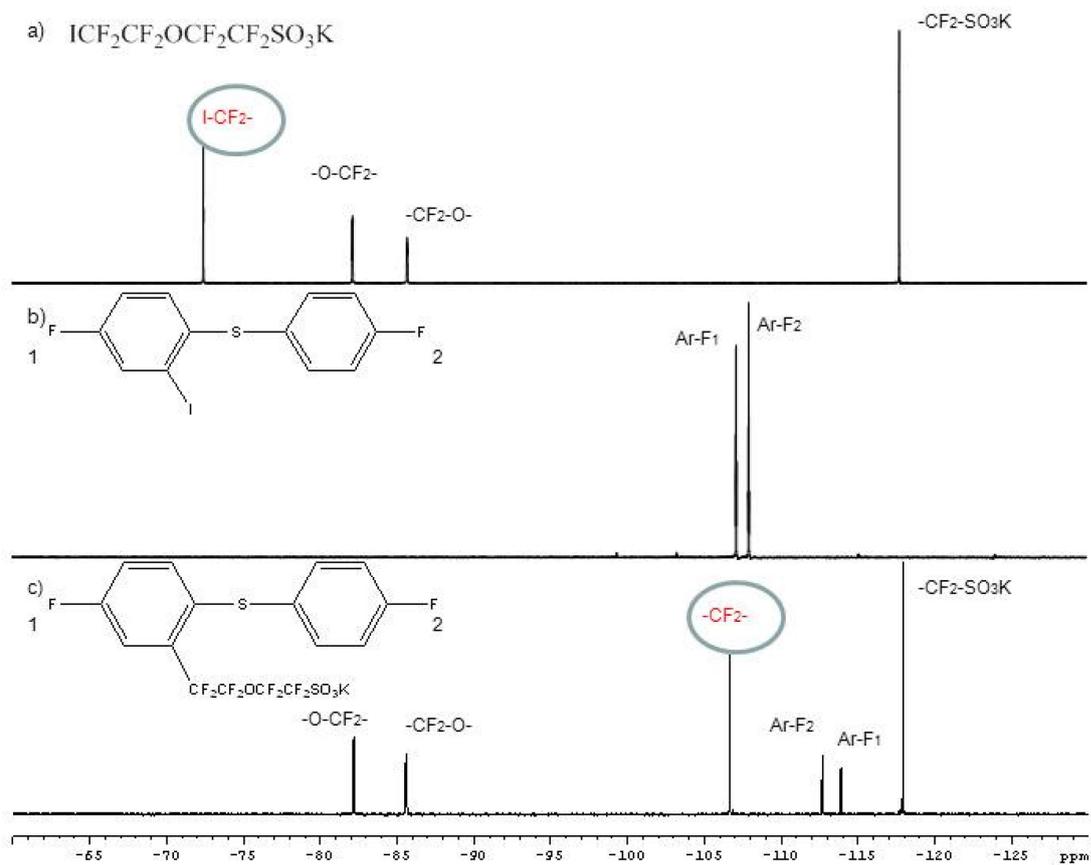
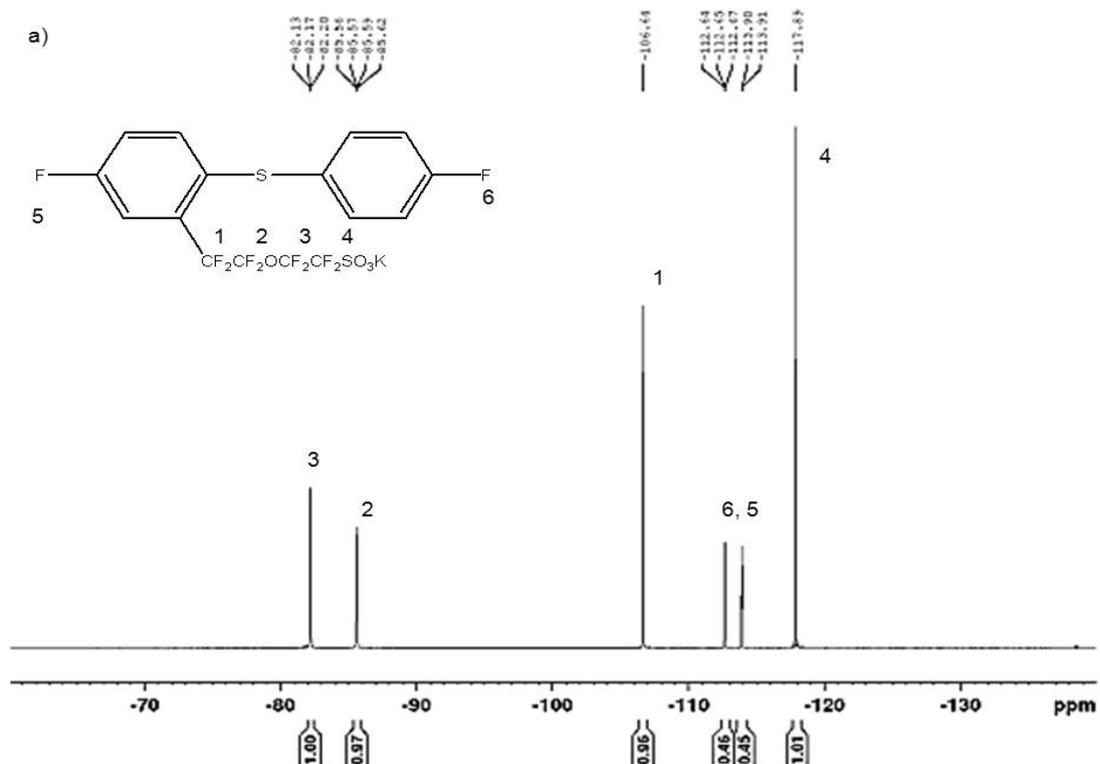


Figure IV.2.1. Superposition of ^{19}F NMR spectra in DMSO-d_6 . a) PSA-K, b) FIPS), c) FPSAPS-K.



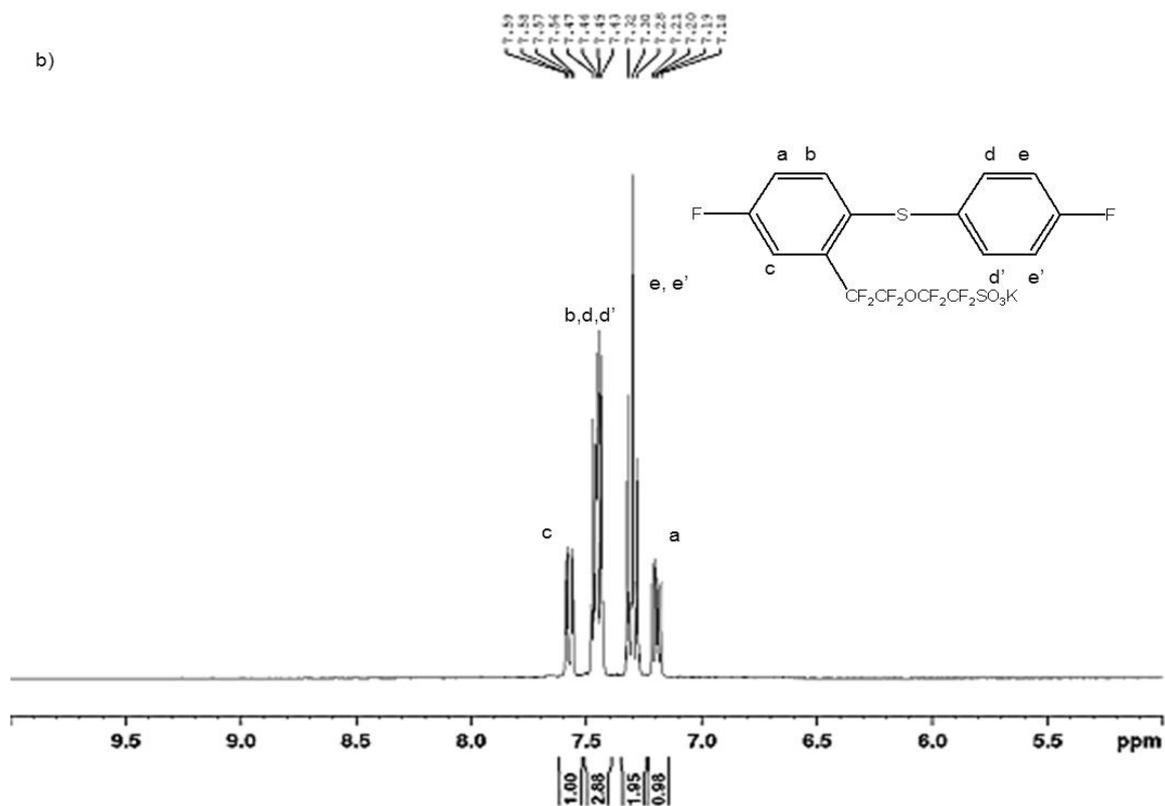


Figure IV.2.2. ^{19}F , ^1H NMR spectra of FPSAPS-K in DMSO-d_6 .

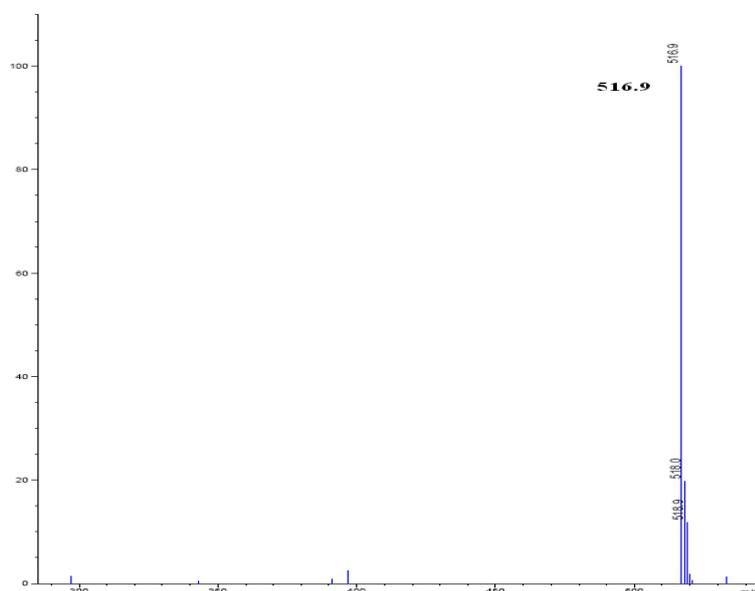
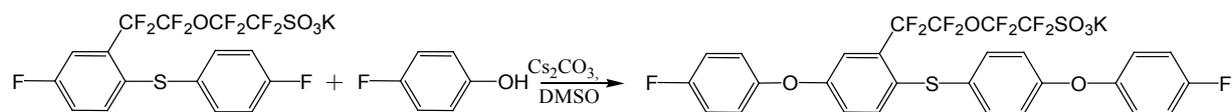


Figure IV.2.3. Mass spectrum of FPSAPS-K monomer.

IV.3. Synthesis of a model compound based on FPSAPS-K



Scheme IV.3.1. Synthesis of a model compound.

As for the other monomers described in the chapter II and III, the reactivity of this monomer towards phenolate compound through a nucleophilic substitution reaction was determined as illustrated in Scheme IV.3.1. Initially, the reaction was carried out at 140°C in DMSO. The progress of the reaction was monitored by ¹⁹F NMR. As it can be seen in Figure IV.3.1, (b) the reaction was uncompleted at 140°C. Indeed, the peaks corresponding to the nuclei labelled F1 and F2 were still present. The intensity of the peak corresponding to F1 was lower than the F2 one, meaning a difference of reactivity between F1 and F2. To get a complete reaction, the reaction mixture was heated to 160°C. In this condition, the peak relative to F1 disappeared rapidly while a longer time was necessary to see the disappearance of the peak corresponding to F2 (see Figure IV.3.1, (c) and (d)).

The greater reactivity of the leaving group F1 can be explain by the electron withdrawing effect of the sulfonated perfluoroalkylgroup grafted on the same phenyl ring in meta position. Although it is well known that the presence of an electron withdrawing group in meta position of the leaving group is much less effective that those in ortho or para position, few research works have been published on the synthesis of poly(aryl ethers) involving difluoroaryl monomer having an electron withdrawing group in meta position. For example Fossum et al.[87] reported on the synthesis of poly(ether sulfone) from 3,5-difluorophenylsulfone. They assumed, to explain the high molecular weight polymer formation, that the electron withdrawing phenylsulfone is activating the electrophilic sites through inductive effects rather than a resonance effect as it is the case for electron withdrawing group in ortho or para position.

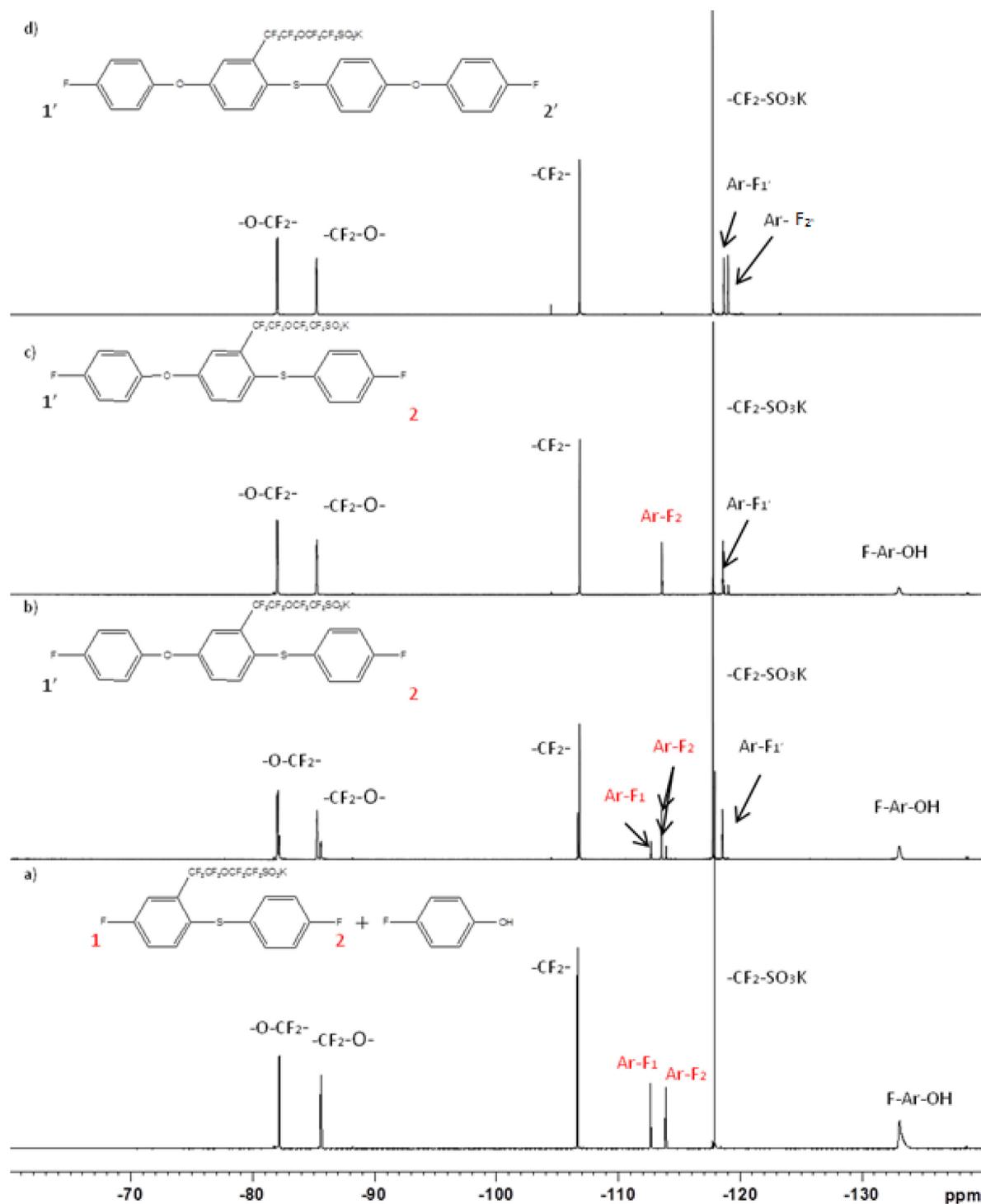
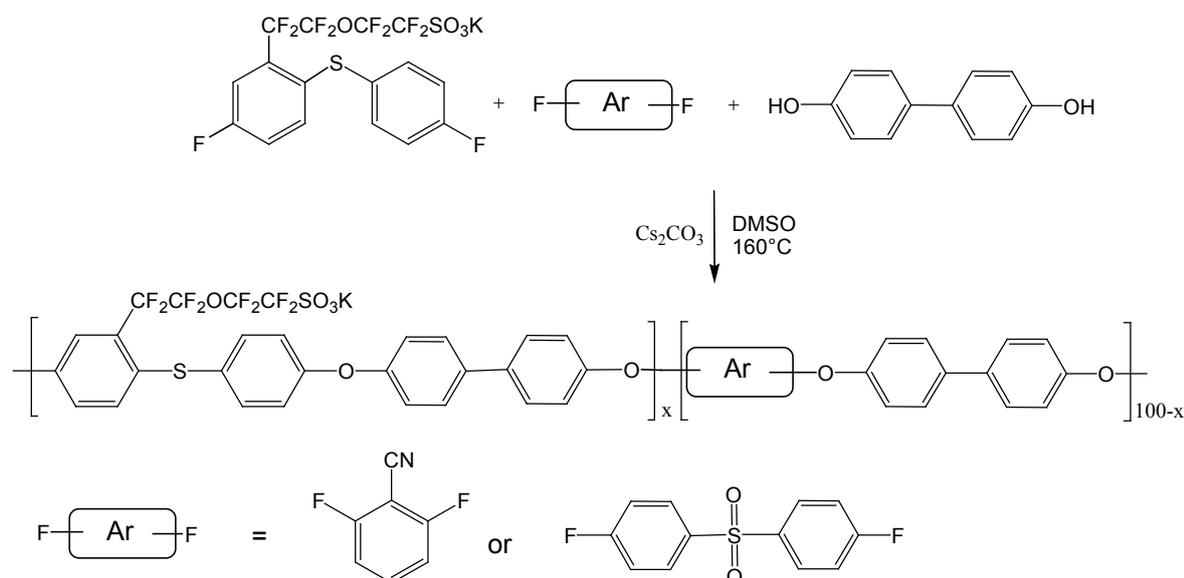


Figure IV.3.1. Spectra of reaction mixture: a) *r.t.*, b) 140°C, after 0 min, c) 160°C after 35 min, d) 160°C after 24h in DMSO-*d*₆.

IV.4. Synthesis of the sulfonated poly(aryl ether sulfide)s copolymers (SPAES)

Based on the Knauss's work[81], the synthesis of different new sulfonated poly(arylene ether sulfide)s copolymers have been envisaged as illustrated in Scheme IV.4.1.

On what we have observed on the synthesis of the model compound, the polymerization reaction to prepare the SPAES copolymers were performed at 160°C in DMSO and in presence of cesium carbonate as base. By varying the molar ratio of FPSAPS-K to nonsulfonated comonomers, copolymers with ion exchange capacity from 1.1 meq/g to 1.5 meq/g were prepared. Two series of SPAES were obtained: sulfonated poly(arylene ether sulfide nitrile)s (SPAES-N) and sulfonated poly(arylene ether sulfide sulfone)s (SPAES-S). Difficulties have been encountered with the synthesis of polymers with IEC=1.3 meq/g for which we did not found clear explanations. Two different methods of polymerization were tested. In the first method all monomers were put together and then the reaction solution was heated at 160°C for 72 hours. After precipitation of the reaction mixture the polymers were isolated as a fine powder from which a brittle membrane was prepared.



Scheme IV.4.1. Synthesis of SPAES copolymers.

In the second approach the polymerization was performed in two-steps. In the first stage, biphenol and sulfonated monomer FPSAPS-K were reacted at 160°C for 24 hours, and then the solution was cooled down. FBN or FPS was added to the mixture and it was heated up to 130°C. The viscosity of the solution increased very quickly and after 2 hours a gel was obtained which was insoluble in various solvents. The polymerization was repeated and stopped before gelling. The obtained polymers were not really soluble in solvents such as DMSO, DMF, DMAc and NMP. To dissolve these polymers a mixture of DMAc and Diglyme was prepared. However, a few days were needed to be completely dissolved.

The chemical structure of the different polymers was confirmed by fluorin and proton NMR. As it can be seen in Figure IV.4.1, the peaks labelled 5 and 6 corresponding to the fluorin leaving groups of the monomer were not appearing on the spectra of the polymers. On the other hand, some peaks relative to nuclei of monomer units were clearly identify on the spectra (see Figure IV.4.2).

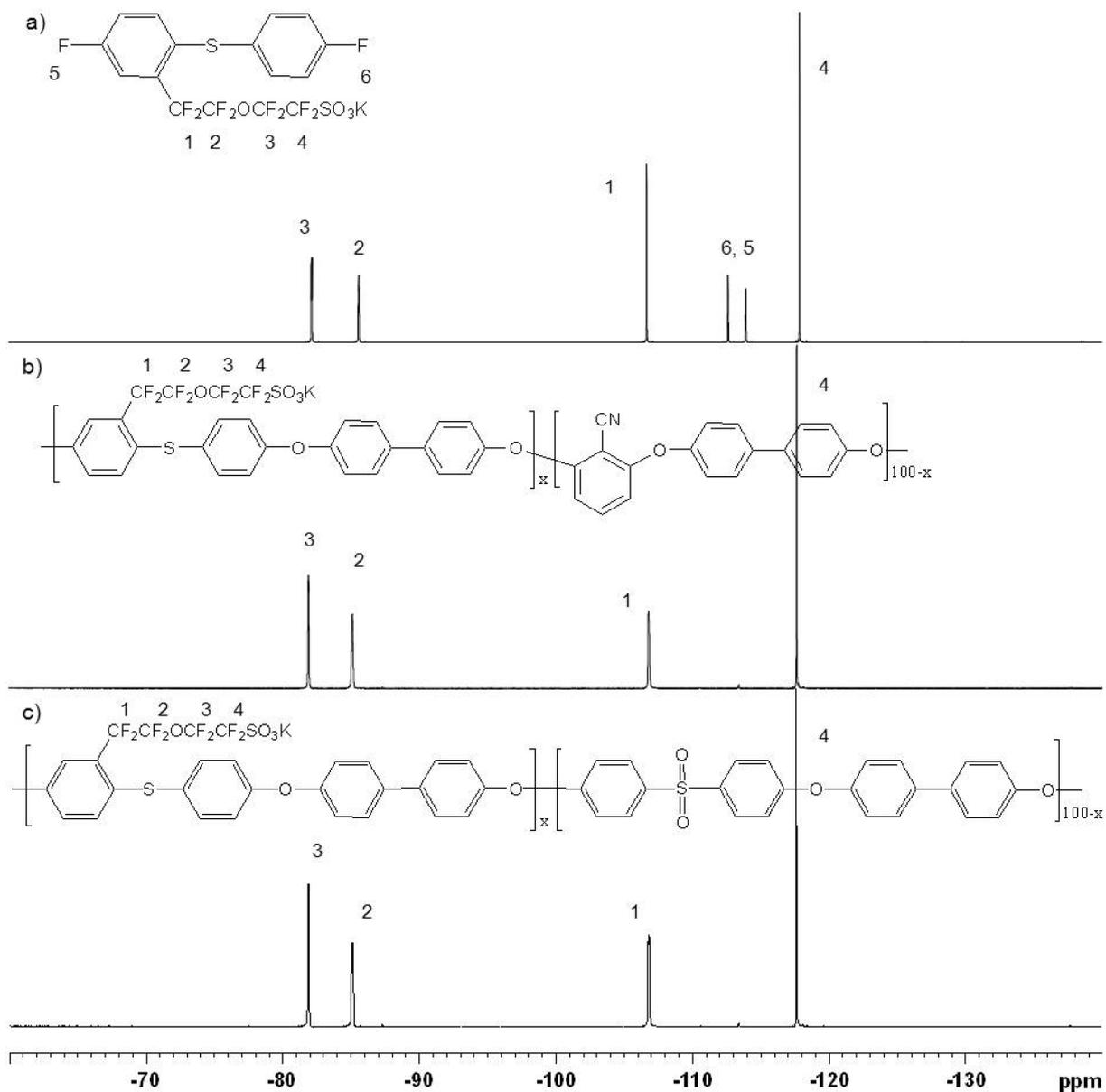


Figure IV.4.1. Spectra ^{19}F NMR: a) monomer FPSAPS-K, b) SPAES-N-1.1, c) SPAES-S-1.1 copolymers in DMSO-d_6 .

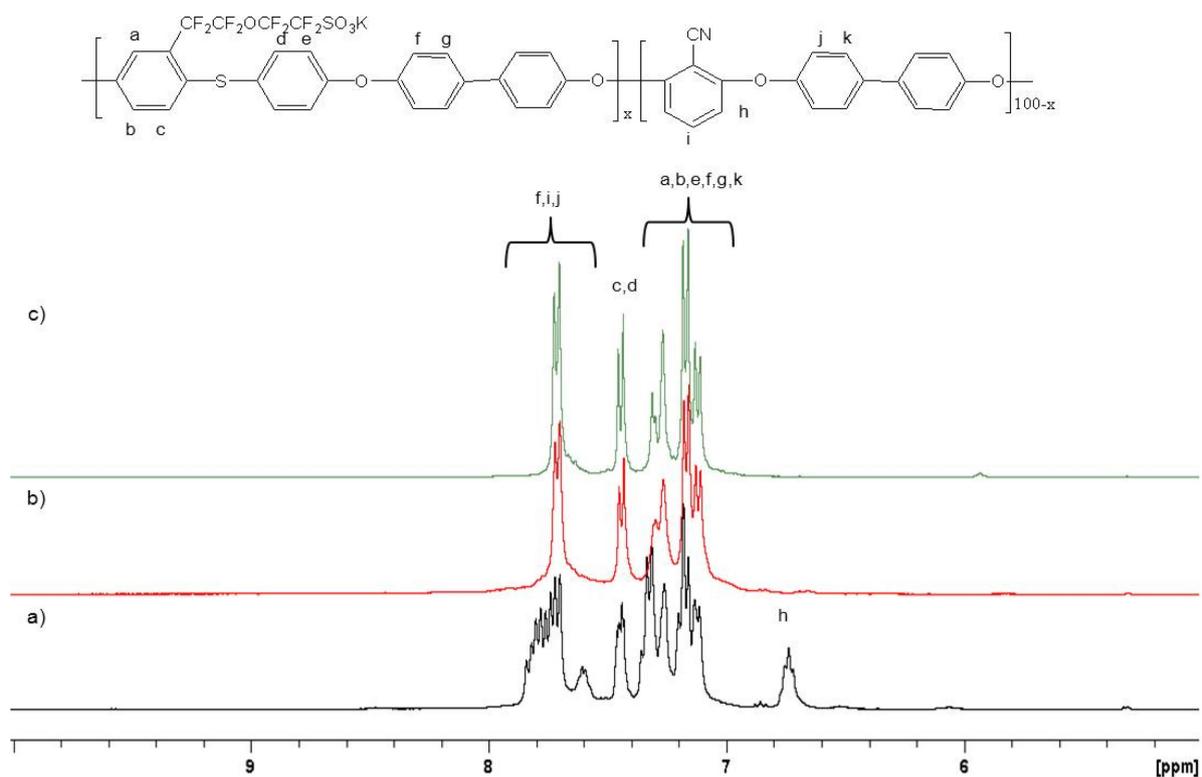


Figure IV.4.2. ^1H NMR spectra: a) SPAES-N-1.1, b) SPAES-N-1.3, c) SPAES-N-1.5 in copolymers DMSO-d_6 .

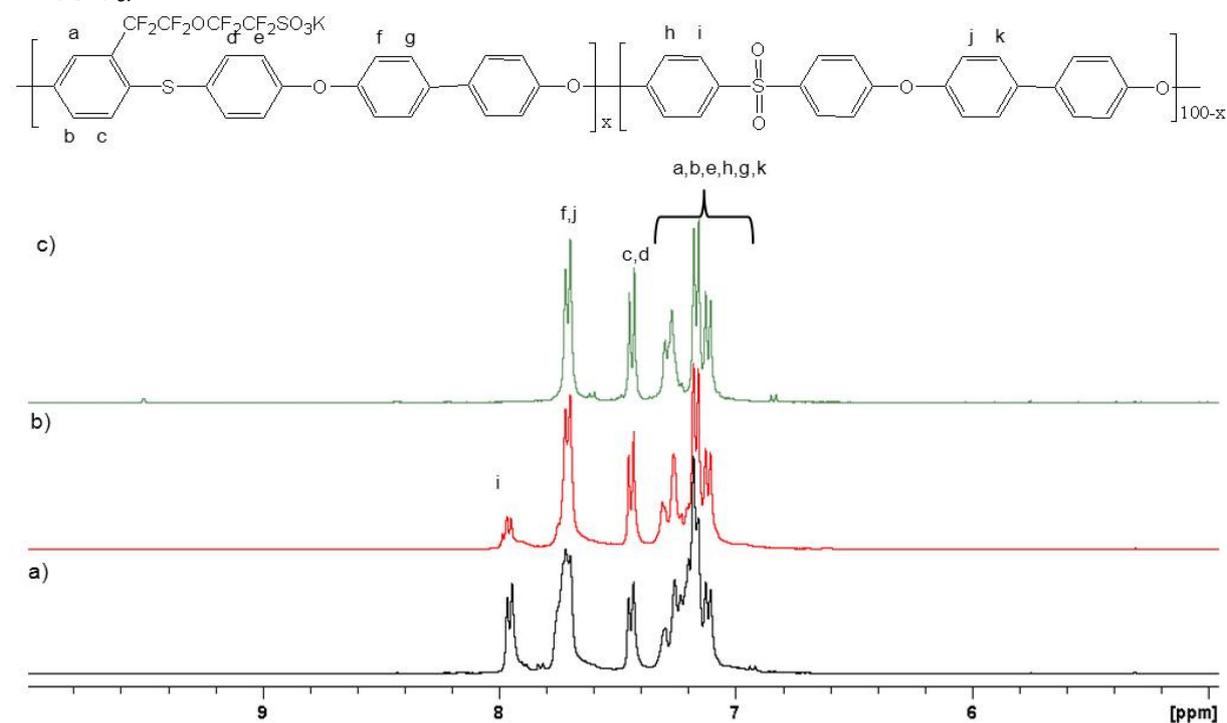


Figure IV.4.3. ^1H NMR spectra: a) SPAES-S-1.1, b) SPAES-S-1.3, c) SPAES-S-1.5 copolymers in DMSO-d_6 .

IV.5. Solubility of SPAES

Sulfonated poly(arylene ether sulfide)s films were prepared by casting solution of polymer dissolved in NMP. The polymers with IEC=1.3 meq/g were dissolved in DMAc/Diglyme (v/v, 50/50) and stirred for a few days.

IV.6. SPAES membranes manufacturing

SPAES films were prepared by casting solution of polymer dissolved in NMP and DMAc/Diglyme. Obtained membranes in K⁺ form gave tough, mechanical resistance material with yellow-brown color. After acidification membranes changed color from yellow to green.

IV.7. Determination of IEC

IV.7.1 Determination of IEC by ¹H NMR analysis

The degree of sulfonation of SPAES copolymers was determined by ¹H NMR. The DS of SPAES-N copolymers were calculated using the formula:

$$DS\% = \frac{(Area\ cd) \div 3}{[(Area\ cd) \div 3 + (Area\ hi) \div 3]} \times 100$$

Area cd - integral value of three protons from sulfonated unit

Area hi - integral value of three protons from non-sulfonated unit

It was not possible to calculate the DS from the spectrum of SPAES-N-1.3 copolymer because the characteristic peaks from unsulfonated units were missing.

Spectra in Figure IV.4.3 were used to determine the DS of SPAES-S copolymers. The percentage of DS of sulfonated unit in SPAES-S copolymers was calculated by:

$$DS\% = \frac{(Area\ cd) \div 3}{[(Area\ cd) \div 3 + (Area\ i) \div 4]} \times 100$$

Area cd - integral value of three protons from sulfonated unit

Area i - integral value of four protons from non-sulfonated unit

Values for calculated DS and IEC for sulfonated poly(arylene ether sulfide)s copolymers are presented in Table IV.7.1.

Table IV.7.1. IEC determination by ^1H NMR spectra.

Copolymer	DS expected	IEC theoretical (meq/g)	DS RMN	IEC RMN (meq/g)
SPAES-N-1.1	54%	1.1	44%	1.0
SPAES-N-1.3	73%	1.3	-	-
SPAES-N-1.5	99%	1.5	100%	1.51
SPAES-S-1.1	62%	1.1	56%	1.0
SPAES-S-1.3	79%	1.3	73%	1.2
SPAES-S-1.5	99%	1.5	100%	1.51

The discrepancy between expected and experimental DS values can be explained in part by the difficulty to determine the accurate integral value due to peak overlapping.

IV.7.2. Determination of IEC by titration

As mentioned early in the precedent chapter, two titration methods were used. However, the titration in non-aqueous solution was found to be more precise method for determination of IEC. Thanks to good solubility of membranes in DGME titration can be more precise compare to aqueous method where exchange of ions is more difficult.

Table IV.7.2.1. Expected and experimental IEC values of SPAES.

copolymer	SPAES-N-1.1	SPAES-N-1.3	SPAES-N-1.5	SPAES-S-1.1	SPAES-S-1.3	SPAES-S-1.5
IEC theoretical (meq/g)	1.1	1.3	1.5	1.1	1.3	1.5
IEC _{Aqu}	0.90±0.05	1.31±0.07	1.37±0.07	1.08±0.05	1.10±0.06	1.28±0.06
IEC _{Non-aqu}	1.05±0.05	1.33±0.07	1.40±0.07	1.10±0.06	1.33±0.07	1.43±0.07

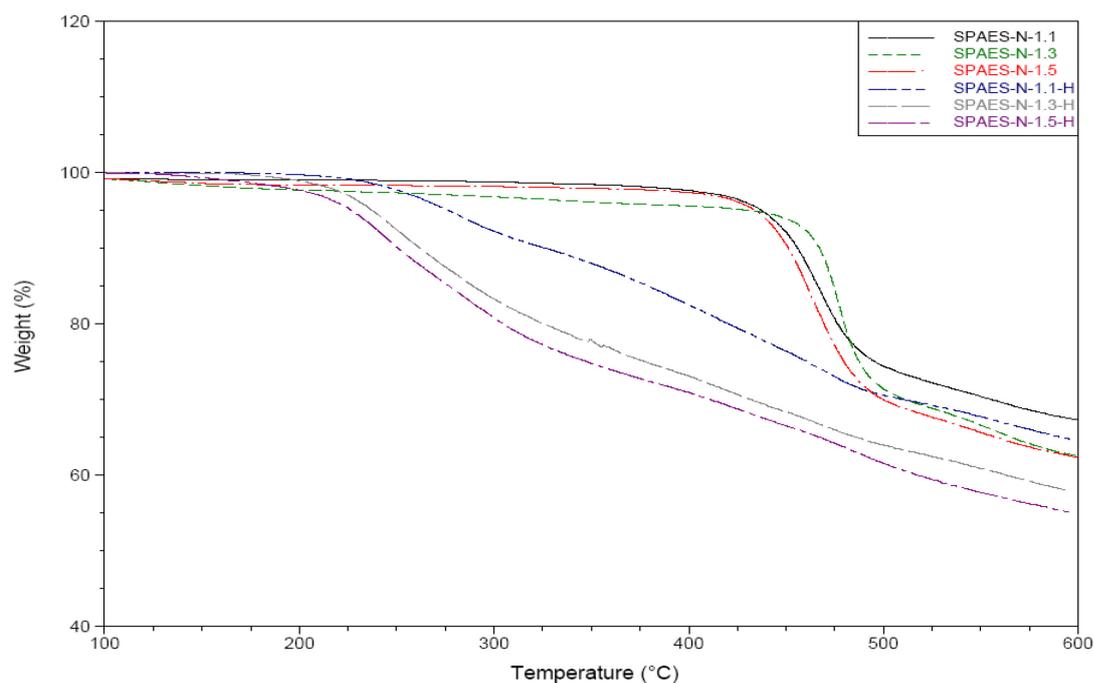
± 5% of error

IV.8. Thermal properties of SPAES

Thermal properties of SPAES copolymers including T_g and thermal decomposition temperatures were investigated by TGA and DSC analyses. As shown in Figure IV.8.1, the polymers in potassium form exhibited a weight loss around 430°C due to main chain loss. SPAES membranes in acid form (ex.: SPAES-N-1.1-H) exhibited a two-step degradation pattern. The first weight loss from 230°C to 280°C may be attributed to sulfonic acid group degradation. The second weight loss was due to the degradation of the main polymer chain (420°C) (see Table IV.8.1).

DSC measurements were achieved to determine the T_g of polymers in K^+ form. Data from second scan were used for T_g evaluation (see Table IV.8.1). It is noteworthy that the T_g of copolymers containing the benzonitrile monomer unit slightly increases with the IEC.

a)



b)

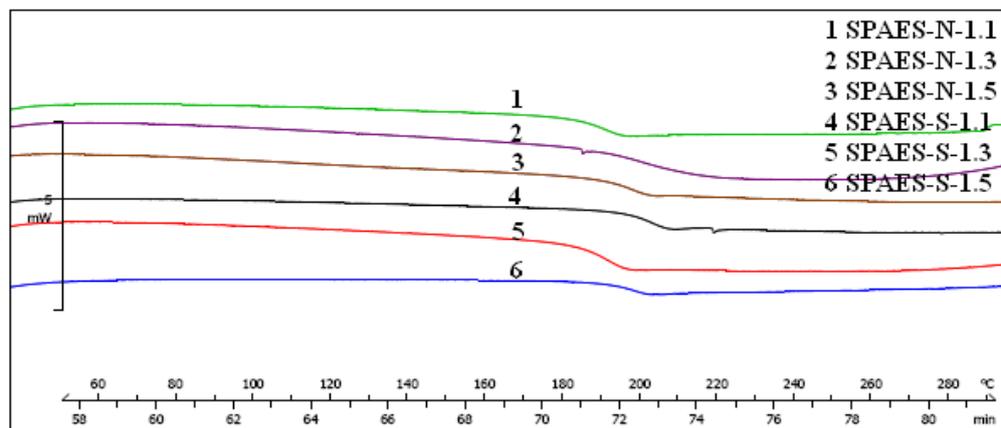


Figure IV.8.1. a) TGA thermogram of the SPAES-N in K^+ and H^+ form, b) DSC traces of the SPAES-N and SPAES-S copolymers in the K^+ form.

In general the grafting of flexible side chains along to a polymer chain drops the T_g , for this reason these results could appear surprising unless we consider that the ionic group interact strongly and so reducing the chain segment mobilities. However, this phenomenon was not observed with the series of polymers containing the sulfone monomer unit. Moreover, it seems to be the inversed effect. It is clear that the T_g variation of these polymers cannot be only related to the presence of ionic side chains. The main chain rigidity should also be taken into account as well as way of preparation of polymers.

Table IV.8.1. Thermal property data of SPAES.

copolymer	SPAES-N-1.1	SPAES-N-1.3	SPAES-N-1.5	SPAES-S-1.1	SPAES-S-1.3	SPAES-S-1.5
IEC(meq/g)	1.1	1.3	1.5	1.1	1.3	1.5
T_d (°C)*	436	429	433	427	442	427
T_d (°C)**	276	236	224	239	245	233
T_g (°C)	189	201	197	202	191	197

T_d - the degradation temperature at 5% weight loss * - T_d measured by TGA in the K^+ form,

** - T_d measured by TGA in the H^+ form

IV.9. Water uptake properties of SPAES polymers

As reported in chapter II.9, the water swelling of the SPAES membranes in acid form was determined at different temperatures. Figure IV.9.1 shows results for all SPAES membranes. For the same series of membranes, as it was expected, higher is the IEC of membranes more water is absorbed.

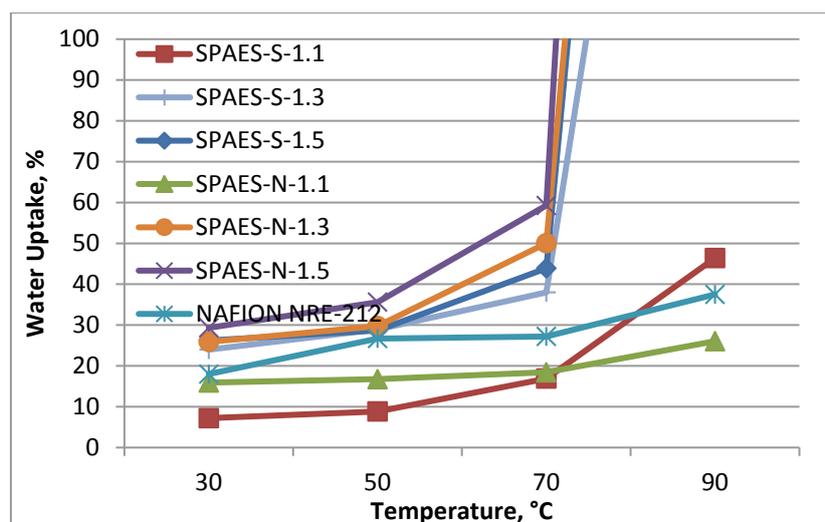


Figure IV.9.1. Temperature dependence of water uptake of the SPAES-N and the SPAES-S membranes.

It worth to note that the membranes SPAES-S-1.1 and SPAES-N-1.1 have a lower uptake than Nafion 212 up to 80°C.

Table IV.9.1. Hydratation number of SPAES membranes at different temperatures.

copolymer	SPAES-N-	SPAES-N-	SPAES-N-	SPAES-S-1.1	SPAES-S-1.3	SPAES-S-1.5
	1.1	1.3	1.5			
λ (H ₂ O/SO ₃ H)						
30°C	8	11	11	4	10	10
50°C	8.5	13	13	4.5	12	11
70°C	9	21	22	8.5	16	16
90°C	13	213	282	23	128	177

IV.10. Ionic conductivity of SPAES polymers

The ionic conductivities of the different membranes were measured as described in chapter II.10. As illustrated in Figure IV.10.1, ionic conductivities of membranes based on SPAES-N and SPAES-S polymers were measured in the temperature range 50 to 90°C under 95% RH.

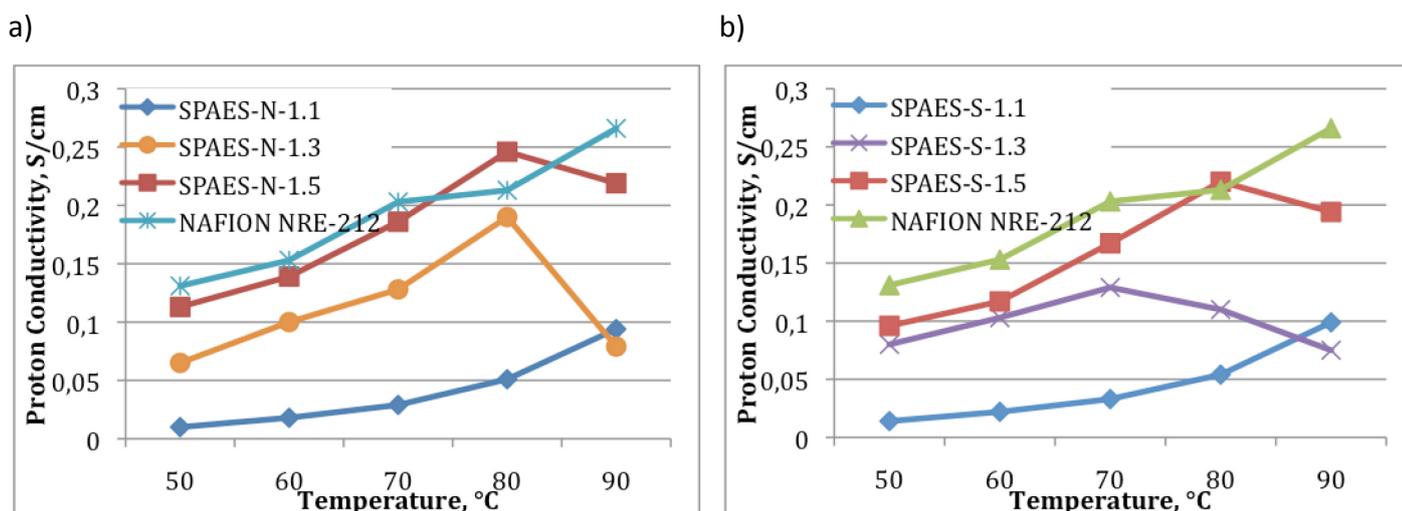


Figure IV.10.1. Proton conductivity as a function of temperature of SPAES membranes and Nafion NRE-212 at 95% relative humidity.

Significant drop of proton conductivity was observed for the samples with IEC 1.3 and 1.5. This behavior can be explained by the high swelling of membranes and Their dimensional changes during analysis. It can be noted that the membranes based on SPAES-N and SPAES-S with an equal IEC do not display a significant conductivity differences. Interestingly enough is the quite similar conductivity of Nafion membrane and the SPAES-N-1.5 and SPAES-S-1.5 membranes up to 80°C show that at low temperature membranes exhibited slight differences in the proton conductivity under different RH. Although, significant changes of the proton conductivity under low and high relative humidity was noticed. SPAES-N containing in the polymer main chain benzonitrile with IEC=1.1 meq/g displayed lower proton conductivity than the copolymer with sulfone in the structure.

Based on the values listed in Table IV.10.1 and IV.10.2, it appears that the conductivity of the membranes at a given temperature do not increase importantly with RH. An interesting observation is the good conductivities of membranes with IEC 1.3 and 1.5 at low RH.

Table IV.10.1. Proton conductivities versus RH and temperature of sulfonated SPAES-N copolymers.

Temp.	Copolymer								
	SPAES-N-1.1			SPAES-N-1.3			SPAES-N-1.5		
	Proton conductivity (mS/cm)								
Relative Humidity									
50%	70%	95%	50%	70%	95%	50%	70%	95%	
50°C	8	9	10	49	60	65	89	107	113
60°C	9	17	18	82	95	100	110	131	139
70°C	21	27	29	104	116	128	158	177	186
80°C	37	46	51	152	184	190	206	237	246
90°C	78	87	94	89	84	79	159	193	219

Table IV.10.2. Proton conductivities versus RH and temperature of sulfonated SPAES-S copolymers.

Temp.	Copolymer								
	SPAES-S-1.1			SPAES-S-1.3			SPAES-S-1.5		
	Proton conductivity (mS/cm)								
Relative Humidity									
50%	70%	95%	50%	70%	95%	50%	70%	95%	
50°C	12	13	14	65	74	80	77	92	96
60°C	17	20	22	98	102	103	104	112	117
70°C	29	31	33	142	155	129	111	154	167
80°C	50	52	54	122	125	110	185	211	220
90°C	81	96	99	136	88	75	236	217	194

IV.11. Conclusion

A new side-chain type sulfonated aromatic monomer, potassium 4,4'-difluoro-2-perfluorosulfonateddiphenylsulfide (FPSAPS-K) was synthesized and polymerized. Two series of sulfonated poly(arylene ether sulfide)s copolymers were successfully synthesized via nucleophilic substitution polycondensation. Obtained copolymers showed high T_g around 200°C. The resulting polymers gave flexible and tough membranes by solution casting. Membrane SPAES-S-1.1 (IEC=1.1 meq/g, WU=16% at 30°C) showed slightly lower water

uptake than that one of SPAES-N-1.1 (IEC=1.1 meq/g, WU=7% at 30°C) and Nafion at a lower temperature. Membranes with a high ion exchange capacity swell intensively at 90°C.

The proton conductivity of the SPAES membranes seems to more dependent on relative humidity than that of Nafion NER-212. SPAES-N containing in the polymer main chain benzonitrile with IEC=1.1 meq/g displayed lower proton conductivity than the copolymer with sulfone in the structure. The SPAES-N-1.5 membrane shows higher proton conductivity (246 mS/cm) than that of Nafion NER-212 (213 mS/cm) at 80°C under 95%RH. However, SPAES-S-1.5 copolymer showed decreasing performance at 90°C cause by excessive swelling of the membrane.

Chapter V. Synthesis of sulfonated poly(arylene ether ketone sulfone)s and poly(arylene ether ketone benzonitrile)s

V.1. Introduction

Compte tenu de leurs très bonnes propriétés thermique chimique et mécanique, les poly arylène éther cétones ont été à la base de nombreuses études. Dans le domaine des membranes pour pile à combustible, cette famille de polymères aromatiques comme évoquée dans le chapitre bibliographique a fait l'objet de nombreux travaux mettant en évidence leur intérêt comme source alternative aux membranes Nafion. Il nous est donc apparu intéressant de développer de tels polymères porteurs de chaînes latérales perfluorées sulfonées et d'en étudier leurs propriétés. Pour cela, un précurseur diaryl cétone dihalogéné porteur de la chaîne alkyle perfluorée sulfonée a été synthétisé. La préparation de différents poly arylène éthers a été effectuée avec ce monomère original et différents co monomères bisphénol et composés aromatiques difluorés.

V.2. Synthesis of 3-[1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl]-4,4'-difluorobenzophenone (FPSABP-K)

As illustrated in Figure V.2.1, the design of a sulfonated perfluoroalkyl containing benzophenone compound was considered.

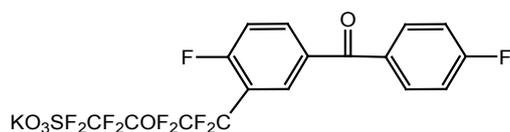
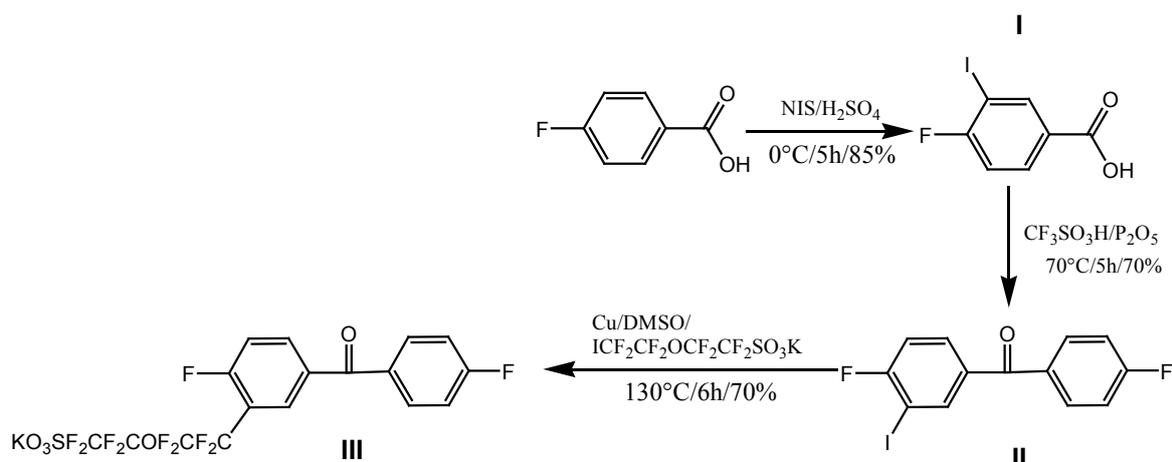


Figure V.2.1. FPSABP-K.

This FPSABP-K monomer was synthesized through a three step process as illustrated in Scheme V.2.1. Initially, the commercially available fluoro benzoic acid compound was converted into corresponding iodinated product (I). With the reaction conditions used, a regioselective iodination was observed[88]. This intermediate compound was then reacted with fluorobenzene via a Friedel Crafts reaction to give the halogenated benzophenone (II). Unless to achieve this reaction using the carboxylic chloride derivative of compound (I) and a lewis acid as catalyst, we found more convenient to use it directly in a presence of Eaton's reagent which is a super acid known to be a good condensating reaction medium in organic synthesis and even in polymer synthesis[89].



Scheme V.2.1. Synthesis of FPSABP-K.

Finally, the desired product was obtained by grafting the sulfonated perfluoroalkyl group on the compound (II) via an Ullmann reaction as already mentioned in the former chapters II, III and IV. The optimal conditions (molar ratio) used for this cross-coupling reaction between PSA-K and compound (II) were: PSA-K/compound (II)/copper bronze/2,2'-bipyridine, 1.0/1.3/3.0/0.2. The reaction was monitored by ^{19}F NMR. Disappearance of the peak

corresponding to the fluorin nuclei of the I-CF₂ group indicated the completion of the reaction (see Fig. V.2.2).

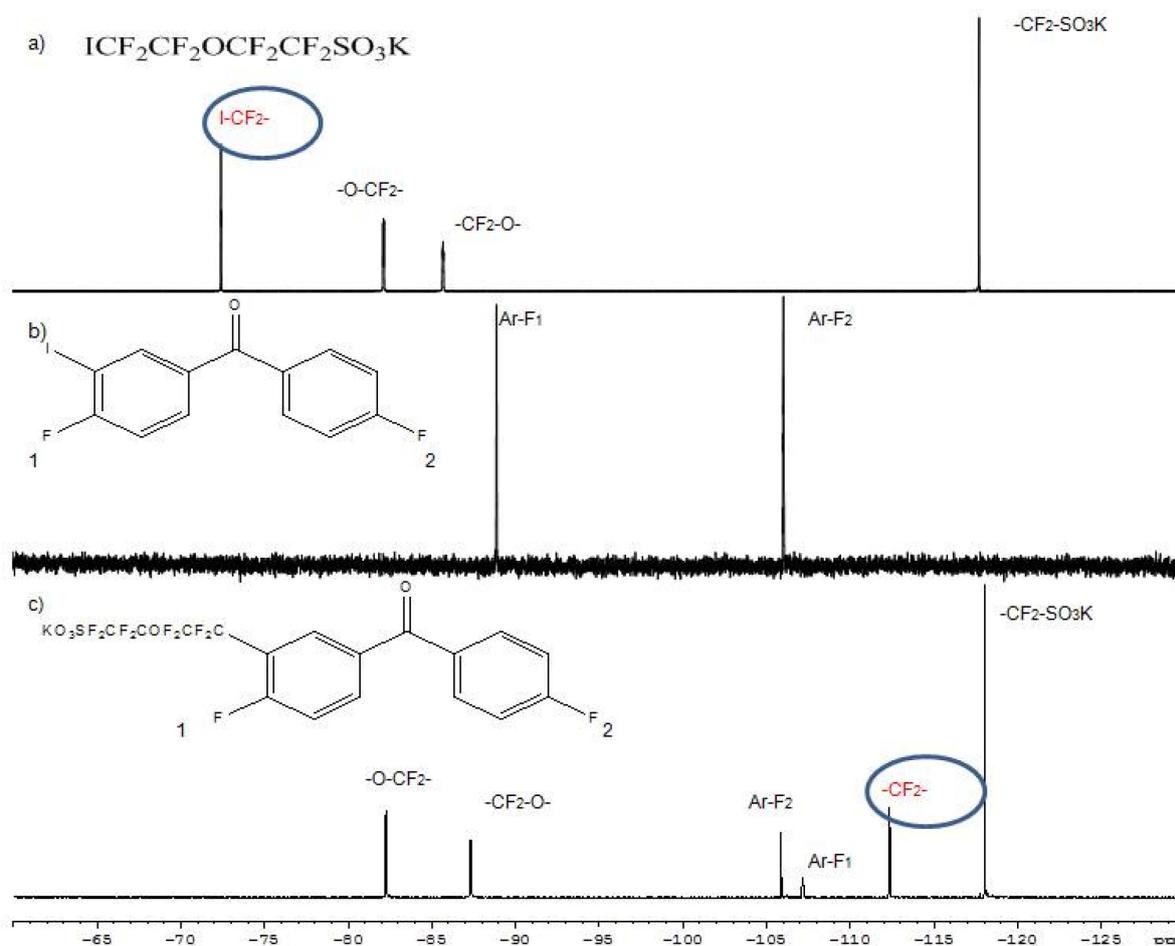


Figure V.2.2. Superposition of ¹⁹F NMR spectra in DMSO-d₆. a) PSA-K, b) FIBP, c) FPSABP-K.

The structure of each intermediate compound and the desired product was confirmed by ¹H NMR. As it can be seen in Figure V.2.3, each peak was assigned to the different protons of the FPSABP-K compound. ¹⁹F NMR was also performed to confirm the grafting of the sulfonated perfluoroalkyl group.

As for the other monomers afore mentioned, one analysis was achieved by HPLC coupled with a mass spectrometer to control its purity. Only one peak was observed by UV detection with the correct mass (see Fig. V.2.4).



Figure. V.2.3. ¹⁹F (top), ¹H NMR (bottom) spectra in DMSO-d₆ of FPSABP-K.

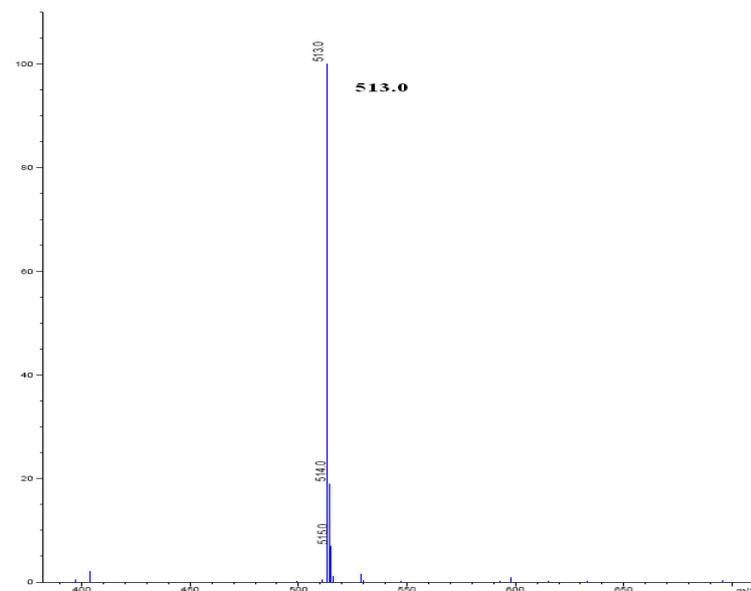
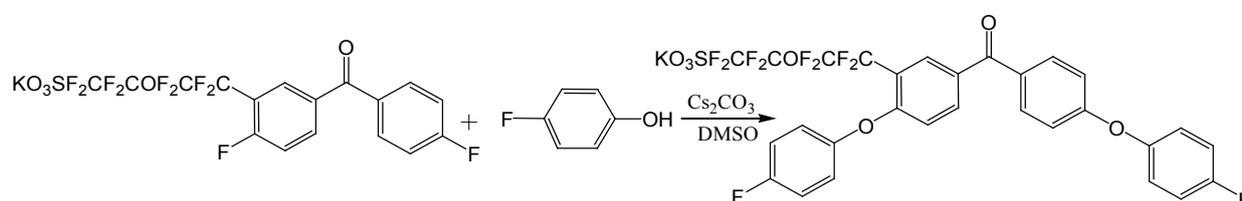


Figure V.2.4. Mass spectrum of FPSABP-K monomer.

V.3. Synthesis of model compound from FPSABP-K monomer

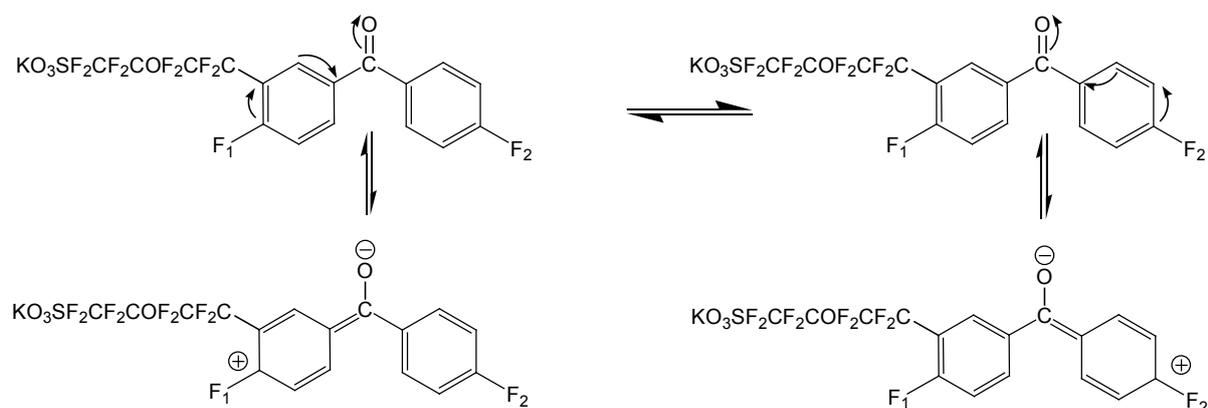
Like the other sulfonated monomers presented in the former chapters, the reactivity of FPSABP-K monomer was tested through a model synthesis involving here also the 4-fluorophenol (FP) in presence of cesium carbonate, and DMSO as solvent (see Scheme V.3.1).



Scheme V.3.1. Model reaction between FPSABP-K and 4-fluorophenol.

During the reaction samples were taken off and analyzed by ^{19}F NMR. The Figure V.3.1 shows different spectra corresponding to the reaction mixture at different stages of the reaction. It is interesting to note (see Fig. V.3.1 (a)) that the reaction is running as soon as the reaction mixture is heated. Indeed, as it can be seen in spectrum (a), the intensity of the peak assigned to F1 is very weak and an other peak due to F2 appears corresponding to the mono substituted FPSABP-K intermediate compound. Noteworthy, the high reactivity of the fluorin F1 that lead to complete conversion of FPSABP-K into mono substituted derivative when the reaction temperature reached 80°C (see spectrum (b)). On the other hand, it is also of interest to observe that the reaction goes to completion at not much to 140°C and in very short time. The total disappearance of the peak at -106.2 ppm corresponding to fluorin nucleus F2 in spectrum (d) comes as an evidence that the reaction is finished.

As it was afore mentioned in chapter III about the 3,4'-FPSAPS-K monomer, the high reactivity of the two fluorin leaving groups of FPSABP-K monomer is due to the activation of the electron-withdrawing carbonyl group. Concerning the difference of reactivity between F1 and F2, it could be taken into account the significant contribution of the electron-withdrawing sulfonate perfluoroalkyl group to the nucleophilic activation of C-F1 through an inductive effect (see Scheme V.3.2).



Scheme V.3.2. Electron withdrawing effect of carbonyl group on the electronic density of different phenyl carbone atoms in FPSABP-K.

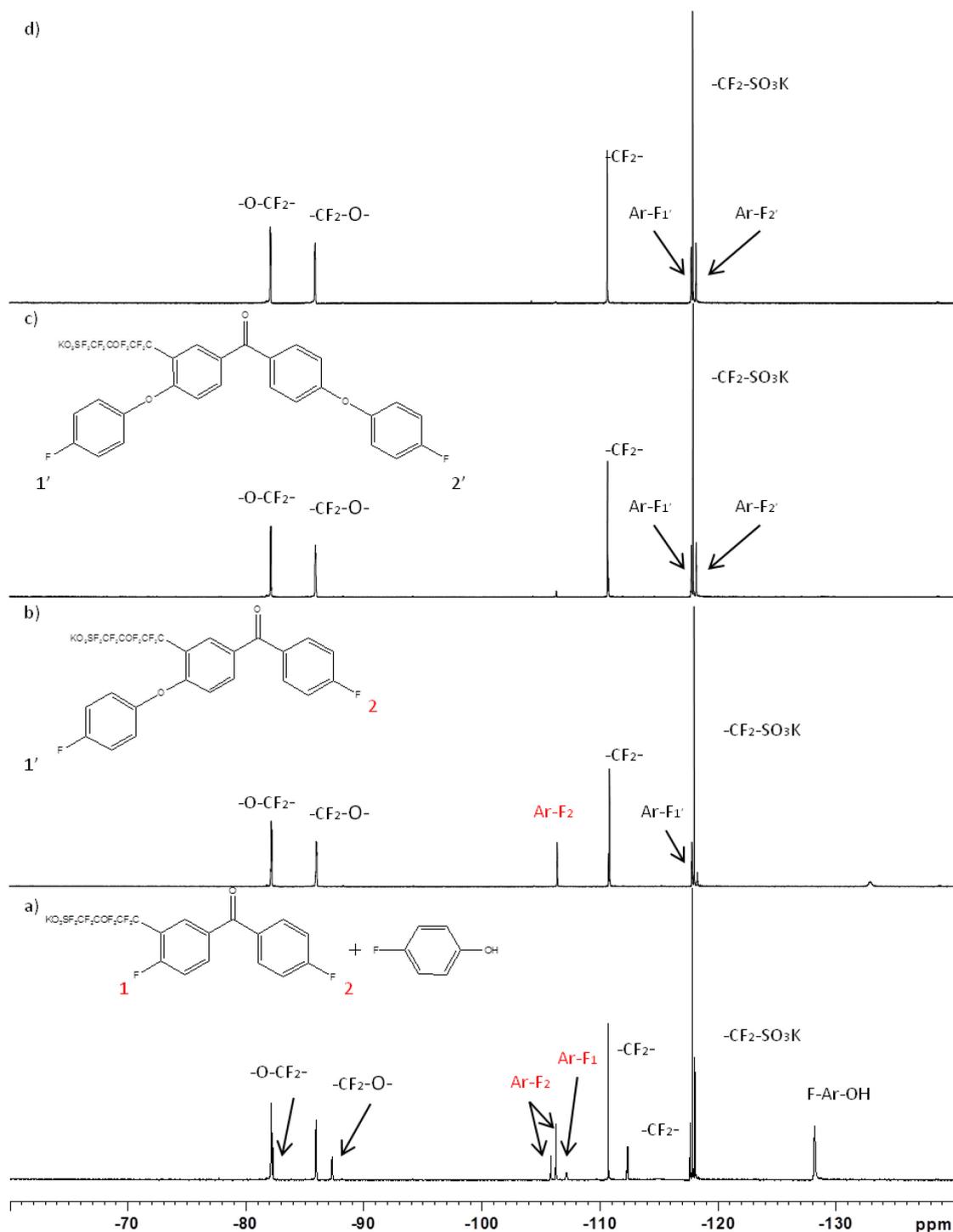
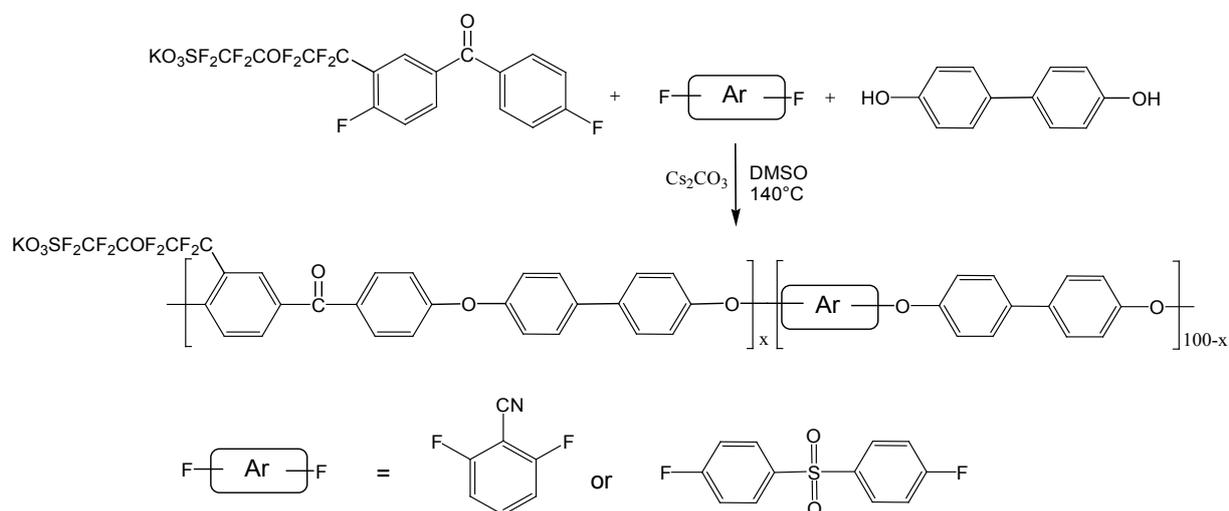


Figure V.3.1. Spectra of samples taken off at different stages of the model reaction between FPSABP-K and 4-fluorophenol: a) when the heating of reaction mixture is started, b) when temperature reached 80°C , c) when temperature reached 140°C , d) after 10 min at 140°C .

V.4. Synthesis of the sulfonated poly(arylene ether ketone sulfone)s and poly(arylene ether ketone benzonitrile)s copolymers

V.4.1. Synthesis of copolymers with biphenol

The sulfonated monomer FPSABP-K was reacted with FBN or FPS and BP (Scheme V.4.1.1). Due to the high reactivity of FPSABP-K shown in the Model Synthesis Section it was thought that the polymerization could be done at 120°C. However, in this case the reaction was extremely slow and controlling of reaction time was difficult. When stirred for too long time the polymer solution began to gel thus forbidding unsupervised overnight reaction. Once a gel was formed, the polymers became insoluble in various solvents. It is difficult to explain the origin of gelatin. In order to limit gel formation different solvents like NMP, DMAc and different salt (potassium carbonate) were tried. However, in each of these cases gels were obtained. Therefore, it was decided to carry out the polymerization at 140°C and this time it can be easily controlled and completed in a day.



Scheme V.4.1.1. Synthesis of sulfonated poly(arylene ether ketone)s copolymers with biphenol.

The viscosity of the polymer solution increased very quickly and the polymerization could be stopped before the formation of a gel. Depending on the difluoro co-monomer involved FPN or FPS, two series of sulfonated poly(arylene ether ketone)s copolymers with ion exchange capacity ranging from 1.1 to 1.5 meq/g were prepared. The structure of these copolymers was confirmed by ^{19}F and ^1H NMR spectra the disappearance of the peaks F_5 and F_6 and the shift of the peak F_1 are observed which confirms a reaction between monomers (Fig. V.4.1.1). These NMR data supports the formation of the supposed structure of the polymers.

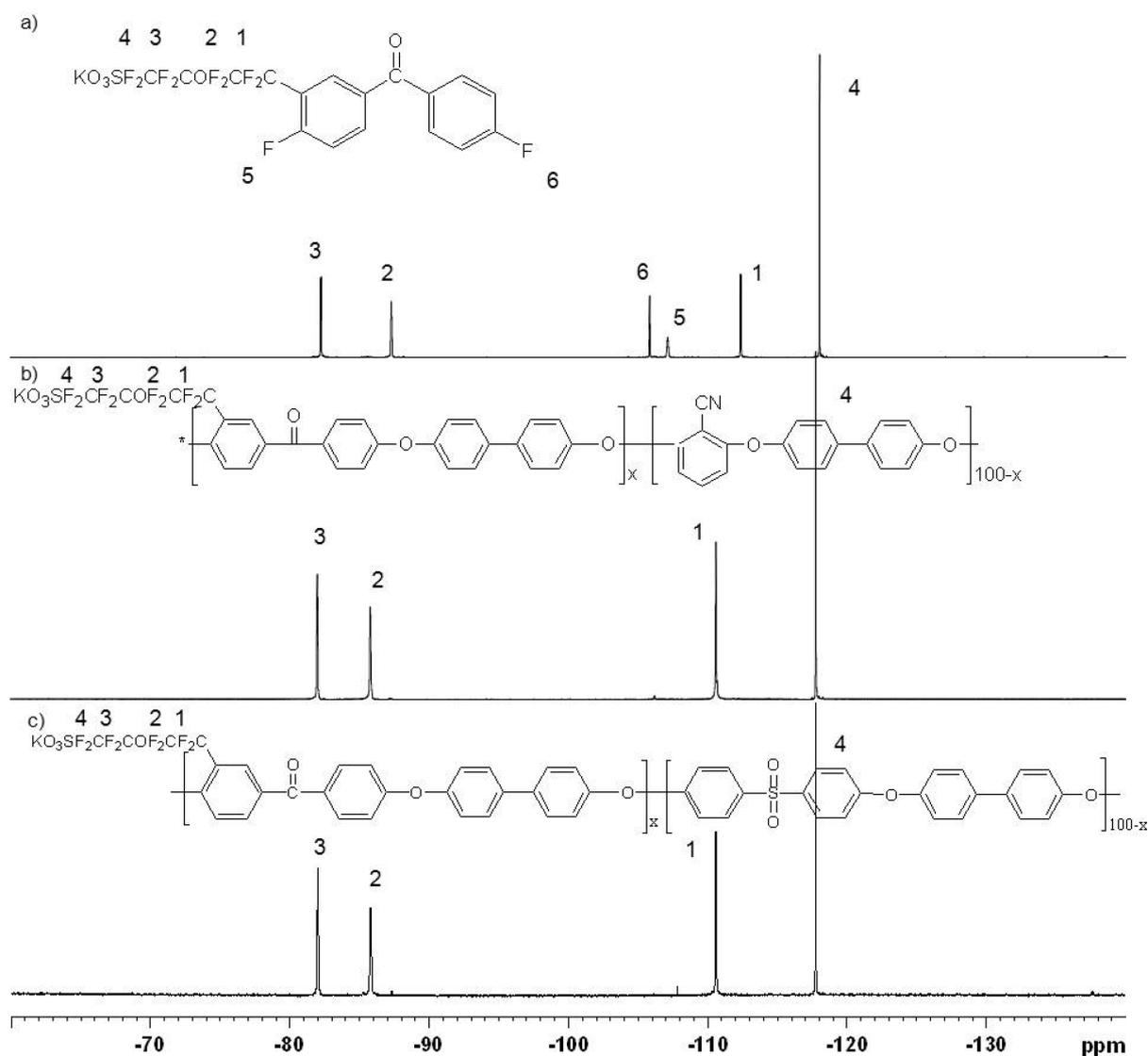


Figure V.4.1.1. Spectra ^{19}F NMR: a) monomer FPSABP-K, b) SPAEK-N-1.1, c) SPAEK-S-1.1 copolymers in DMSO-d_6 .

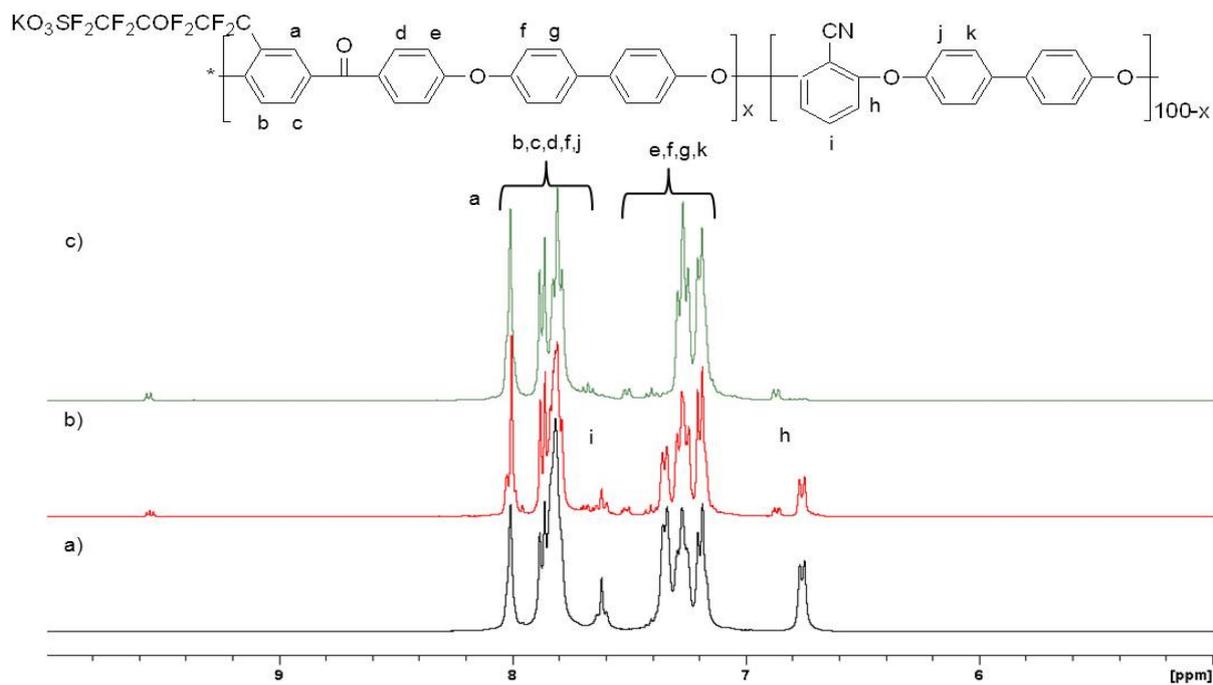


Figure V.4.1.2. ^1H NMR spectra: a) SPAEK-N-1.1, b) SPAEK-N-1.3, c) SPAEK-N-1.5 copolymers in DMSO-d_6 .

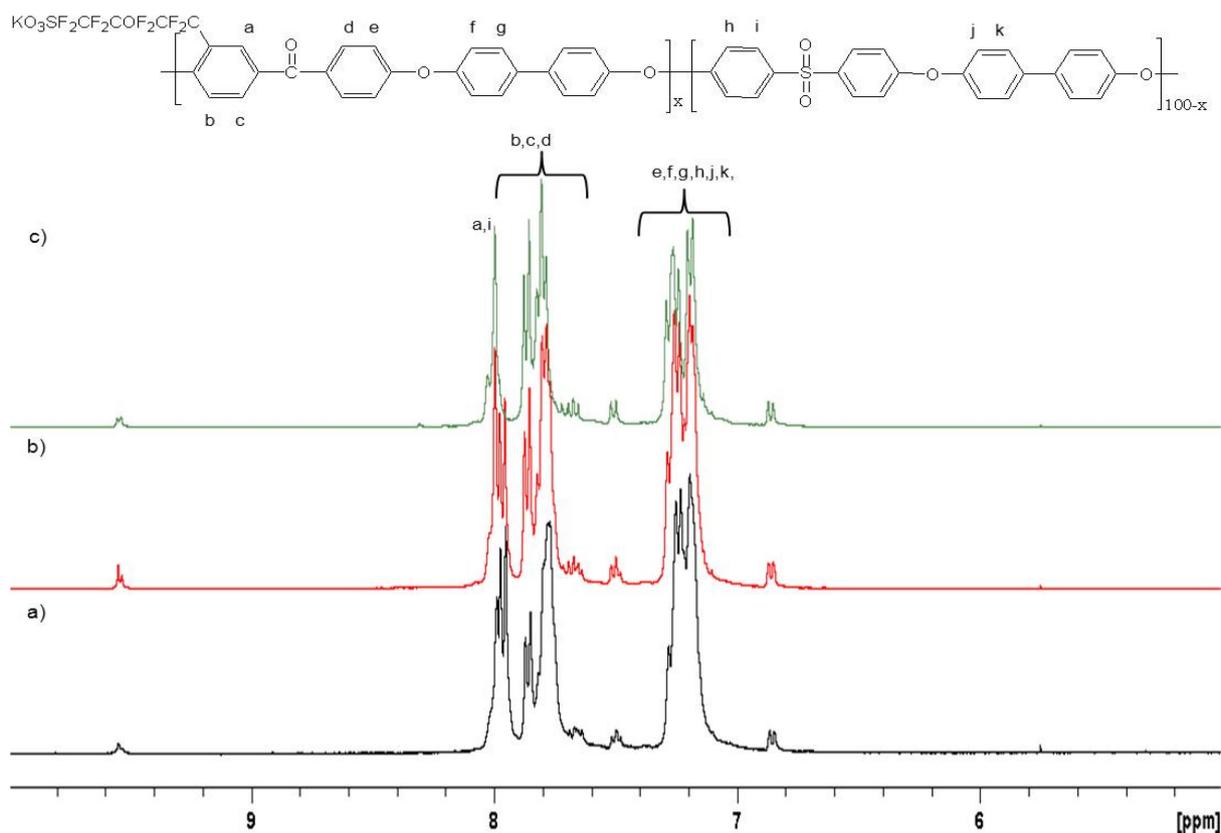
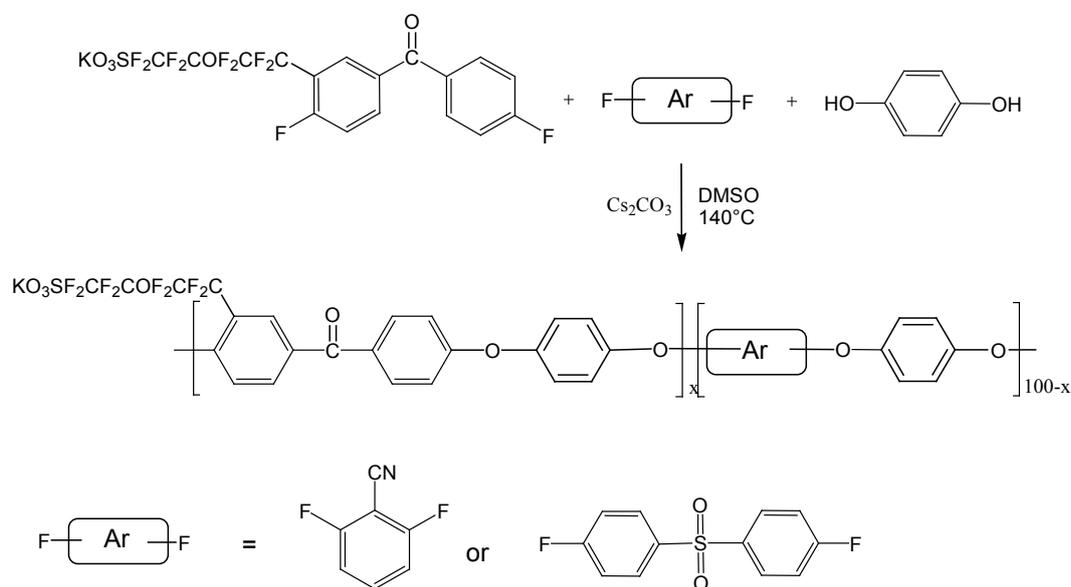


Figure V.4.1.3. ^1H NMR spectra: a) SPAEK-S-1.1, b) SPAEK-S-1.3, c) SPAEK-S-1.5 copolymers in DMSO-d_6 .

V.4.2. Synthesis of copolymers with hydroquinone

With the purpose to obtain SPAEK with higher IEC, comonomer with low molecular mass, hydroquinone (Q) was used instead of biphenol monomer (Scheme V.4.2.1).



Scheme V.4.2.1. Synthesis of sulfonated poly(arylene ether ketone)s copolymers based on hydroquinone.

As the other SPAEK above described, the chemical structure of these polymers was confirmed by ¹⁹F and ¹H NMR spectroscopy, see Figure V.4.2.1, showed the disappearance of the peaks corresponding to fluorides on the aromatic ring of the sulfonated monomer. This confirms that the polymerization was successfully performed.

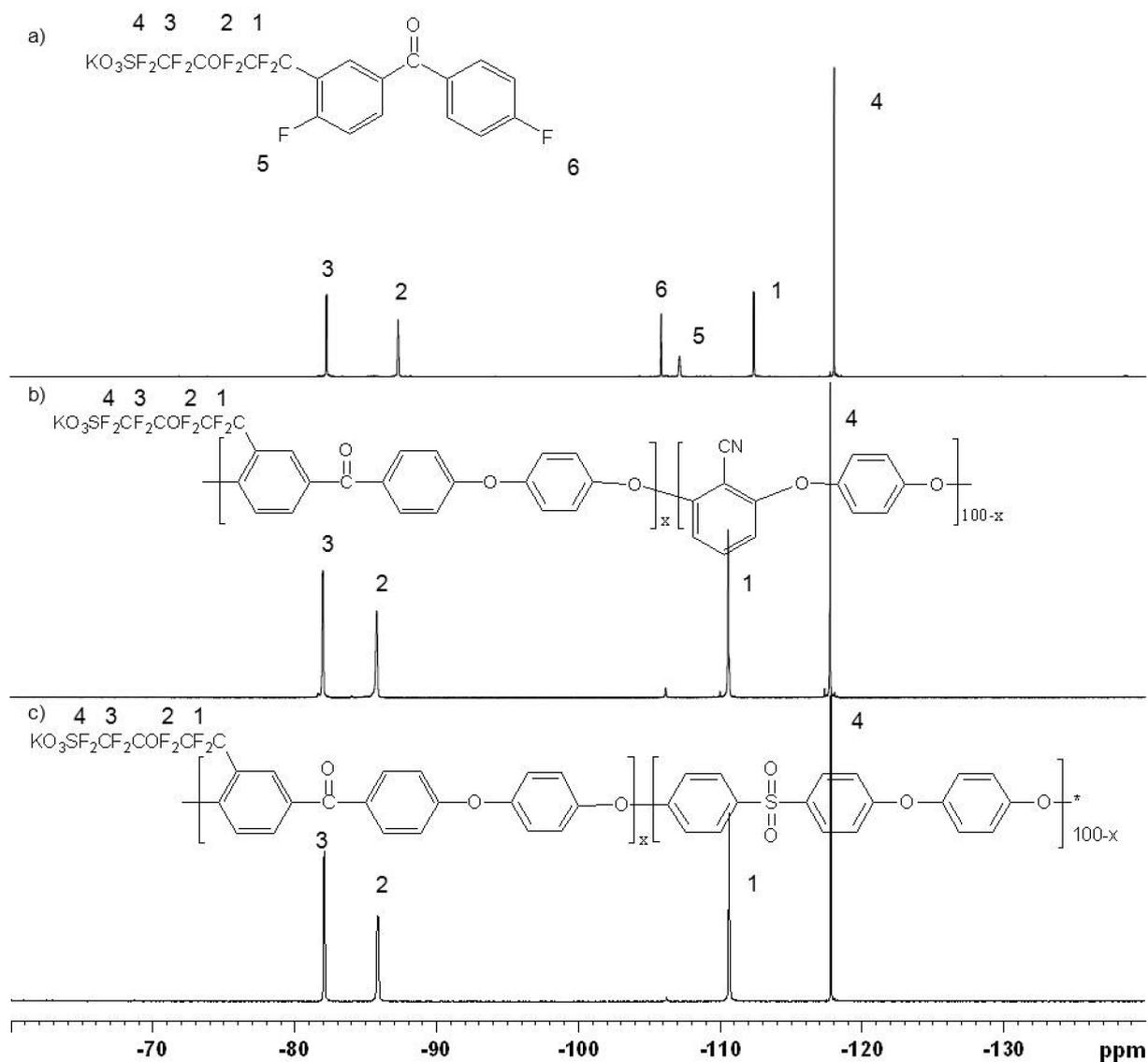


Figure V.4.2.1. Spectra ^{19}F NMR: a) monomer FPSABP-K, b) SPAEK-QN-1.1, c) SPAEK-QS-1.1 copolymers in DMSO-d_6 .

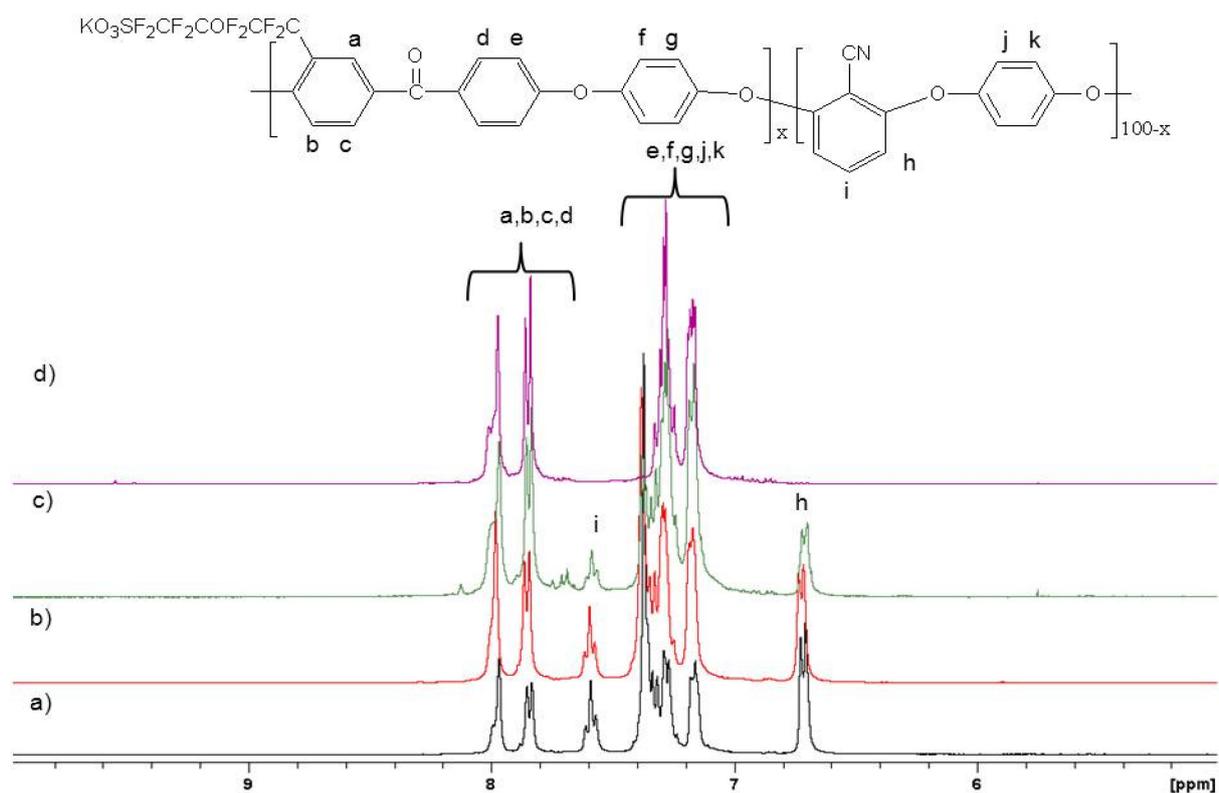


Figure V.4.2.2. ^1H NMR spectra: a) SPAEK-QN-1.1, b) SPAEK-QN-1.3, c) SPAEK-QN-1.5, d) SPAEK-QN-1.71 copolymers in DMSO-d_6 .

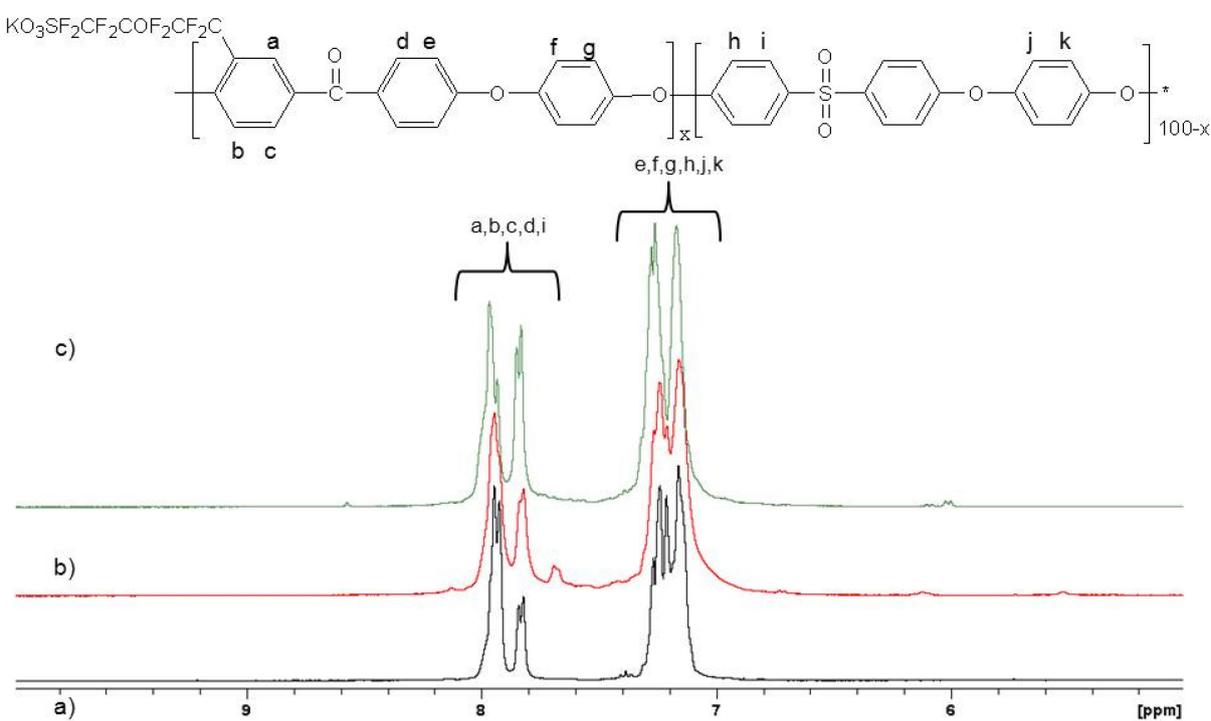


Figure V.4.2.3. ^1H NMR spectra: a) SPAEK-QS-1.1, b) SPAEK-QS-1.3, c) SPAEK-QS-1.5 copolymers in DMSO-d_6 .

V.5. Solubility of SPAEK polymers

All sulfonated poly(arylene ether ketone)s copolymers were not soluble in apolar solvent. SPAEK copolymers containing biphenol unit were soluble only in aprotic polar solvents like DMSO, NMP and DMAc. However, it was necessary to add diglyme in aprotic solvent to completely dissolve the SPAEK-S with IEC=1.1 meq/g. Sulfonated poly(arylene ether ketone)s based on hydroquinone were also found soluble in aprotic solvents. Polymers containing nitrile unit with IEC=1.5 meq/g and IEC=1.71 meq/g were soluble in methanol.

V.6. SPAEK membranes manufacturing

Different membranes were prepared by solution casting method as afore mentioned in the former chapters.

V.7. Determination of IEC of membranes

V.7.1. Determination of IEC by ¹H NMR

The IEC and DS of the different SPAEK copolymers were determined by ¹H NMR spectroscopy. As mentioned in chapter III based on the ¹H proton NMR spectra (Figure V.4.1.2) the DS of SPAEK-N co-polymers was calculated from the following formula:

$$DS \% = \frac{(Area a)}{[(Area a) + (Area hi) \div 3]} \times 100$$

Area a – integration area of one proton from sulfonated unit

Area hi – integration area of three protons from non-sulfonated unit

As regards the DS values of SPAEK-S copolymers, they were calculated from data obtained from the ¹H NMR spectra (see Fig. V.4.1.3) and using the following equation:

$$DS \% = \frac{(Area\ a)}{[(Area\ a) + (Area\ i) \div 4]} \times 100$$

Area a – integration area of one proton from sulfonated unit

Area i – integration area of four protons from non-sulfonated unit

In Table V.7.1. are listed the calculated values for the different SPAEK co-polymers based on the biphenol co-monomer.

Table V.7.1. IEC determination by ¹H NMR spectra of SPAEK.

Copolymer	DS theoretical (mol%)	IEC theoretical (meq/g)	DS RMN	IEC RMN (meq/g)
SPAEC-N-1.1	53%	1.1	42%	1.0
SPAEC-N-1.3	72%	1.3	82%	1.4
SPAEC-N-1.5	98%	1.5	100%	1.51
SPAEC-S-1.1	62%	1.1	68%	1.2
SPAEC-S-1.3	72%	1.3	78%	1.3
SPAEC-S-1.5	98%	1.5	100%	1.51

As it can be seen, the experimental DS values are in relatively good accordance with the calculated ones expected from feed ratio of the sulfonated monomer.

The DS value for co-polymers SPAEK-QN (Fig. VII.3.2.2) was determined from the equation used to calculate the DS of SPAEK-N polymers. However, it was not possible to obtain the DS of SPAEK-QS polymers (Fig. VII.3.2.3) due to the fact that no specific peak of protons in sulfonated and non-sulfonated units appear distinguished in the spectra (Fig. V.4.2.3).

Table V.7.2. IEC determination from ¹H NMR spectra of SPAEK-Q.

Copolymer	DS theoretical (mol%)	IEC theoretical (meq/g)	DS RMN	IEC RMN (meq/g)
SPAEC-QN-1.1	39%	1.1	52%	1.2
SPAEC-QN-1.3	53%	1.3	66%	1.4
SPAEC-QN-1.5	72%	1.5	78%	1.55
SPAEC-QN-1.71	100%	1.71	100%	1.71

V.7.2. Determination of IEC by titration

As reported in chapter II (see paragraph II.7), the aqueous and non-aqueous titration were performed to determine the IEC of the different SPAEK co-polymers. In Tables V.7.2.1 and V.7.2.2 are presented the obtained results which are in good correlation with the calculated values.

Table V.7.2.1. IEC values of SPAEK containing biphenol.

copolymer	SPAEEK-N-1.1	SPAEEK-N-1.3	SPAEEK-N-1.5	SPAEEK-S-1.1	SPAEEK-S-1.3	SPAEEK-S-1.5
IEC theoretic (meq/g)	1.1	1.3	1.5	1.1	1.3	1.5
IEC _{Aqu}	1.0±0.05	1.14±0.06	1.45±0.07	1.05±0.05	1.14±0.06	1.64±0.08
IEC _{Non-aqu}	1.07±0.05	1.29±0.06	1.47±0.07	1.05±0.05	1.29±0.06	1.52±0.08

± 5% of error

Table V.7.2.2. IEC values of SPAEK containing quinone.

Copolymer	SPAEEK-QN-1.1	SPAEEK-QN-1.3	SPAEEK-QN-1.5	SPAEEK-QN-1.7	SPAEEK-QS-1.1	SPAEEK-QS-1.3	SPAEEK-QS-1.5
IEC theoretical (meq/g)	1.1	1.3	1.5	1.71	1.1	1.3	1.5
IEC _{Aqu}	1.08±0.05	1.25±0.06	1.38±0.07	1.68±0.08	1.20±0.06	1.15±0.06	1.5±0.08
IEC _{Non-aqu}	1.15±0.06	1.28±0.06	1.44±0.07	1.65±0.08	1.08±0.05	1.29±0.06	1.5±0.08

± 5% of error

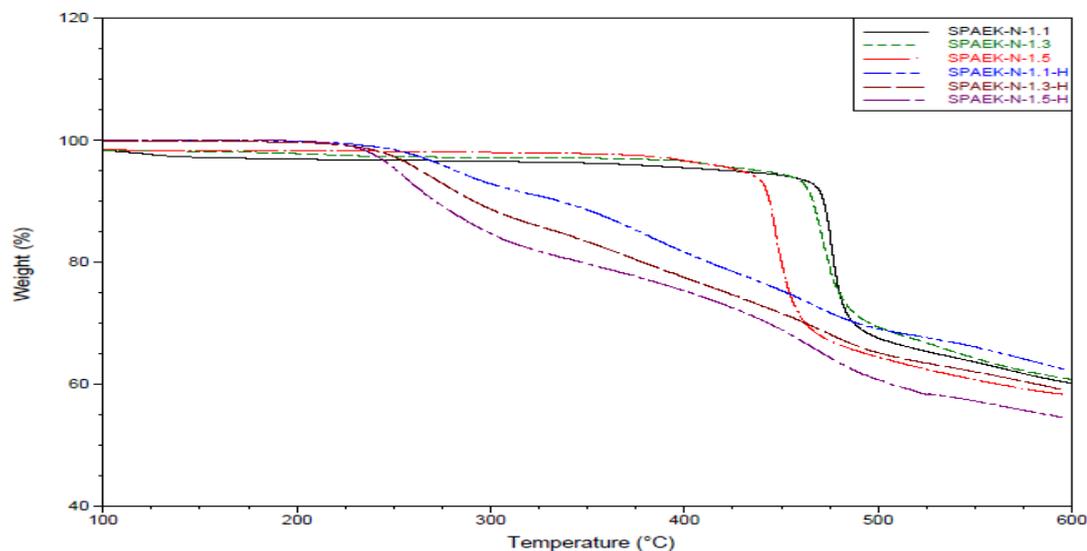
V.8. Thermal properties of SPAEK polymers

V.8.1 SPAEK containing biphenol unit

The thermal stability of these polymers was investigated by TG analysis. As reported in Table V.8.1.1, SPAEK polymers in K⁺ form show an onset of degradation in the range of 420-440°C. With respect to the polymers in H⁺ form it was observed (see Figure V.8.1.1) a two-step

weight loss process: the first one attributed to the sulfonic acid group degradation and the second one due to the chain degradation.

a)



b)

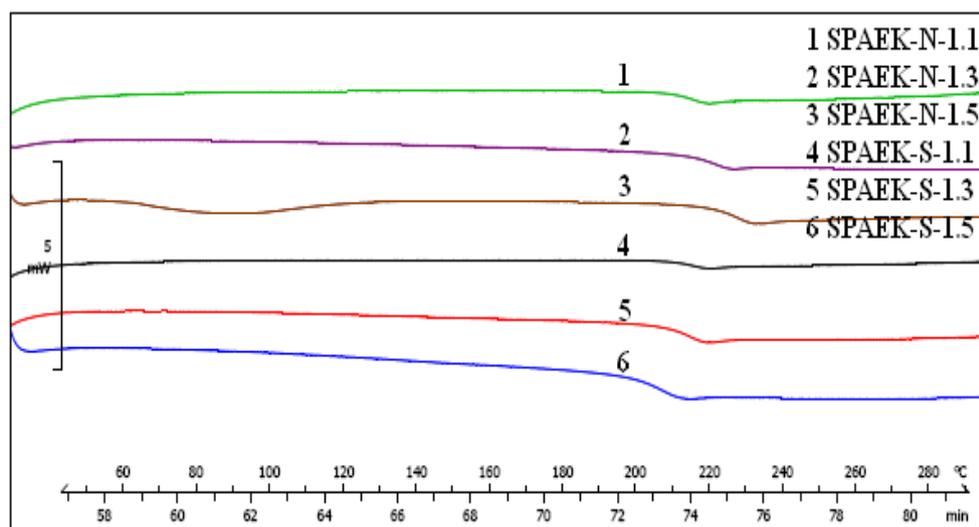


Figure V.8.1.1. a) TGA traces of the SPAEK-N in K^+ and H^+ form b) DSC heating traces of the SPAEK-N and SPAEK-S copolymers in the K^+ form.

As observed with the SPAES polymers (see chapter IV.8), the variation of T_g as a function of the extent of sulfonated side chains bonded to the polymer chain seems also depend on the chain rigidity (see Figure V.8.1.1.b). It can be assumed that the chain rigidity higher for the

polymers containing benzonitrile unit induce better chain packing which afford better interactions of sulfonated side chains. Conversely, the less chain rigidity of polymers containing diphenylsulfone unit could allowed a better side chain flexibility.

Table V.8.1.1. Thermal property data of SPAEK-N and SPAEK-S co-polymers.

copolymer	SPAEC-N-1.1	SPAEC-N-1.3	SPAEC-N-1.5	SPAEC-S-1.1	SPAEC-S-1.3	SPAEC-S-1.5
IEC(meq/g)	1.1	1.3	1.5	1.1	1.3	1.5
T _d (°C)*	423	439	428	417	423	430
T _d (°C)**	282	264	251	252	253	248
T _g (°C)	213	220	226	215	213	207

* - Measured by TGA in the K⁺ form, ** - Measured by TGA in the H⁺ form

V.8.2. SPAEK containing quinone unit

The thermal stability of these polymers was also investigated by the TG analysis. The results are shown in Table V.8.2.1. For the same IEC, the onset of degradation of these polymers is lower than those of SPAEK polymer based on biphenol monomer.

Table V.8.2.1. Property data of SPAEK-NQ and SPAEK-SQ.

copolymer	SPAEC-QN-1.1	SPAEC-QN-1.3	SPAEC-QN-1.5	SPAEC-QN-1.7	SPAEC-QS-1.1	SPAEC-QS-1.3	SPAEC-QS-1.5
IEC(meq/g)	1.1	1.3	1.5	1.71	1.1	1.3	1.5
T _d (°C)*	393	412	361	416	405	344	345
T _d (°C)**	295	274	257	243	260	252	244
T _g (°C)	148	192	190	208	212	172	194

* - Measured by TGA in the K⁺ form, ** - Measured by TGA in the H⁺ form

The T_g of polymers obtained from DSC analysis are presented in Table V.8.2.1. As observed for the SPAEK-N, the T_g value of SPAEK-QN polymer increases with the IEC. However, for SPAEK-QS it was not possible to establish a relation between T_g and IEC.

V.9. Water uptake of SPAEK polymers

The water uptake measurements of SPAEK membranes were performed as mentioned in chapter II.9.

V.9.1. Water uptake of biphenol containing SPAEK polymers

Figure V.9.1.1 shows the water uptake values of the SPAEK membranes in the acid form as a function of temperature. As it can be seen, the polymers with a IEC of 1.1 mequiv/g have relatively similar behavior to Nafion membrane. The water uptake is even lower up to 70°C for the SPAEK-S-1.1 membrane and up to 90°C for the SPAEK-N-1.1 membrane. For the polymers with the IEC of 1.3, the water uptake variation is comparable to the Nafion membrane up to 70°C but over this temperature their water uptake increase drastically in respect of Nafion membrane.

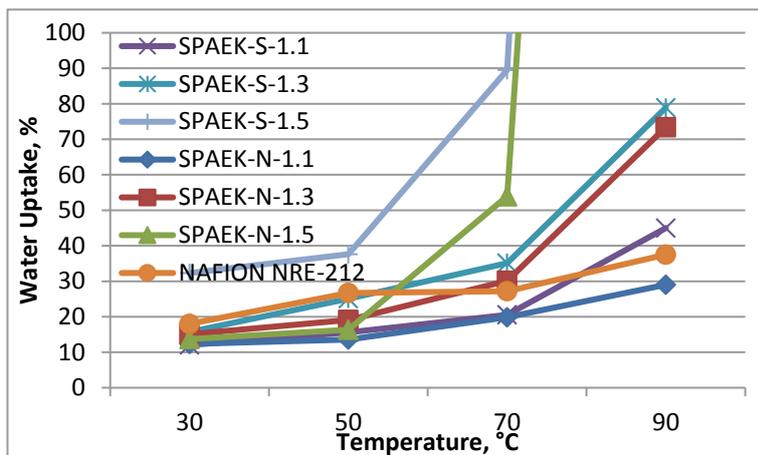


Figure V.9.1.1. Temperature dependence of water uptake of SPAEK-N and SPAEK-S membranes.

However, the water uptake for membranes with IEC=1.5 meq/g is very important over 50°C which is real drawback for fuel cell application.

Table V.9.1.1. Hydration number of SPAEK membranes at different temperatures.

copolymer	SPA EK-N-1.1	SPA EK-N-1.3	SPA EK-N-1.5	SPA EK-S-1.1	SPA EK-S-1.3	SPA EK-S-1.5
	λ (H ₂ O/SO ₃ H)					
30°C	6	6	11	6.1	7	12
50°C	7	8	14	7.9	11	14
70°C	10	13	54	10.4	15	33
90°C	15	73	-	23	34	-

V.9.2. Water uptake of hydroquinone containing SPAEK polymers

Based on the results reported in Figure V.9.2.1 it can be considered that the water uptake behavior versus the temperature and the IEC of these polymers is relatively similar to those of biphenol based SPAEK. As regards the polymer with IEC=1.71 meq/g the water swelling is very important even at low temperature and dissolved completely at 50°C.

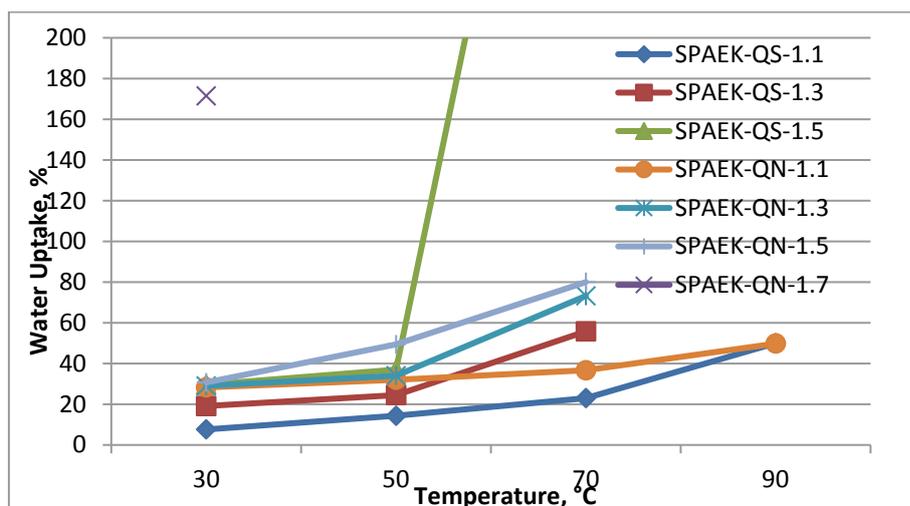


Figure V.9.2.1. Temperature dependence of water uptake of SPAEK-QN and SPAEK-QS membranes.

Table V.9.2.1. Hydration number of SPAEK membranes at different temperatures.

copolymer	SPA EK-QN-1.1	SPA EK-QN-1.3	SPA EK-QN-1.5	SPA EK-QN-1.7	SPA EK-QS-1.1	SPA EK-QS-1.3	SPA EK-QS-1.5
	λ (H ₂ O/SO ₃ H)						
30°C	14.3	12.4	11.4	55.7	3.8	8.2	10.9
50°C	16.2	14.5	18.3	-	7.2	10.5	13.7
70°C	18.5	31.2	29.6	-	11.6	23.8	178.8
90°C	25.1	-	-	-	25.2	-	-

- Membrane dissolved in water

SPAEK membranes based on biphenol have lower water uptake in comparison with quinone containing SPAEK membranes.

V.10. Ionic conductivity of SPAEK polymers

V.10.1. Ionic conductivity of biphenol containing SPAEK polymers

First, the ionic conductivities of these polymers were measured at 95% RH and different temperatures. As illustrated in Figure V.10.1.1, the conductivities increased both with temperature and relative humidity. However, only polymers with IEC=1.5 afforded interesting conductivity values.

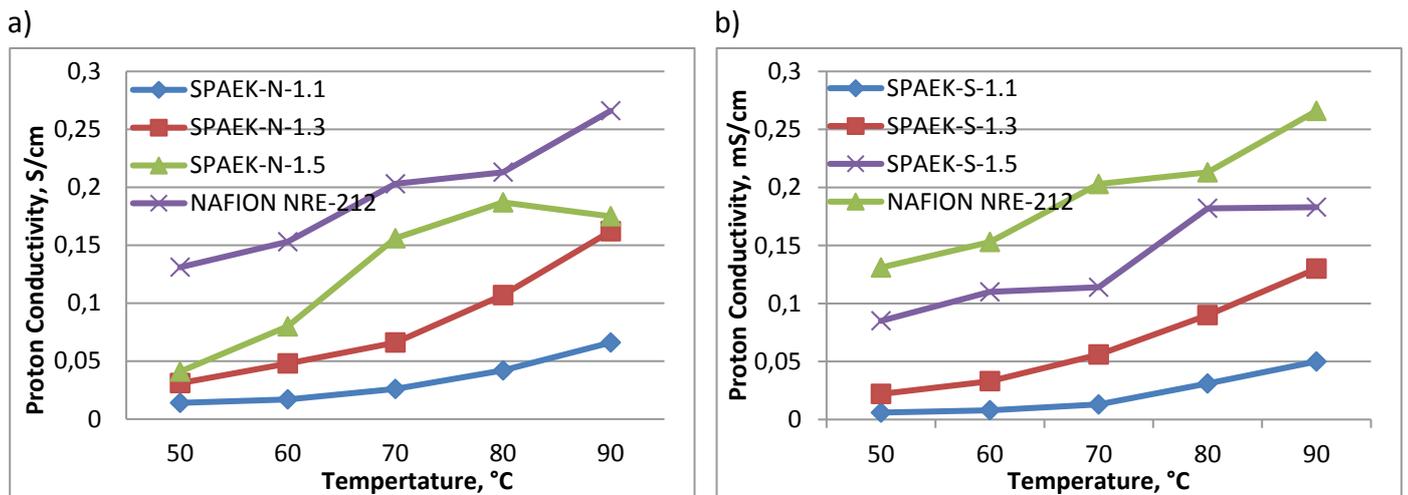


Figure V.10.1.1. Ionic conductivity as a function of temperature a) SPAEK-N, b) SPAEK-S membranes and Nafion NRE212 under 95% relative humidity.

Table V.10.1.1. Ionic conductivity of the sulfonated SPAEK-N copolymers.

Temp.	Copolymer								
	SPA EK-N-1.1			SPA EK-N-1.3			SPA EK-N-1.5		
	Proton conductivity (mS/cm)								
Relative Humidity									
	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	12	13	14	19	28	31	75	56	41
60°C	12	13	17	38	45	48	86	94	80
70°C	24	25	26	51	61	66	109	142	156
80°C	34	39	42	82	102	107	122	175	187
90°C	50	56	60	134	154	162	170	175	175

Table V.10.1.2. Ionic conductivity of the sulfonated SPAEK-S copolymers.

Temp.	Copolymer								
	SPA EK-S-1.1			SPA EK-S-1.3			SPA EK-S-1.5		
	Proton conductivity (mS/cm)								
Relative Humidity									
	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	4	5	6	18	21	22	67	79	85
60°C	7	8	8	23	30	33	94	106	110
70°C	9	12	13	52	55	56	132	138	144
80°C	28	29	31	81	86	90	153	180	182
90°C	41	47	50	113	125	130	193	189	183

Results in Table V.10.1.1 and Table V.10.1.2 of the SPAEK-N membranes showed higher conductivity than that of the SPAEK-S membranes at all range. The SPAEK-N membranes had higher water uptake than that of the SPAEK-S which explain higher conductivity. These results confirm that the polymer structure has high influence on membrane performance.

V.10.2. Proton conductivity of quinone containing SPAEK polymers

Like the SPAEK based on biphenol monomers, conductivities increase with IEC and temperature (Fig V.10.2.1).

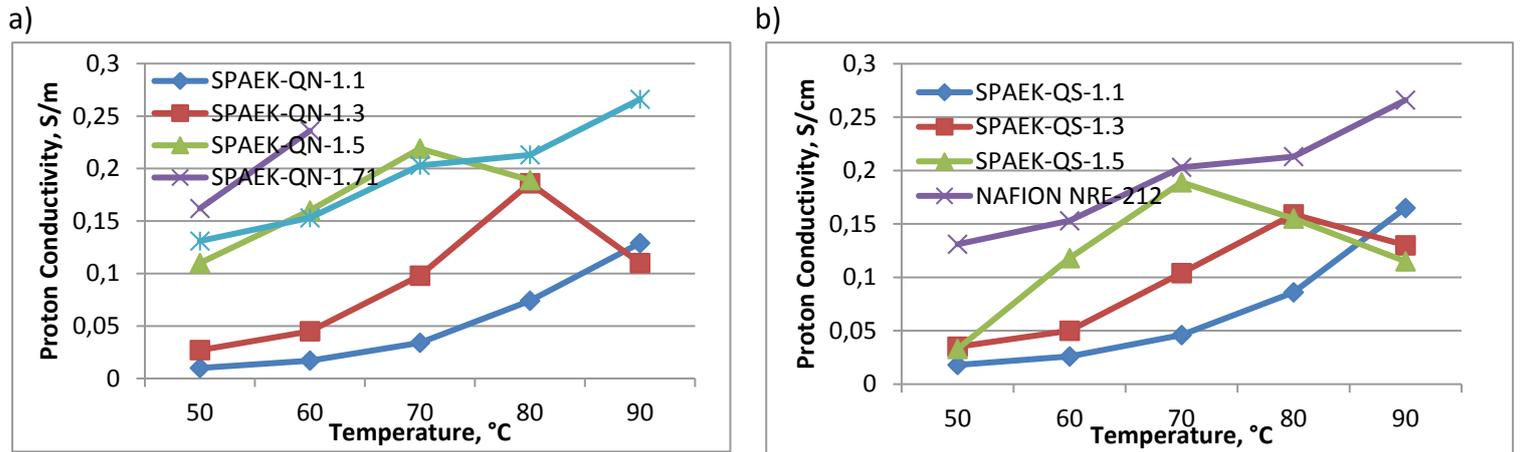


Figure V.10.2.1. Ionic conductivity as a function of temperature a) SPAEK-QN, b) SPAEK-QS membranes and Nafion NRE212 under 95% relative humidity.

However, the increase in conductivity is higher for the polymers with IEC=1.1 mequiv/g. It worth also to note that the conductivities obtained for the polymers SPAEK-QN-1.5 are very close to Nafion up to 70°C. Better conductivities than Nafion were determined with the SPAEK-QN-1.7 up to 60°C but unfortunately the conductivity could not be measured above this temperature because of excessive membrane swelling. All results are summarized in Table V.10.2.1 and Table V.10.2.2.

Table V.10.2.1. Ionic conductivity of the sulfonated SPAEK-QN copolymers.

Temp.	Copolymer											
	SPAEEK-QN-1.1			SPAEEK-QN-1.3			SPAEEK-QN-1.5			SPAEEK-QN-1.71		
	Proton conductivity (mS/cm)											
	Relative Humidity											
	50%	70%	95%	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	8	9	10	21	25	25	88	102	110	155	160	162
60°C	12	15	17	42	44	45	130	150	160	183	220	236
70°C	23	30	34	60	88	98	160	196	219	248	278	-
80°C	52	68	74	138	172	186	176	198	189			
90°C	93	119	129	158	141	110	190	-	-			

Table V.10.2.2. Ionic conductivity of the sulfonated SPAEK-QS copolymers.

Temp.	Copolymer								
	SPAEEK-QS-1.1			SPAEEK-QS-1.3			SPAEEK-QS-1.5		
	Proton conductivity (mS/cm)								
	Relative Humidity								
	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	16	17	18	25	31	35	23	28	32
60°C	23	25	26	41	48	50	106	115	118
70°C	36	42	46	87	101	104	127	170	189
80°C	58	77	86	144	166	159	162	184	155
90°C	134	156	165	165	157	130	175	125	115

V.11. Conclusion

Monomer FPSABF-K with pendant perfluoroalkyl sulfonic acid was successfully synthesized. Poly(arylene ether ketone)s were effectively synthesized by the aromatic nucleophilic substitution. All membranes showed very strong mechanical properties. Poly(arylene ether ketone sulfone)s co-polymers exhibited higher water uptake and proton conductivity than that poly(arylene ether ketone benzonitrile)s co-polymers. These results confirmed that chemical structure has high influences on membrane properties. All data confirmed that synthesized SPAEK are candidates for proton exchange membrane fuel cell applications. However, some properties could be enhanced by changing chemical architecture to improve their performance.

Chapter VI. Synthesis poly(arylene ether)s block copolymers

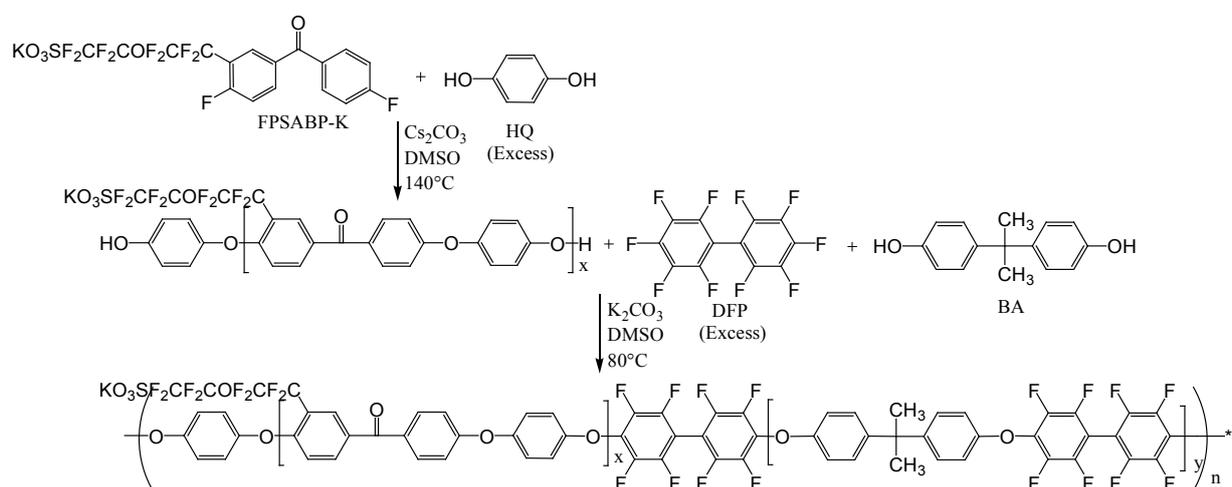
VI.1. Introduction

Comme il a été mentionné dans le chapitre bibliographique, l'approche copolymère à blocs a été utilisée pour développer des membranes conductrices protoniques. Les travaux publiés comme ceux réalisés dans le groupe de J. McGrath[90] montrent que les blocs contenant les groupes acide sulfonique (blocs hydrophiles) tendent à s'organiser et former des domaines distinctes de ceux contenant les blocs non sulfonés (blocs hydrophobes) et dont la connection entre eux va dépendre de la proportion des motifs sulfonés présents dans la chaîne et de la longueur respective des blocs. Les conséquences généralement constatées dues à cette morphologie biphasique sont une meilleure conductivité ionique et dans certains cas un gonflement à l'eau moindre en comparaison avec des copolymères sulfonés de type statistiques. Dans le cadre de ce travail, il nous est apparu intéressant de développer des copolymères à blocs et ce à partir de l'un des précurseurs sulfonés décrits dans les chapitres précédents. Le choix s'est porté sur le FPSABP-K du fait de sa très bonne réactivité. Ces copolymères ont été synthétisés par la méthode dite en deux étapes successives. Les propriétés ainsi que la morphologie des membranes ont été également étudiées.

VI.2. Highly fluorinated sulfonated block poly(arylene ether ketone)s (BSPAEEK-F)

FPSABP-K was chosen as a monomer for the synthesis of sulfonated block copolymers, because of its good reactivity. Series of block co-polymers with different sulfonated block lengths were prepared.

As it can be seen in Scheme VI.2.1, the block copolymers were synthesized by a two stages one-pot polymerization. In this polymerization process, the sulfonated blocks are formed first by reacting sulfonated monomer FPSABP-K and hydroquinone (HQ). The desired length of these blocks is determined by the monomer feed ratio, sulfonated block with $M_n = 4000$ (4k), 6000 (6k) and 8000 (8k) were prepared. Subsequently, 4,4'-decafluorodiphenyl (DFP) and bisphenol A (BPA) were added to the reaction mixture to extend the polymer chain. By controlling the amount of DFP, hydrophobic block with $M_n = 4000$ (4k) were obtained. DFB was chosen because of great reactivity in the nucleophilic aromatic substitution reactions which allowed to perform polymerisation at a temperature lower than 120°C and then prevent side reactions like trans etherification reaction. The polymerization was carried out at 80°C for 2-3 h.



Scheme VI.2.1. Synthesis route of BSPAEK-F polymer.

DMSO was chosen as a good solvent for the block polymerization of poly(arylene ether ketone)s 8k-4k and 6k-4k. However, block copolymer 4k-4k showed lower solubility in DMSO. Therefore, DMAc was preferred as polymerisation solvent.

Figure VI.2.1 shows the ^{19}F NMR spectrum of the sulfonated block copolymer 8k-4k. All the peaks characteristic of the fluorine nuclei of both sulfonated perfluoro alkyl side chains and DFB monomer were clearly depicted. The chemical structure of these polymers was also confirmed by ^1H NMR spectra (see spectra Figure VI.2.2.).

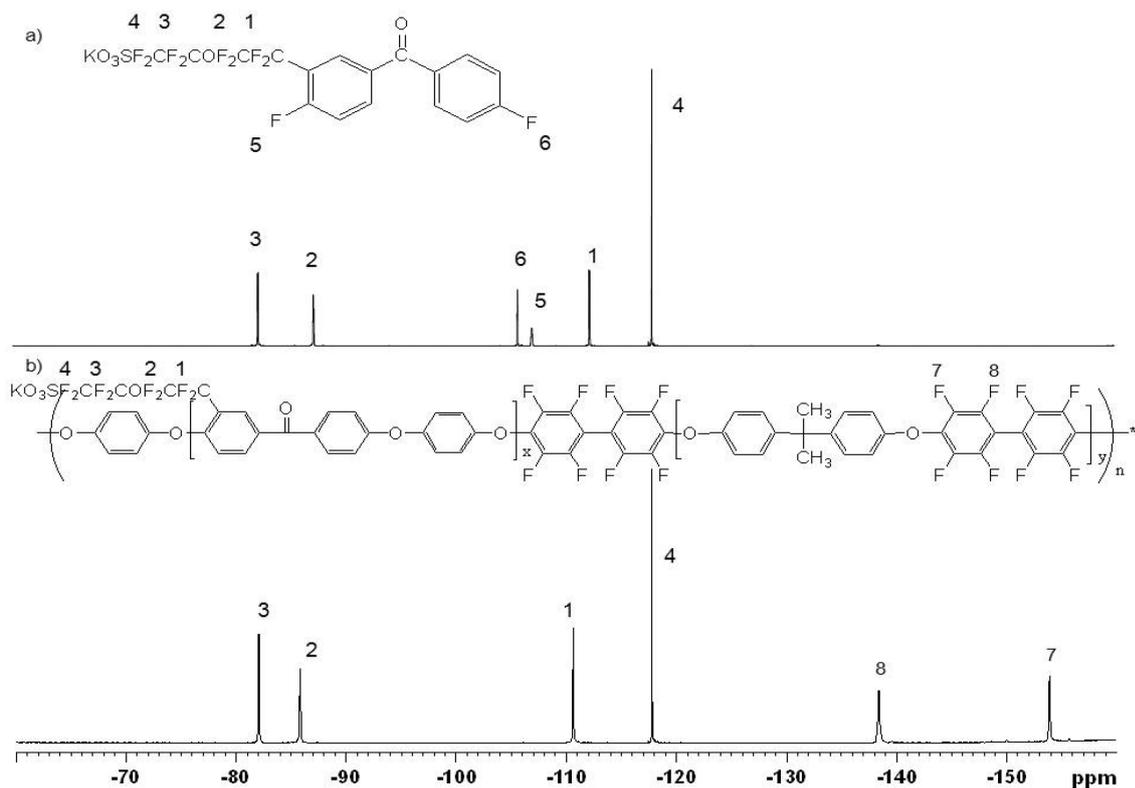


Figure VI.2.1. ^{19}F NMR spectra: a) FPSABP-K, b) BSPAEK-F-8k-4k block copolymer in DMSO-d_6 .

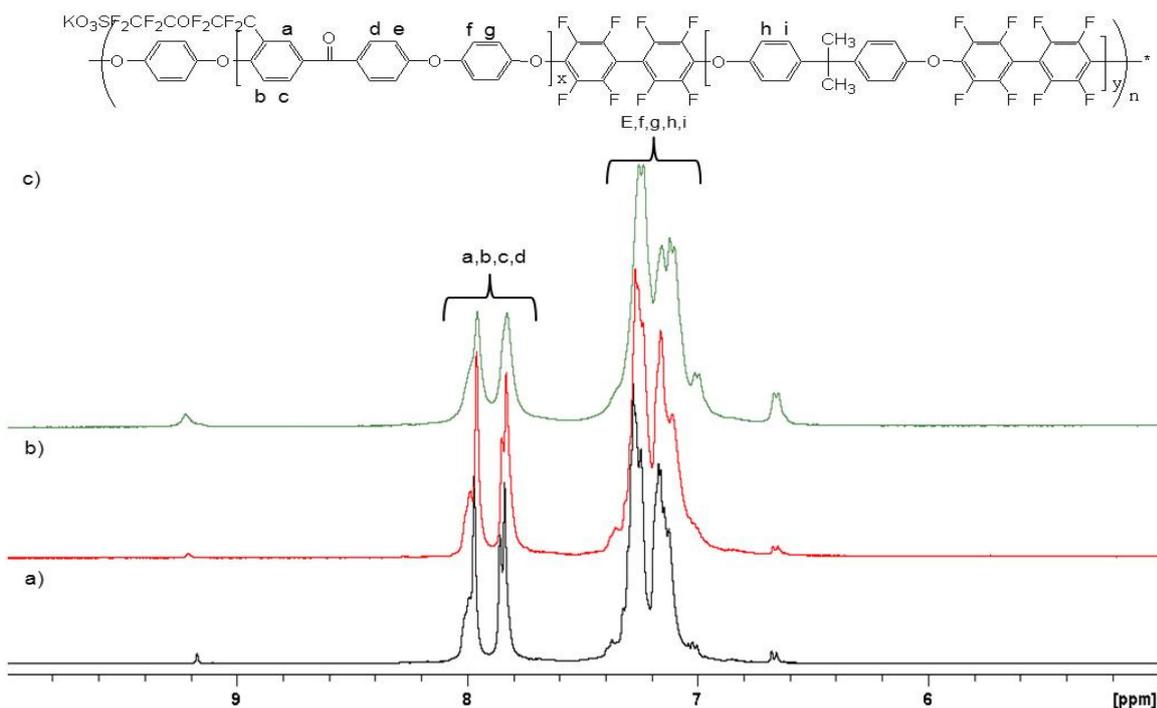
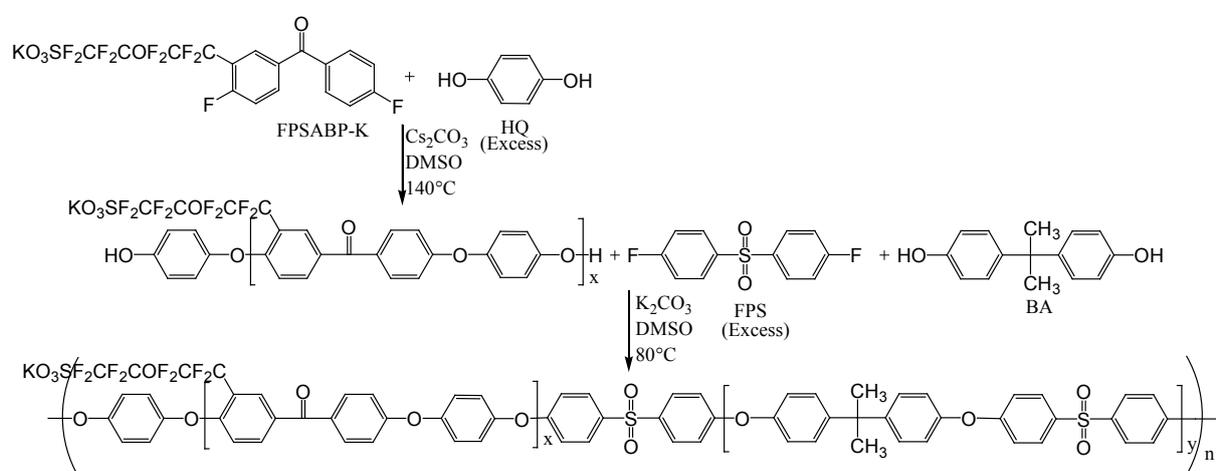


Figure VI.2.2. ^1H NMR spectra: a) BSPAEK-F-8k-4k, b) BSPAEK-F-6k-4k, c) BSPAEK-F-4k-4k copolymers in DMSO-d_6 .

VI.3. Sulfonated block poly(arylene ether ketone sulfone)s (BSPAEK-S)

A new approach was focused on the synthesis of sulfonated multiblock poly(arylene ether ketone sulfone)s. Block copolymers were prepared using the same methodology that the BSPAEK-F polymers (Scheme VI.3.1). Only the DFB monomer was replaced by the difluorodiphenyl sulfone monomer which also display a great reactivity in S_NAr reaction at temperature lower than 120°C . This polymerization reaction was then proceeded smoothly at 80°C .



Scheme VI.3.1. Synthesis route of BSPAEK-S polymer.

The chemical structure of these polymers were confirmed by both ^{19}F and ^1H NMR as illustrated in Figures VI.3.1, VI.3.2.

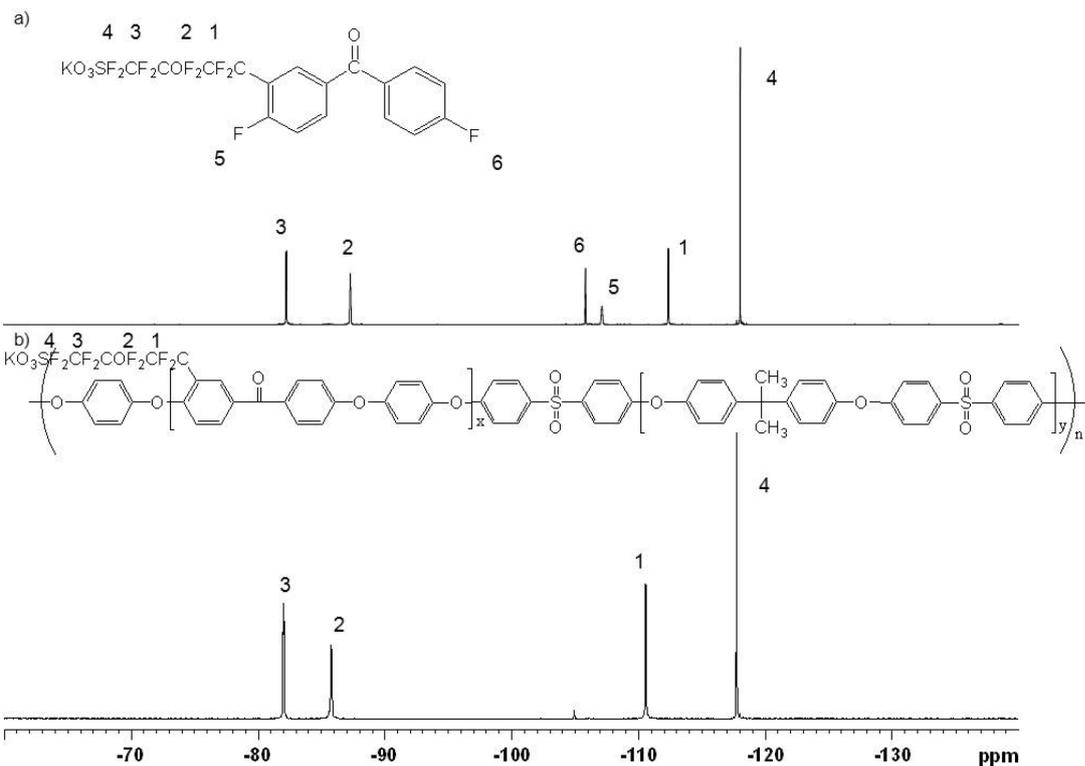


Figure VI.3.1. ^{19}F NMR spectra: a) FPSABP-K, b) BSPAEK-S-8k-4k copolymer in DMSO-d_6 .

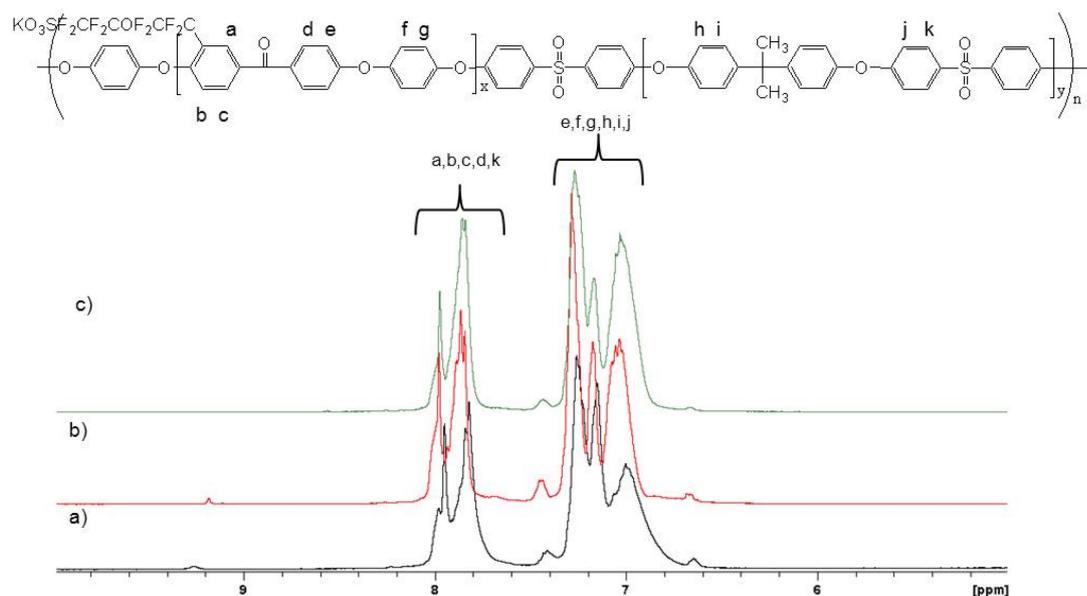
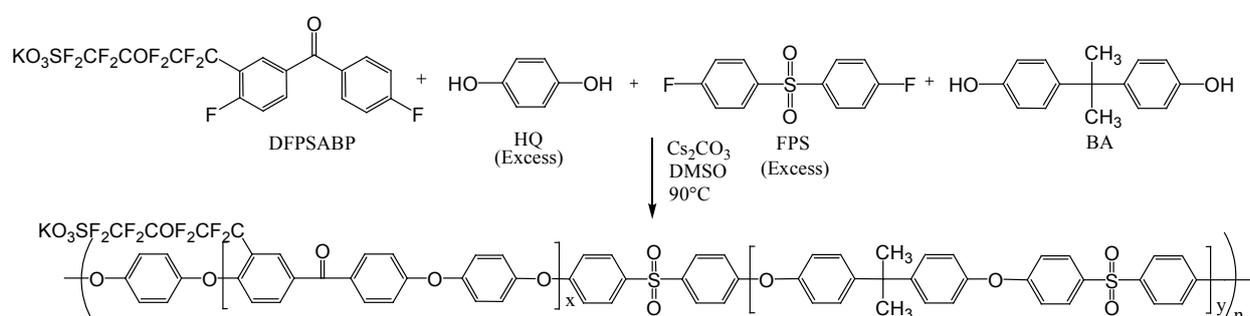


Figure VI.3.2. ^1H NMR spectra: a) BSPAEK-S-8k-4k, b) BSPAEK-S-6k-4k, c) BSPAEK-S-4k-4k copolymers in DMSO-d_6 .

VI.4. Statistic sulfonated poly(arylene ether ketone sulfone)s copolymer (statSPAEEK)

In this approach the idea was to synthesize statistic copolymer and then compare its properties with block copolymers. Statistic sulfonated poly(arylene ether ketone sulfone)s copolymer (statSPAEEK-S) was synthesized by polycondensation. The preparation of this copolymer is based on the chemical reaction of the DFPSABP-K, HQ, FPS and BPA. All monomers were reacted in one step polymerisation. Scheme VI.4.1 shows the synthetic procedure. Monomer ratio was the same as in the case of block copolymer BSPAEK-S-6k-4k.



Scheme VI.4.1. Synthesis route of statSPAEEK-S.

The ^{19}F NMR spectra of this copolymer are shown in Figure VI.4.1. The peaks corresponding to the fluorine leaving groups F_5 and F_6 of sulfonated monomer disappeared. ^1H NMR spectra showed significant difference between polymer structure as it was expected (see Figure VI.4.2).

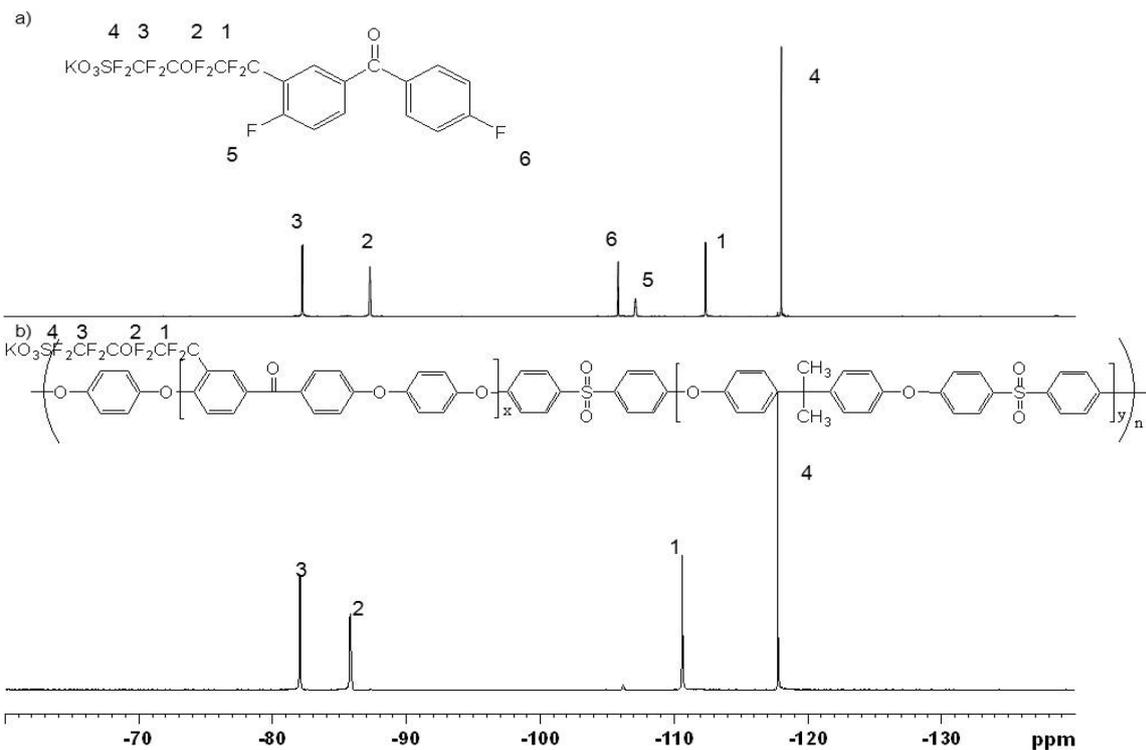


Figure VI.4.1. ^{19}F NMR spectra in DMSO-d_6 : a) FPSABP-K, b) statSPAEK-S copolymer in DMSO-d_6 .

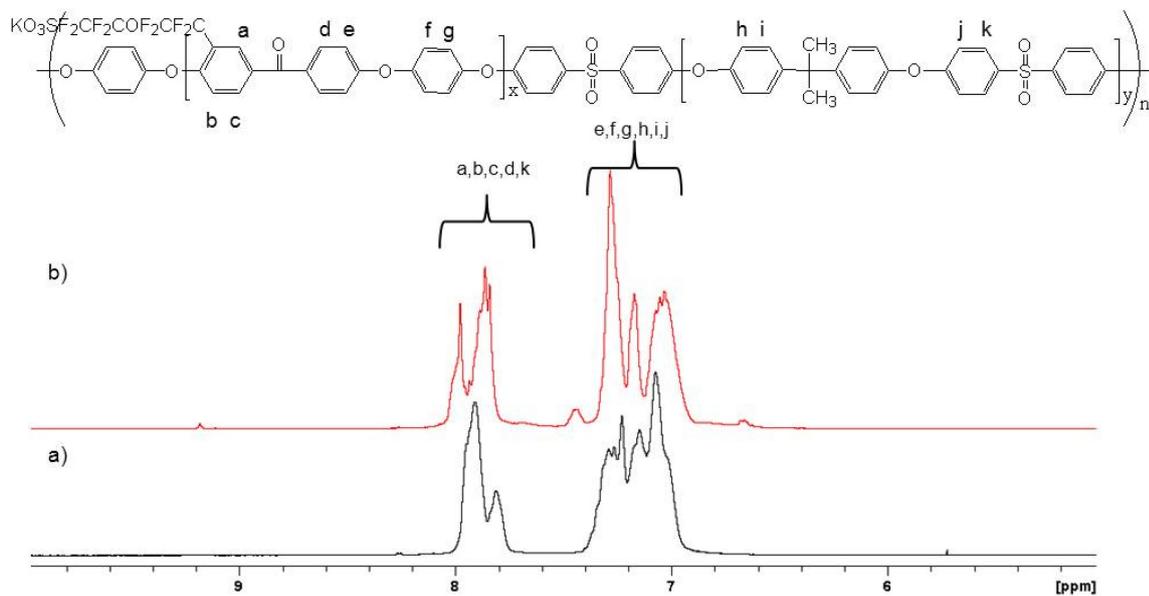


Figure VI.4.2. ^1H NMR spectra: a) statSPAEK-S, b) BSPAEK-S-6k-4k copolymers in DMSO-d_6 .

VI.5. Solubility of BSPAEK and statSPAER

Sulfonated block copolymers were not soluble in apolar solvents like cyclohexane and chloroform. In methanol all copolymers swelled but did not dissolve. The block copolymers with shorter hydrophilic block than $M_n=8000$ were a little or completely dissolved in THF which is moderately polar solvent and can dissolve a wide range of nonpolar and polar chemical compounds. All block copolymers were well dissolve in aprotic polar solvents (DMAc, DMSO, NMP). For this reason NMP for membrane preparation was used.

Statistic copolymer (statSPAEK-S) showed the same properties of the solubility as the block BSPAEK-S-6k-4k copolymer.

VI.6. BSPAEK and statSPAEK membranes manufacturing

Membrane casting was done in NMP and yielded tough, flexible membranes for all block copolymers BSPAEK-F.

Block copolymers BSPAEK-S-8k-4k and BSPAEK-S-4k-4k gave tough membranes. Although, block copolymer BSPAEK-S-6k-4k formed a very brittle film. This occurrence can be explained by cyclisation of polymers main bonds. The best way to obtain a membrane with good mechanical properties was purification of the polymer by extraction process performed in a Soxhlet extractor. Isopropanol and methanol were tested as extraction solvents. Best results were obtained with methanol and yielded a pure polymer after 48 h. The extracted block copolymer gave a tough, flexible membrane with yellow-brown color.

VI.7. Morphological characterization

VI.7.1. Transmission electron microscopy (TEM)

The chemical structure of the polymers affects morphology and hence conductivity. Microphase separation in block copolymers structure is resulted by mixing of different segments. For this reason multiblock copolymers based on hydrophilic and hydrophobic blocks formed phase separated morphologies[91]. Different morphologies can be controlled by factors like, the extent of dissimilarity between block and the chain length of each block. The multiblock polymer architecture with high IEC values enhanced the formation of proton transportation channel which contributed to high proton conduction in a wide range of relative humidity[46].

Morphology of the sulfonated membranes can be investigated by transmission electron microscopy (TEM) analysis. It is important to convert membranes in salt form into heavy metals such as lead or silver which can enhance contrast[60]. In this approach as a contrast lead (II) acetate trihydrate, cesium chloride and lead (II) nitrate were selected. As it can be seen in Figure VI.7.1.1, lead (II) nitrate showed better contrast between hydrophilic and hydrophobic organization. For this reason this compound was employed for this study.

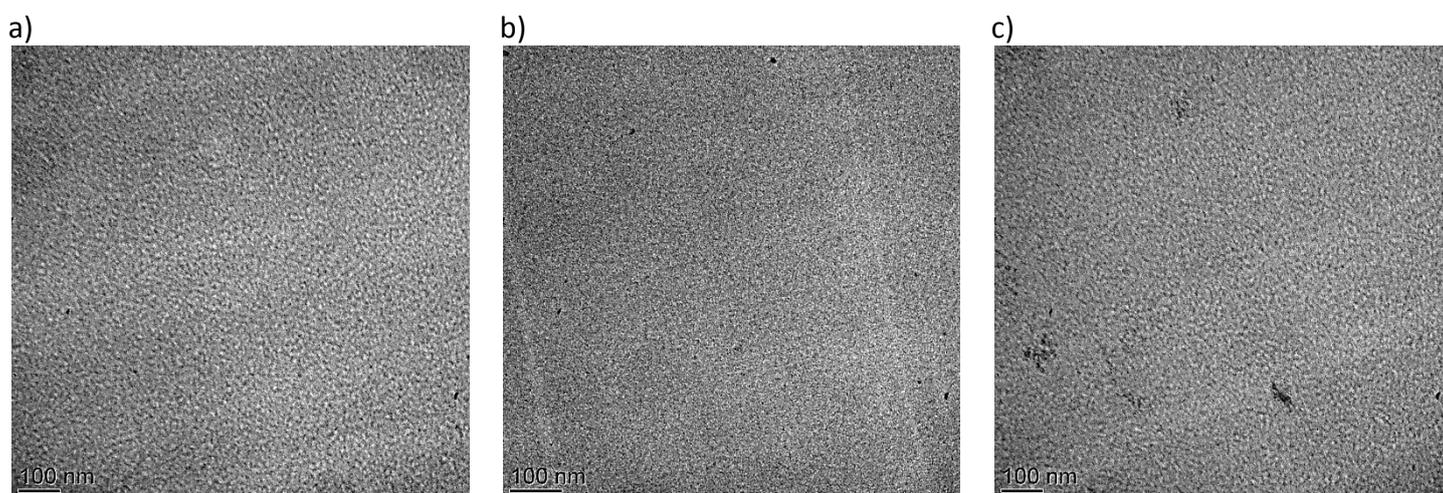


Figure VI.7.1.1. TEM photographs of BSPAEK-S-8k-4k membranes: a) exchanged with $Pb(CH_3COO)_2$ aqueous solution, b) exchanged with $CsCl$, c) exchanged with $Pb(NO_3)_2$. Scale bars = 100 nm.

VI.7.1.1. Microstructure of BSPAEK-F

Morphology of BSPAEK-F membranes were investigated by TEM analysis. Figure VI.7.1.1.1 shows TEM images of lead-ion exchanged samples. The dark areas are assigned to regions of high ionicity and bright areas to hydrophobic regions. The EDX analysis was performed to confirm this phenomenon.

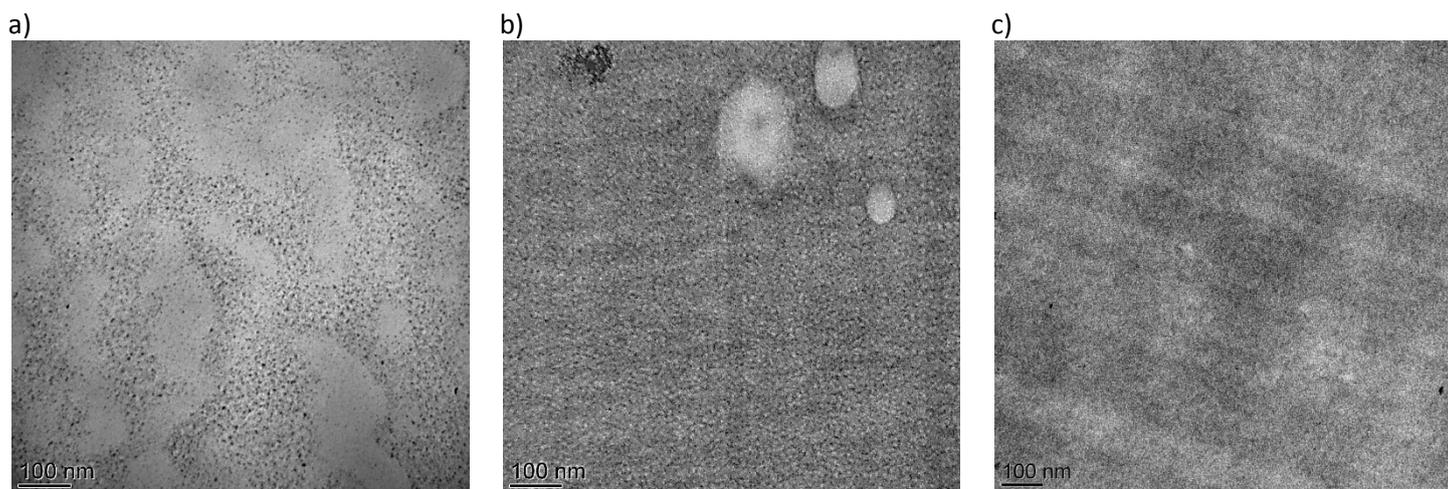


Figure VI.7.1.1.1. TEM photographs of a) BSPAEK-F-8k-4k, b) BSPAEK-F-6k-4k, c) BSPAEK-F-4k-4k membranes exchanged with $Pb(NO_3)_2$. Scale bars = 100 nm.

A phase-separated morphology was observed in all three series of highly fluorinated block copolymers. However, in contrast hydrophilic aggregates were smaller for membrane BSPAEK-F-4k-4k and dependent on the block length. The interface between sulfonated domains and hydrophobic areas is much less sharp. It is reasonable that the hydrophilic domains became larger with increasing length of the hydrophilic block due to increasing concentration of sulfonic acid groups.

VI.7.1.2. Microstructure of the BSPAEK

As is seen in Figure VI.7.1.2.1, the effect of block length on the morphology is noticeable. Comparison among the three membranes with different length of the hydrophilic block revealed that the clusters became larger as increasing the block length. These results lead to

the conclusion that both IEC and block length are main factors in determining the membrane morphology.

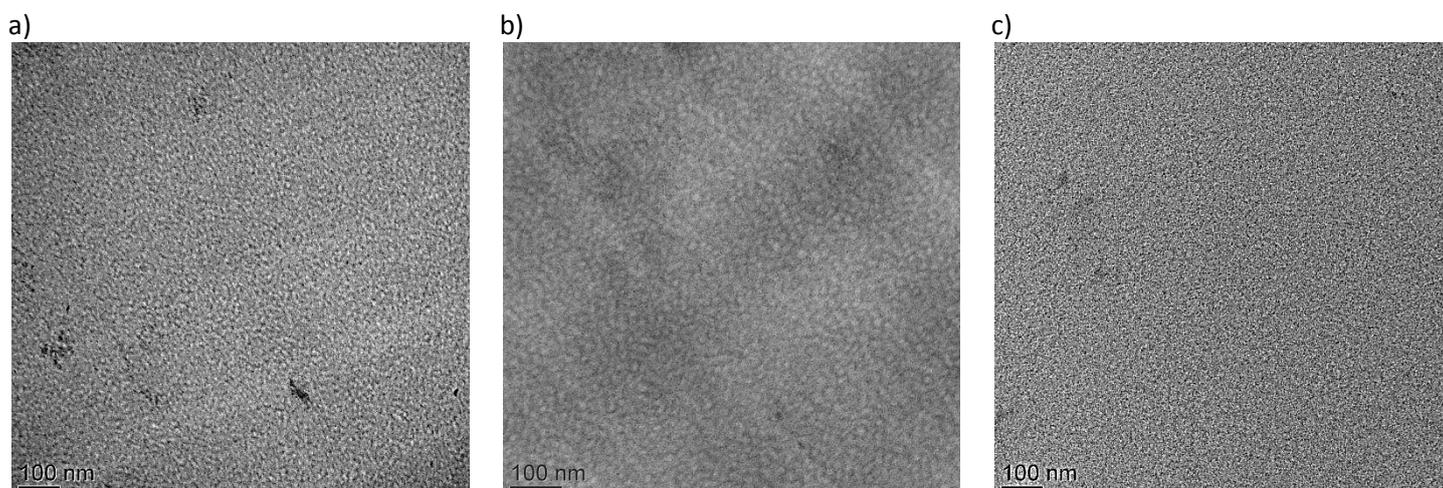


Figure VI.7.1.2.1. TEM photographs of a) BSPAEK-S-8k-4k, b) BSPAEK-S-6k-4k, c) BSPAEK-S-4k-4k membranes exchanged with $Pb(NO_3)_2$. Scale bars = 100 nm.

These series of the sulfonated copolymers possessed a micro morphology characterized by 5-10 nm ionic clusters. For membranes with higher IEC (Figure VI.7.1.2.1. a and b) a phase-separated morphology was observed with sharply visible ionic cluster. The hydrophilic domains are connected to each other.

As it was mentioned before BSPAEK-S-6k-4k polymer gave a very brittle membrane. After extraction of the block copolymer a tough membrane was obtained. These two films were analyzed by TEM. As it can be seen in Figure VI.7.1.2.2, many of big sharply visible circles are present. Their widths are between 250 to 500 nm. Image of the membrane after extraction (Figure VI.7.1.2.2 b) shows disappearance of the circles. Origin of these circles is caused by the cyclisation reaction which occurred during the polymerization. EDX analysis indicated that inside of the circles perfluoroalkyl sulfonated chains are not present.

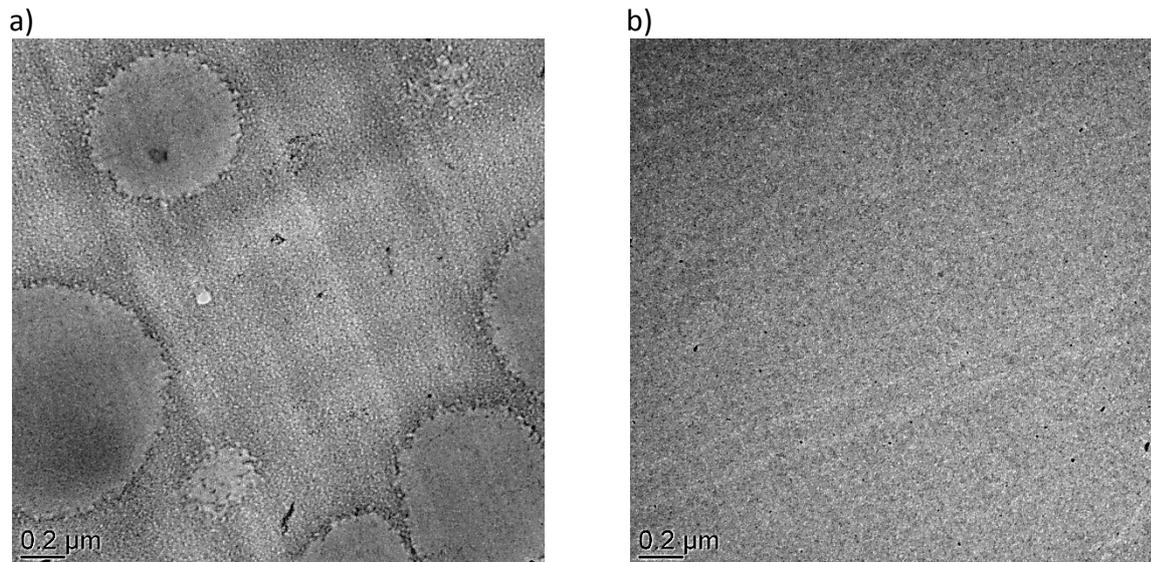


Figure VI.7.1.2.2. TEM photographs of BSPAEK-S-6k-4k membranes exchanged with $Pb(NO_3)_2$. a) before extraction, b) after extraction. Scale bars = 0.2 μm .

VI.7.1.3. Microstructure of statSPAEEK

Phase separation of the statistic copolymer is less developed than that of block copolymer. In the image of the statistic polymer some very small domains whose size was not uniform were dispersed in the continuous hydrophobic phase. For the block polymer more obvious phase-separation microstructure was noticed.

That result confirmed that block copolymers have more developed phase-separation. The dark regions are connected to each other and form channels and networks that extend through the whole sample surface. This confirms that nanophase separation takes place in this hydrophilic/hydrophobic block copolymer.

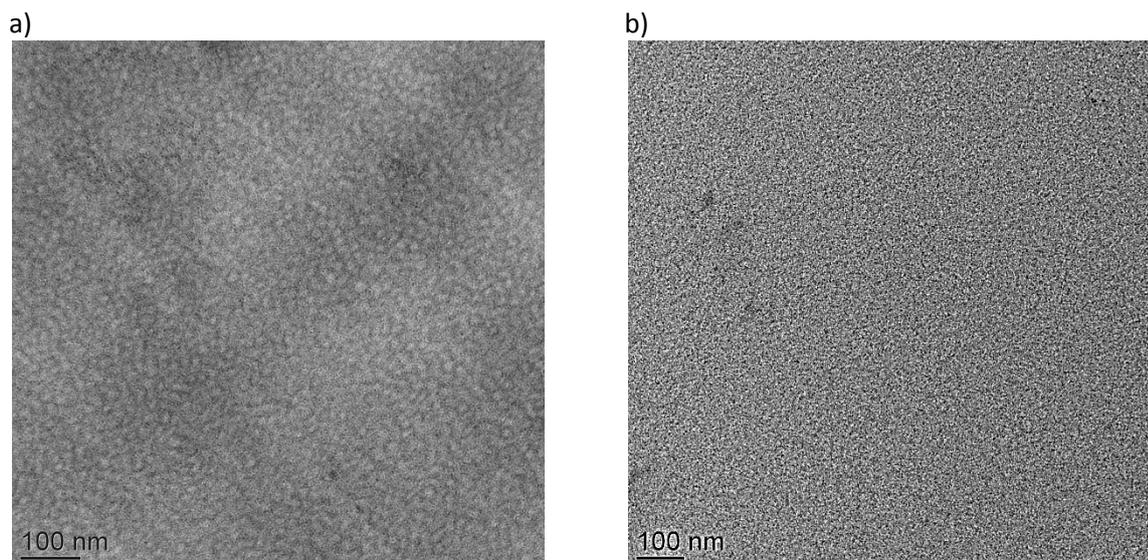


Figure VI.7.1.3.1. TEM photographs of a) BSPAEK-S-6k-4k, b) statSPAEEK-S membranes exchanged with $Pb(NO_3)_2$. Scale bars = 100 nm.

VI.7.1.4. Effect of film casting conditions on the microphase separation of BSPAEK membranes

It was noticed that all membranes have microphase separation, however, the film prepared by the classic method (BSPAEEK-S-8k-4k) showed well visible ionic clusters.

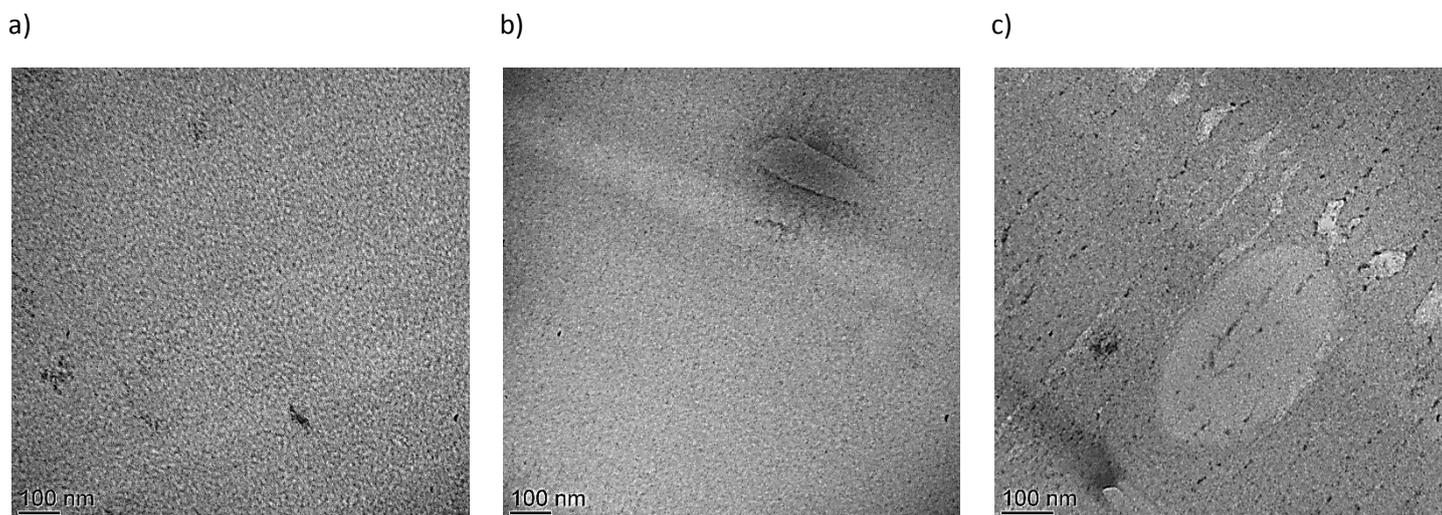


Figure VI.7.1.4.1. TEM photographs of a) BSPAEK-S-8k-4k, b) BSPAEK-S-8k-4k-180°C, c) BSPAEK-S-8k-4k-50°C membranes exchanged with $Pb(NO_3)_2$. Scale bars = 100 nm.

Membrane prepared at 50°C (BSPA EK-S-8k-4k-50°C) was very brittle which may be caused by lateral organization of the segments. Comparison among the three membranes confirms that film casting conditions have high influence on the microphase separation. By drying a membrane below its T_g temperature, the organization of the membrane is differently developed. The way of membrane preparation can influence not only phase organization but also properties like water uptake as well as proton conductivity.

VI.7.2. Atomic force microscopy (AFM)

The tapping mode AFM phase images of the membranes were reordered under ambient conditions $2 \times 2 \mu\text{m}^2$ size scale to investigate its microstructure. As can be seen in Figure VI.7.2.1 and VI.7.2.2, the phase image presented a clear hydrophilic/hydrophobic phase separation which is provoked by multiblock structure.

The dark and bright regions are assigned to the soft hydrophilic structure containing sulfonic groups and the hard hydrophobic structure. As is seen in Figure VI.7.2.1 and VI.7.2.2, the effect of block length on the morphology is noticeable. The AFM phase images correspond to their aggregated ionic groups and the lighter regions to their hydrophobic backbones. The sizes of both the lighter hydrophobic and darker hydrophilic regions appear to increase as block length increases from 4 to 8 kg/mol.

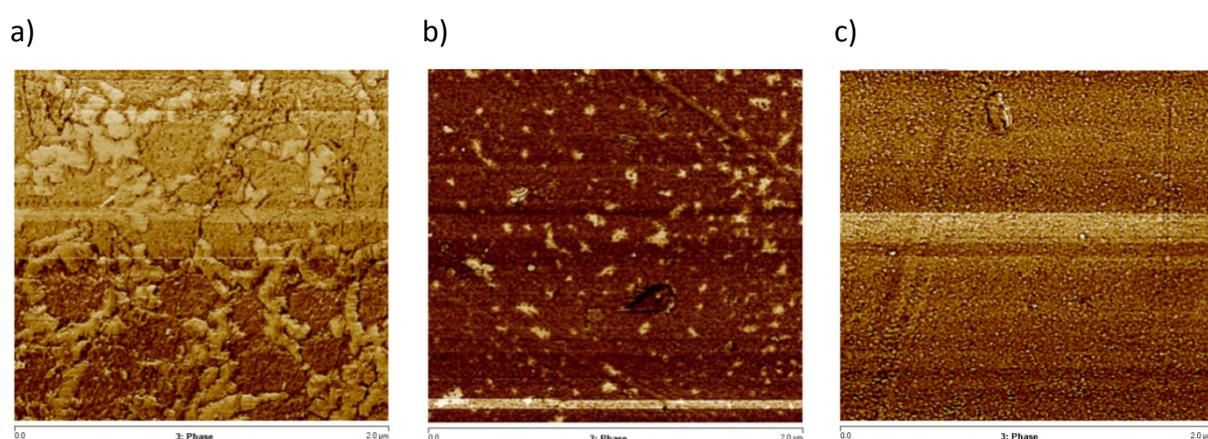


Figure VI.7.2.1. Tapping mode AFM phase image of block copolymers: a) BSPAEK-S-8k-4k, b) BSPAEK-S-8k-4k and c) BSPAEK-S-4k-4k.

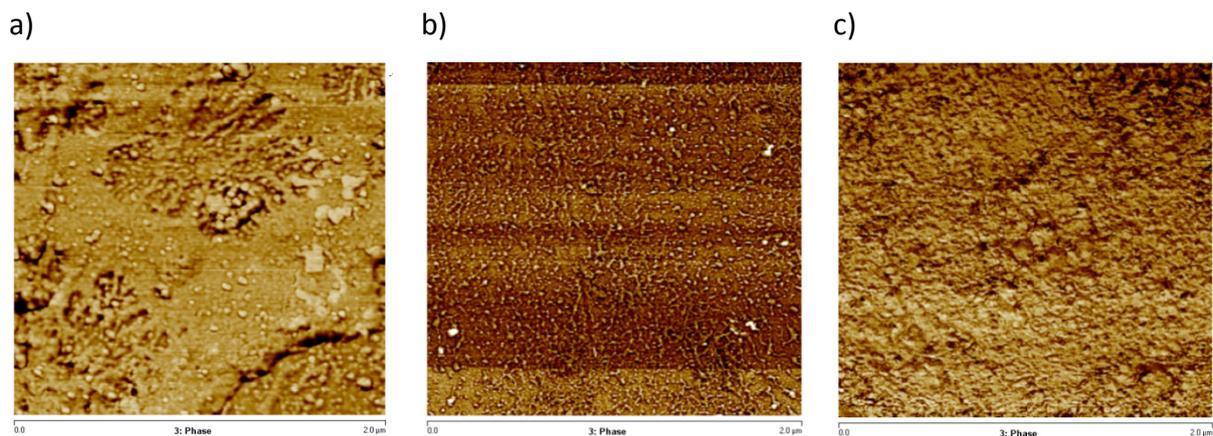


Figure VI.7.2.2. Tapping mode AFM phase image of block of block copolymers: a) BSPAEK-F-8k-4k, b) BSPAEK-F-6k-4k and c) BSPAEK-F-4k-4k.

VI.8. Determination of IEC by titration

The titration of non-aqueous solution was used to determined IEC of block copolymers (see Table VI.8.1).

Titration confirmed the theoretical ion exchange capacity of block and statistic copolymers.

Table VI.8.1. Expected and Experimental IEC values of BSPAEK and statSPAEEK.

copolymer	BSPAEEK F-8k-4k	BSPAEEK F-6k-4k	BSPAEEK F-4k-4k	BSPAEEK S-8k-4k	BSPAEEK S-6k-4k	BSPAEEK S-4k-4k	statSPAEEK S
IEC theoretical (meq/g)	1.1	0.9	0.7	1.05	1.0	0.6	1.0
IEC _{AQU}	1.1±0.06	0.73±0.4	0.6±0.03	1.07±0.5	1.06±0.05	0.55±0.3	0.88±0.04
IEC _{Non-aqu}	1.05±0.05	0.95±0.05	0.79±0.04	1.06±0.05	0.95±0.05	0.78±0.04	0.93±0.05

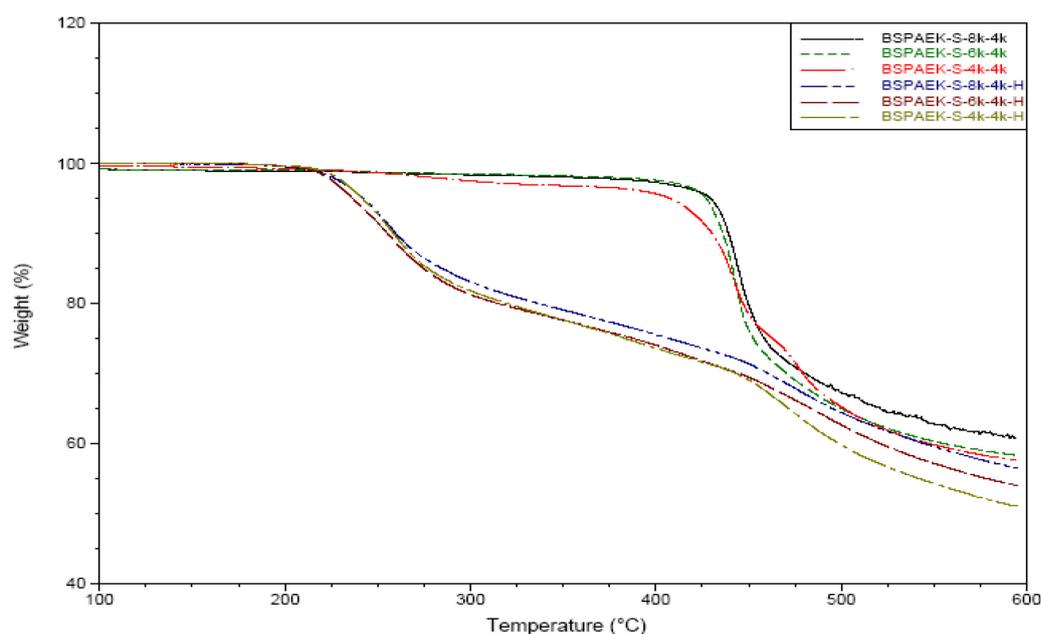
± 5% of error

VI.9. Thermal stability

VI.9.1. Thermal stability of BSPAEK

Thermal stabilities of sulfonated block copolymers were investigated by TGA in both K⁺ and H⁺ forms. As shown in Figure VI.9.1.1, the polymer BSPAEK in potassium form exhibited a one-step degradation at around 420°C due to main chain degradation. Sulfonated block copolymers with sulfone moieties in the main polymer bond have slightly higher T_d temperatures than that of the highly fluorinated block copolymers (Table VI.9.1.1). As it is shown in Figure VI.9.1.1.a and b, TGA curves of membranes in acid forms exhibited two-step weight loss. The initial weight loss step started at around 230-300°C and the second one at around 420°C.

a)



b)

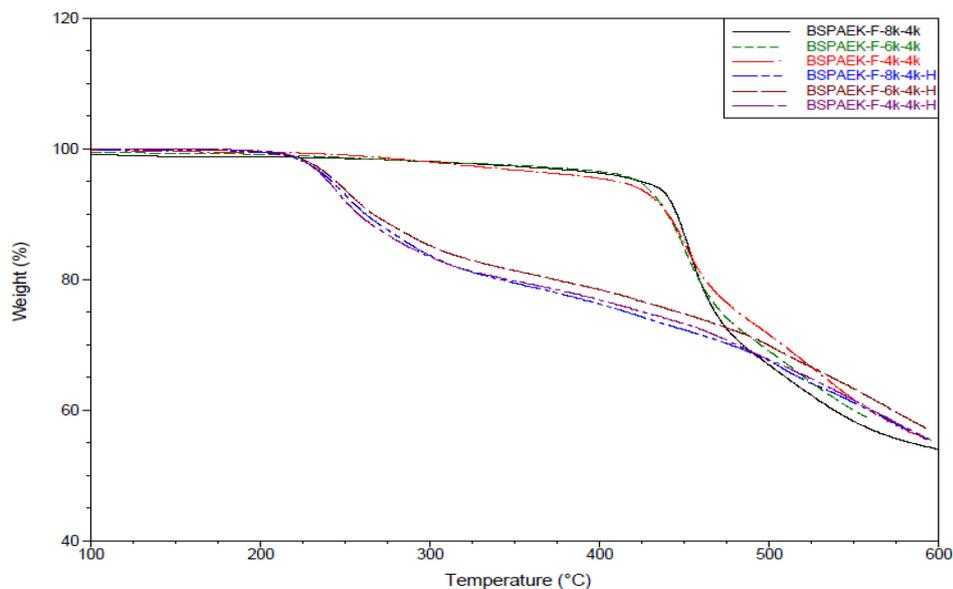


Figure VI.9.1.1. TGA thermogram of the sulfonated block copolymers: a) BSPAEK-S, b) BSPAEK-F, in K^+ form and H^+ form.

The first weight loss is attributed to the desulfonation of sulfonic groups and the second one is attributed to the decomposition of the main polymer chains. There are no significant differences between polymers with different hydrophilic and hydrophobic oligomer lengths.

DSC was conducted to characterize the thermal transition of the multiblock copolymers in the potassium form. As it is shown in Figure VI.9.1.2, two glass transitions were found in sulfonated block copolymers. T_g of the multiblock copolymers are summarized in Table VI.9.1.1. The lower T_g (I) was assigned to the T_g of the hydrophobic segment which was found to be more flexible than hydrophilic block. The higher T_g (II) was associated to the hydrophilic, sulfonated block which is more rigid segment. This nanophase separation is expected because hydrophilic and hydrophobic segments in both block copolymers are different in terms of their chemical structure. It suggests that the hydrophobic segment has a more flexible backbone than the hydrophilic block, which has very rigid polymer chain. DSC analysis confirmed nanophase separation between hydrophilic/hydrophobic segments. However, in the case of the sulfonated block BSPAEK-S-4k-4k, which has short blocks ($M_n=4000$), only one glass transition was detected ($T_g=184^\circ\text{C}$). For block copolymers with

different size segments this effect is more visible because longer hydrophilic blocks increase the immiscibility between segments, which favoring the nanophase separation in the multiblock systems.

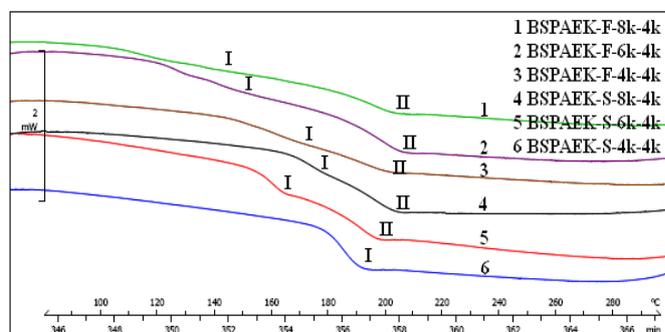


Figure VI.9.1.2. DSC traces of the BSPAEK-F and BSPAEK-S copolymers in the K^+ form (N_2 , $10^\circ C \text{ min}^{-1}$).

Table VI.9.1.1. Thermal property data of BSPAEK.

copolymer	BSPA EK F-8k-4k	BSPA EK F-6k-4k	BSPA EK F-4k-4k	BSPA EK S-8k-4k	BSPA EK S-6k-4k	BSPA EK S-4k-4k	statSPA EK S
IEC(meq/g)	1.1	0.9	0.7	1.05	1.0	0.6	1.0
T_d ($^\circ C$)*	425	422	410	429	427	407	422
T_d ($^\circ C$)**	242	239	240	242	236	241	240
T_g ($^\circ C$)	I. 113 II. 194	I. 129 II. 196	I. 152 II. 199	I. 164 II. 201	I. 153 II. 190	I. 184	I. 202

* - Measured by TGA in the K^+ form, ** - Measured by TGA in the H^+ form

VI.9.2. Thermal stability of statSPA EK

Thermal stability of statistic copolymer was compared to sulfonated block poly(arylene ether ketone sulfone)s copolymer consisting of hydrophilic block of 6000 g/mol and hydrophobic block of 4000 g/mol. The aim of this investigation was to demonstrate the nanophase separation of the sulfonated block copolymer. Thermo gravimetric analysis was used to study the thermal stability of the copolymers. As it is shown in Figure VI.9.2.1, T_d of statistic copolymer and sulfonated block are around $422^\circ C$ and $427^\circ C$, respectively. TGA curves of the membrane in the acid form showed a degradation close to $240^\circ C$ for both polymers. Then DSC was employed to study the glass transition temperatures of the copolymers.

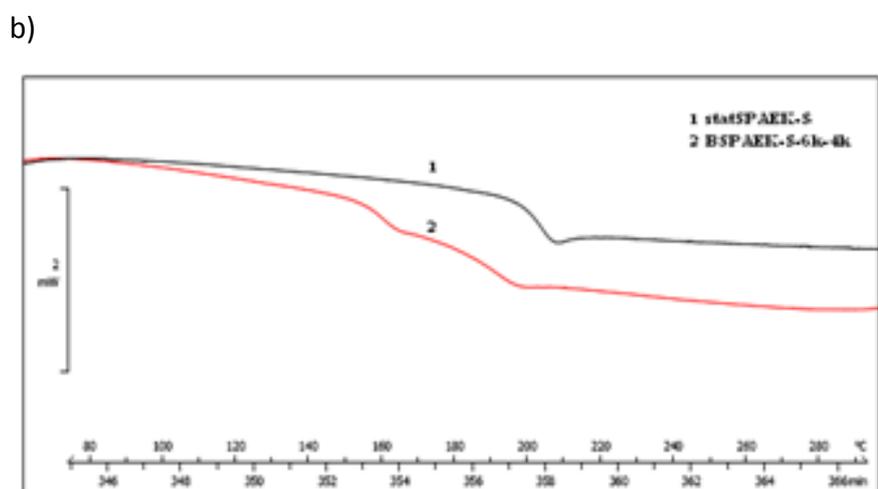
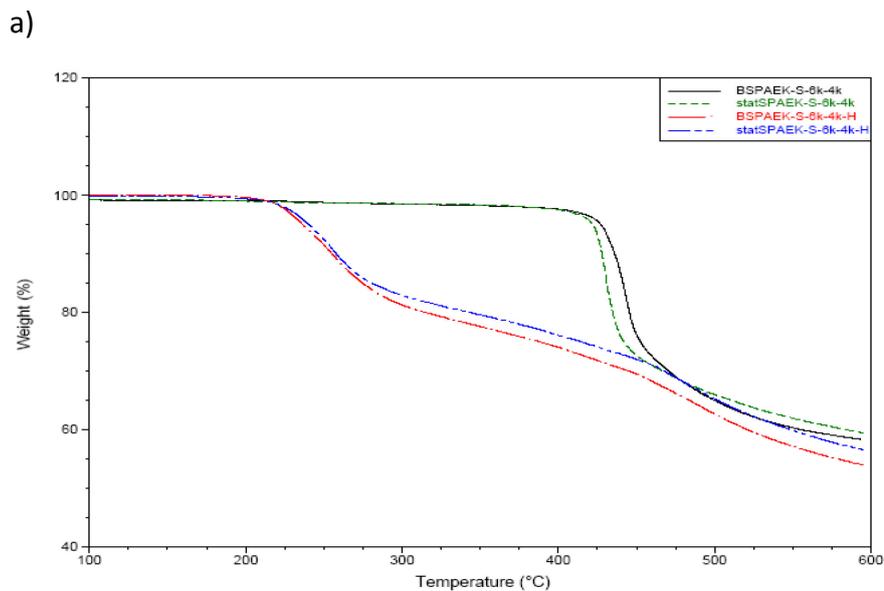


Figure VI.9.2.1. a) TGA thermogram of the statistic polymer and sulfonated block in K^+ and H^+ form, b) DSC traces of the statSPAEEK-S and BSPAEK-S-6k-4k.

Figure VI.9.2.1 b shows the DSC thermogram of both polymers (statSPAEEK-S and BSPAEK-S-6k-4k). As a result, two separate T_g 's can be observed for the BSPAEK-S-6k-4k copolymer and only one T_g for statSPAEEK-S copolymer (Table VI.9.1.1).

VI.10. Water uptake

VI.10.1. Water uptake properties of BSPAEK polymers

The hydrophilic-hydrophobic nanophase separation morphology of the sulfonated block copolymers is considered to have a particularly significant influence on water uptake which may facilitate proton transportation at even low humidity. With increasing sulfonated chain length, the phase separation between the hydrophobic and the hydrophilic segments became more apparent. This effect influences the water uptake of sulfonated block copolymers. The increase in water uptake with increasing block length may suggest the formation of ordered hydrophilic domains within the copolymer.

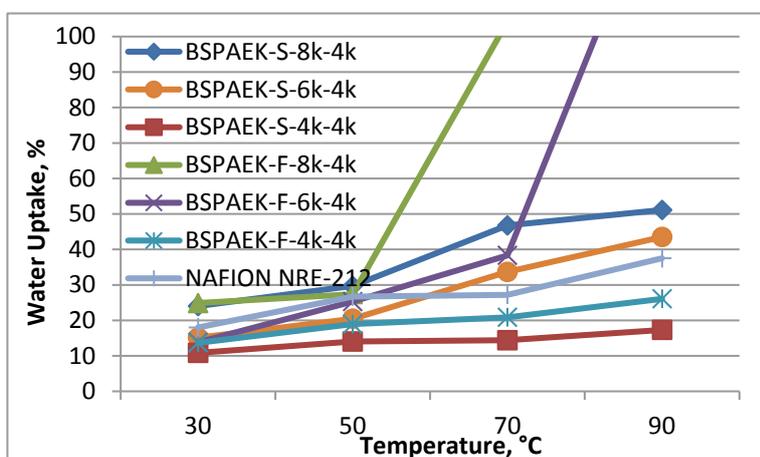


Figure VI.10.1.1. Temperature dependence of water uptake of the BSPAEK-S and BSPAEK-F membranes.

Block copolymers with decafluorodiphenyl in the structure extensively swelled even at low temperature. In this case the major factors of swelling are the chemical structure of the hydrophobic segment and length of the hydrophilic block. Introducing very hydrophobic decafluorodiphenyl monomer to block copolymer created better phase separation between two segments. That creates well developed channels which can absorb more water.

Table VI.10.1.1. Hydration number of BSPAEK membranes at different temperatures.

copolymer	BSPAEK F-8k-4k	BSPAEK F-6k-4k	BSPAEK F-4k-4k	BSPAEK S-8k-4k	BSPAEK S-6k-4k	BSPAEK S-4k-4k	statSPAEK
IEC(meq/g)	1.1	0.9	0.7	1.05	1.0	0.6	1.0
	λ (H ₂ O/SO ₃ H)						
30°C	13	8.5	11	13	8	10	5
50°C	14	16	15	16	11	13	7
70°C	53	24	17	26	19	13	10
90°C	153	90	21	28	24	16	17

As it is shown in Table VI.10.1.1, highly fluorinated block copolymers (BSPAEK-F) exhibited higher water molecules absorption than block copolymers with diphenyl sulfone (BSPAEK-S) in the polymer main chain. This behavior explained the high water uptake of BSPAEK-F membranes. The statistic copolymer showed hydration numbers lower than that of corresponding block copolymer at all range of temperature.

VI.10.2. Effect of film casting conditions on the water uptake of BSPAEK membranes

The effect of membrane preparation on water uptake was investigated. BSPAEK-S-8k-4k copolymer was chosen for this test. From a polymer solution three films were prepared at following different conditions: the first polymer film was dried according to a typical sequences which is discussed in experimental part. The second film was heated at 50°C during 48 h and the last polymer film was heated for one hour at 50°C and then at 180°C for 24 h. Water uptakes of sulfonated block membranes are presented in Figure VI.10.2.1.

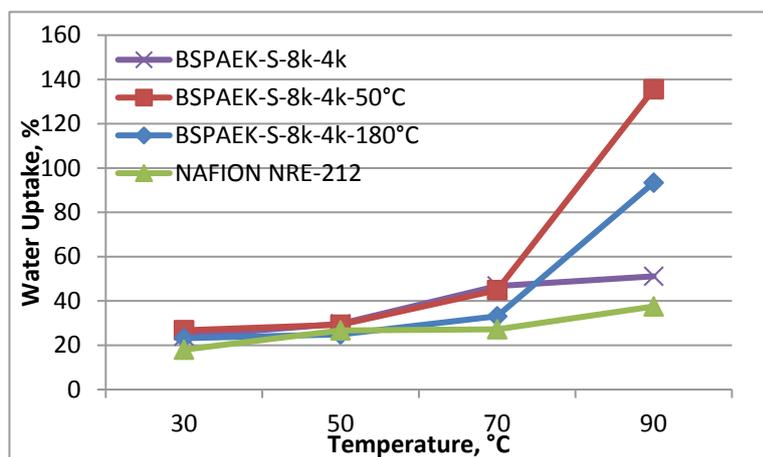


Figure VI.10.2.1. Temperature dependence of water uptake of the BSPAEK-S-8k-4k membranes prepared with different casting film methods.

As it is seen in Figure VI.10.2.1, membrane BSPAEK-8k-4k-50°C prepared at 50°C swelled more than the film prepared by the classic method (BSPAEK-8k-4k). A significant difference was observed at high temperature, where the membrane prepared at 50°C (BSPAEK-8k-4k-50°C) swelled extensively, WU=136%. The membrane prepared at 180°C (BSPAEK-8k-4k-180°C) showed water uptake values of around 93% and for the film prepared by the classic method the water uptake value is only 51%. The casting temperature has a high impact on the copolymer organization which is responsible for morphology changes as discussed in Section VI.7.1.4.

Table VI.10.2.1. Hydration number of BSPAEK-S membranes with different casting film methods.

copolymer	λ (H ₂ O/SO ₃ H)			
	30°C	50°C	70°C	90°C
BSPAEK-S 8k-4k-50°C	14	15.5	24	72
BSPAEK-S 8k-4k-180°C	12	13	17.5	49
BSPAEK-S 8k-4k	13	16.5	26	28

The membrane prepared at 50°C showed higher absorption of water molecules per sulfonic acid groups than the membranes prepared following the classical procedure (Table VI.10.2.1).

VI.10.3. Water uptake of statSPAEEK

The water uptake of the block copolymer BSPAEK-S-6k-4k was compared with the water uptake of the statistic copolymer, statSPAEEK-S. As it is shown in Figure VI.10.3.1, the water uptake of both copolymers membranes increased with increasing temperature. However, the block copolymer swelled more than the statistic copolymer in all range of temperature.

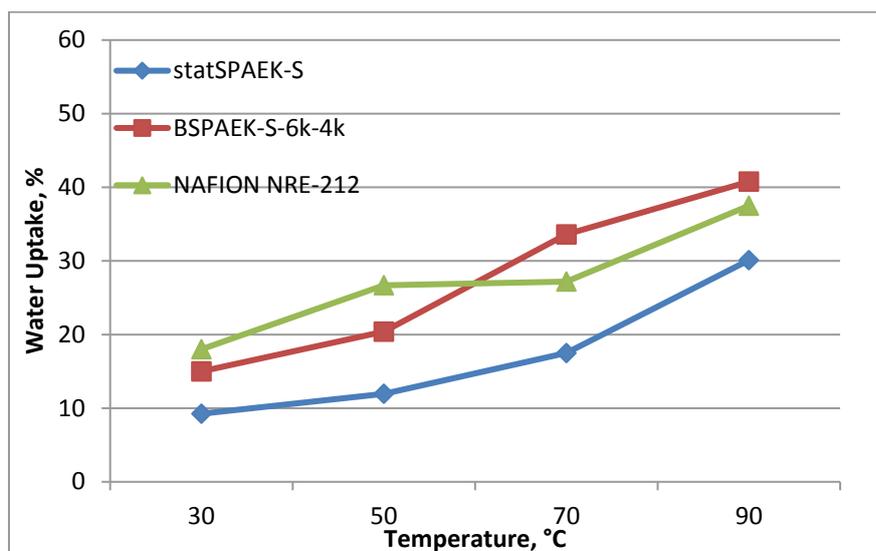


Figure VI.10.3.1. Temperature dependence of water uptake of the BSPAEK-S-6k-4k and statSPAEEK membranes.

VI.11. Ionic conductivity

VI.11.1. Ionic conductivity of BSPAEK

Ionic conductivities of the block copolymers were measured in the RH range of 50-95% at different temperatures. Results are summarized in Table VI.11.1.1. The proton conductivities of highly fluorinated block copolymers are higher than that of BSPAEK-S copolymers for example: BSPAEK-F-8k-4k, IEC=1.1 meq/g, 0.206 S/cm at 90°C and BSPAEK-S-8k-4k, IEC=1.1 meq/g, 0.185 S/cm at 90°C. These results indicate that chemical structure of block polymers highly influence proton conductivity.

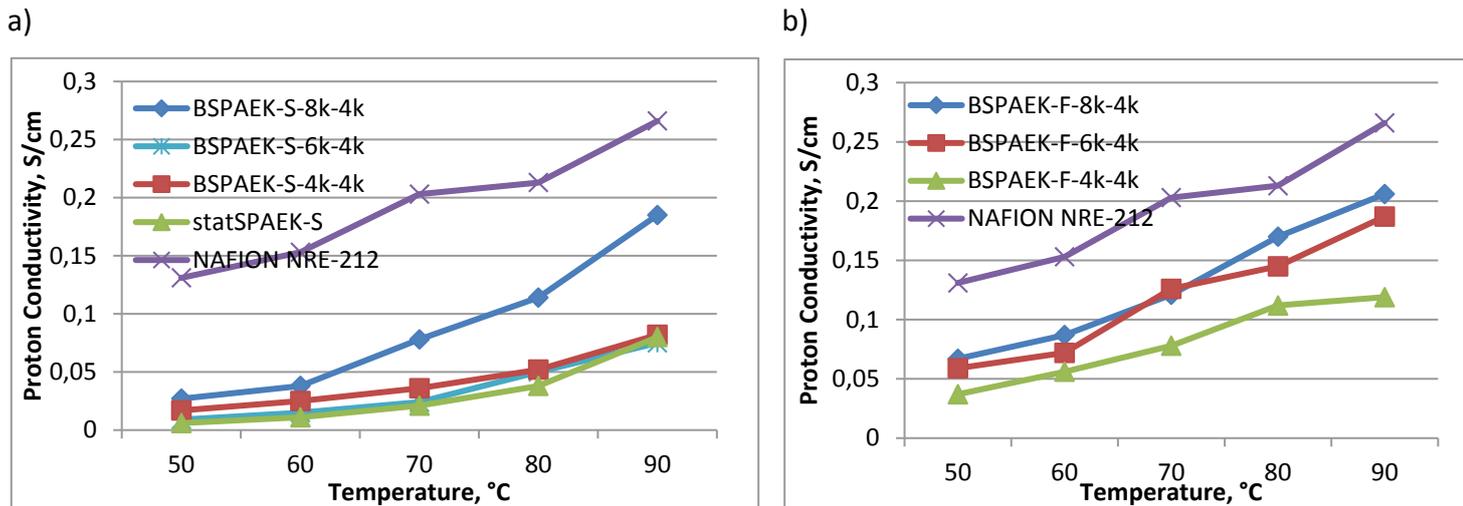


Figure VI.11.1.1. Proton conductivity as a function of temperature of: a) BSPAEK-S, b) BSPAEK-F membranes and Nafion NRE-212 at 95% relative humidity.

As is seen in Figure VI.11.1.1, statistic copolymer showed slightly lower proton conductivity than its corresponding block copolymer, BSPAEK-S-6k-4k. This occurrence can be explained by block's polymers good phase separation between the hydrophilic and hydrophobic domains. Usually, high water uptake of block polymers leads to the high proton conductivities, in contrast to the random copolymers. The proton conductivity of the block copolymers under partially hydrated condition are improved with increasing length of the segments[48]. Highly fluorinated BSPAEK-F membranes showed high water uptake (BSPAEK-F WU=300%) than that of BSPAEK-S (WU=51) which can explain high conductivity.

Table VI.11.1.1. Proton conductivities versus RH and temperature of BSPAEK-S and statSPAEEK copolymers.

Temp.	Block Copolymer											
	BSPAEEK-S-8k-4k			BSPAEEK-S-6k-4k			BSPAEEK-S-4k-4k			statSPAEEK-S		
	Proton conductivity (mS/cm)											
	Relative Humidity (%)											
	50%	70%	95%	50%	70%	95%	50%	70%	95%	50%	70%	95%
50°C	23	26	27	7	8	9	9	11	13	5	5	6
60°C	32	36	38	12	14	15	23	24	25	8	10	11
70°C	69	73	78	20	23	24	31	32	36	19	20	21
80°C	73	102	114	38	47	50	45	51	52	33	36	38
90°C	154	176	185	67	71	75	72	77	82	61	74	80

Table VI.11.1.2. Proton conductivities versus RH and temperature of highly BSPAEK-F copolymers.

Temp.	Block Copolymer								
	BSPA EK-F-8k-4k			BSPA EK-F-6k-4k			BSPA EK-F-4k-4k		
	50%RH	70%RH	95%RH	50%RH	70%RH	95%RH	50%RH	70%RH	95%RH
50°C	56	61	67	46	56	59	30	34	37
60°C	68	80	87	57	64	72	47	55	56
70°C	102	102	121	122	124	126	59	63	78
80°C	137	158	170	127	140	145	95	106	112
90°C	216	211	206	179	186	187	103	116	119

VI.11.2. Effect of film casting conditions on ionic conductivity of BSPAEK

Influences of membrane preparation condition on proton conductivity were investigated. The proton conductivities of the BSPAEK-S-8k-4k membranes are plotted as a function of RH and compared with that of Nafion NRE-212 membrane (see Figure VI.11.2.1). The BSPAEK-S-180°C membrane showed slightly higher proton conductivity at 70 RH (0.18 S/cm). Membrane which was prepared at 50°C showed significantly lower proton conductivity than these membranes prepared by the classic method and membrane prepared at 180°C.

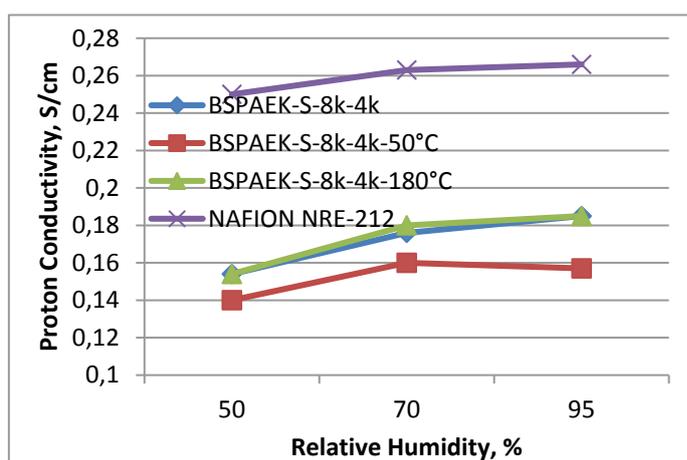


Figure VI.11.2.1. Proton conductivity as a function of RH at 90°C of the BSPAEK-S-8k-4k membranes performed at different casting film methods.

Figure VI.11.2.1 shows the RH dependence of proton conductivities at 90°C. The proton conductivity of the membranes decreases rapidly with decreasing relative humidity from 95

to 50% RH. These results showed that membrane preparation can influence of the membrane. Higher proton conductivities of the membrane prepared by classic method (BSPA EK-S-8k-4k) and at 180°C (BSPA EK-S-8k-4k-180°C) showed better phase separation where the hydrophilic domains are well dispersed and connected to each other. This phenomenon consequences in formation of proton transportation channels, resulting in high proton conductivity in the whole range of relative humidity.

Table VI.11.2.1. Proton conductivities versus RH and temperature of BSPAEK-S-8k4k copolymers performed in different film casting conditions.

Temp.	Block Copolymer								
	BSPA EK-S-8k-4k-50°C			BSPA EK-S-8k-4k-180°C			BSPA EK-S-8k-4k		
	Proton conductivity (mS/cm)								
	50%RH	70%RH	95%RH	50%RH	70%RH	95%RH	50%RH	70%RH	95%RH
50°C	15	21	24	19	27	31	23	26	27
60°C	41	44	46	19	33	40	32	36	38
70°C	60	72	78	39	57	65	69	73	78
80°C	99	124	135	97	111	117	73	102	114
90°C	140	160	157	154	180	198	154	176	185

VI.12. Conclusion

Hydrophilic/hydrophobic multiblock copolymers based on poly(arylene ether ketone)s were synthesized and characterized. Proton conductivity increased with increase of IEC and length of hydrophilic segment for both series of block copolymers. Longer block length seems to be very effective in increasing proton conductivity which proven by the morphological observations. Tapping-mode AFM studies showed clear nano-phase separation between hydrophilic and hydrophobic domains. Well-connected hydrophilic domains worked as proton transportation channels which resulting with high proton conduction. The highly sulfonated multiblock copolymer structure demonstrated that this strategy is a promising way to achieve high-performance PEM materials.

VII. Conclusion générale

Ce travail avait pour but de mettre au point de nouveaux polymères conducteurs ioniques, de type poly éther aromatiques susceptibles d'être utilisés comme membranes de piles à combustible. Pour cela, il a été choisi d'introduire des groupes latéraux de type perfluoro alkyl sulfoné sur les chaînes des polymères. Pour réaliser la synthèse de ces polymères, la stratégie adoptée est celle qui consiste à réaliser la polymérisation en impliquant des précurseurs contenant dans leur structure le motif perfluoro alkyle sulfoné.

La préparation de ces polymères a donc nécessité dans un premier temps la synthèse de ces précurseurs. Ainsi quatre monomères originaux ont été développés. Pour chacun d'entre eux, un schéma de synthèse a été mis au point. La réactivité de ces monomères a été préalablement testée à partir de réactions modèles. Ces études ont montré que le FPSAB-K et le FPSAPS-K monomères avaient une réactivité relativement modeste dans une réaction de type SNAr utilisée pour la synthèse des polymère. Les deux autres monomères 3,4'-FPSAPS-K et FPSABP-K ont par contre, montré une bien meilleure réactivité qui peut s'expliquer par la présence dans la structure de ces monomères de motifs sulfone pour le 3,4'-FPSAPS-K et cétone pour le FPSABP-K qui tendent à sensiblement accroître dans le cas d'une réaction de type SNAr, la réactivité des carbones des noyaux aromatiques en position ortho et para de ces motifs dû à leur effet électro attracteur.

A partir de ces monomères différents polymères aromatiques à chaînes latérales perfluoro alkyle sulfonées ont été préparés en utilisant comme co-monomères des composés commercialement disponibles. En fonction de la structure du monomère sulfoné utilisé pour la synthèse des polymères, on peut les différencier en quatre catégories de polymères aromatiques à savoir:

- les poly(arylène éther)s
- les poly(arylène éther sulfure)s
- les, poly(arylène éther sulfone)s
- et les poly(arylène éther cétone)s

Pour chacune de ces séries, des polymères avec différents CEI ont été préparés. Si pour la plupart de ces polymères, on peut considérer que les unités sulfonées sont réparties dans les chaînes macromoléculaires de façon statistique, on a toutefois obtenu une série de copolymères à blocs en adaptant le procédé de polymérisation qui consiste à réaliser la réaction de polymérisation en deux étapes successives. Ainsi, des copolymères à blocs sulfonés avec des tailles de blocs sulfoné et non sulfoné bien définies ont été préparés.

Une étude des propriétés thermiques de ces polymères a notamment révélé que ceux-ci présentaient une T_g relativement élevée comprise entre 190°C et 230°C. Dans le cas particulier des copolymères à blocs deux T_g ont été observées.

Des membranes auto-portantes ont été préparées avec pratiquement l'ensemble de ces polymères en utilisant la méthode de coulée évaporation.

Les propriétés de gonflement de ces membranes ont été également étudiées mettant en évidence l'influence de la CEI du polymère. L'effet de la température sur le gonflement a été observé de façon plus marquée avec les CEI les plus fortes. Dans le cas des copolymères à blocs une variation du gonflement en fonction de la longueur du bloc sulfoné a été constatée. Il a également été constaté que la nature du bloc hydrophobe avait une influence sur le gonflement.

Les copolymères à blocs avec DFP dans le segment hydrophobe contenant le précurseur décafluorobiphenyl ont montré des absorptions d'eau plus élevées que les copolymères dont les blocs hydrophobes contiennent le motif diphenylsulfone.

En ce qui concerne la conductivité ionique les résultats montrent que les polymères synthétisés ont des conductivités inférieures à celles du Nafion. Toutefois avec les polymères ayant les CEI les plus élevées des valeurs de conductivité proches de celles du Nafion ont été obtenues.

On peut aussi souligner que les copolymères à blocs ont montré des conductivités significatives même avec une faible CEI (CEI = 1,1 mEq/g). La morphologie biphasique des membranes préparées avec les copolymères à blocs est un facteur prépondérant pour expliquer leur bonne conductivité.

Pour améliorer les propriétés de ces polymères aromatiques à chaînes latérales perfluoro alkyl sulfonées notamment celles relatives au gonflement à l'eau et au transport des charges ioniques, la voie des copolymères à blocs semblent être la plus prometteuse. Pour cela il serait intéressant d'augmenter la taille des blocs sulfonés pour améliorer la conductivité mais aussi d'accroître la rigidité des blocs hydrophobe pour réduire le gonflement des membranes. A ce titre on peut penser que former des blocs hydrophobes (non sulfonés) présentant un caractère semi-cristallin (par exemple cétone bloc), serait de nature à améliorer les propriétés de gonflement des membranes.

References

1. WHITTINGHAM M S, SAVINELL R F, and ZAWODZINSKI T. Introduction: Batteries and Fuel Cells. *Chemical Reviews*, 2004, vol. 104, n°. 10, pp. 4243-4244.
2. WINTER M and BRODD R J. What Are Batteries, Fuel Cells, and Supercapacitors. *Chemical Reviews*, 2004, vol. 104, pp. 4245-4269.
3. YU X, ROY A, DUNN S, et al. Synthesis and Characterization of Sulfonated-Fluorinated, Hydrophilic-Hydrophobic Multiblock Copolymers for Proton Exchange Membranes. *Macromolecular Symposia*, 2006, vol. 245-246, n°. 1, pp. 439-449.
4. GROVE W R. On Voltaic Series and the Combination of Gases by Platinum. *London and Edinburgh Philosophical Magazine and Journal of Science*, 1839, pp. 127-130.
5. Fuel Cell Today. Johnson Matthey Public Limited Company, [en ligne], Disponible sur: <<http://www.fuelcelltoday.com/technologies>> (consulté le 10.01.2014).
6. RESNICK P R. A Short History of Nafion®. *Matériaux et nouvelles technologies*, 2006, n°. 301-302, pp. 144-147.
7. COLOMBAN P. Proton Conductor : Solid, Membranes and Gel Materials and Devices. Cambridge University Press, 1992.
8. KREUER K D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *Journal of Membrane Science*, 2001, vol. 185, pp. 29-39.
9. KOBAYASHI T, RIKUKAWA M, SANUI K, et al. Proton-conducting polymers derived from poly(ether-etherketone) and poly(4-phenoxybenzoyl-1,4-phenylene). *Solid State Ionics*, 1998, vol. 106, pp. 219-225.
10. NOHE R, LEDJEFF K, BAUERB M, et al. Partially sulfonated poly (arylene ether sulfone) -A versatile proton conducting membrane material for modern energy conversion technologies. *Journal of Membrane Science*, 1993, vol. 83, pp. 211-220.
11. WANG F, HICKNER M, KIMA Y S, et al. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. *Journal of Membrane Science*, 2002, vol. 197, pp. 231-242.
12. OROUJZADEH M, MEHDIPOUR-ATAEI S, and ESFANDEH M. Preparation and properties of novel sulfonated poly(arylene ether ketone) random copolymers for polymer electrolyte membrane fuel cells. *European Polymer Journal*, 2013, vol. 49, n°. 6, pp. 1673-1681.
13. GAO Y, ROBERTSON G, MIKHAILENKO S D, et al. Synthesis of Copoly(aryl ether ether nitrile)s Containing Sulfonic Acid Groups for PEM Application. *Macromolecules*, 2005, vol. 38, pp. 3237-3245.
14. LIU B, ROBERTSON G P, KIM D-S, et al. Aromatic Poly(ether ketone)s with Pendant Sulfonic Acid Phenyl Groups Prepared by a Mild Sulfonation Method for Proton Exchange Membranes. *Macromolecules*, 2007, vol. 40, pp. 1934-1944.
15. MEIER-HAACK J, KOMBER H, VOGEL C, et al. Side-Chain Sulfonated Poly(arylene ether)s for Fuel Cell Applications. *Macromolecular Symposia*, 2007, vol. 254, n°. 1, pp. 322-328.

16. LAFITTE B, PUCHNER M, and JANNASCH P. Proton Conducting Polysulfone Ionomers Carrying Sulfoaryloxybenzoyl Side Chains. *Macromolecular Rapid Communications*, 2005, vol. 26, n°. 18, pp. 1464-1468.
17. KIM D S, ROBERTSON G P, KIM Y S a, et al. Copoly(arylene ether)s Containing Pendant Sulfonic Acid Groups as Proton Exchange Membranes. *Macromolecules*, 2009, vol. 42, pp. 957-963.
18. SANKIR M, KIM Y S, PIVOVAR B S, et al. Proton exchange membrane for DMFC and H₂/air fuel cells: Synthesis and characterization of partially fluorinated disulfonated poly(arylene ether benzonitrile) copolymers. *Journal of Membrane Science*, 2007, vol. 299, n°. 1-2, pp. 8-18.
19. GAO Y, ROBERTSON G P, GUIVER M D, et al. Sulfonated copoly(phthalazinone ether ketone nitrile)s as proton exchange membrane materials. *Journal of Membrane Science*, 2006, vol. 278, n°. 1-2, pp. 26-34.
20. KARLSSON L. Polysulfone ionomers for proton-conducting fuel cell membranes: sulfoalkylated polysulfones. *Journal of Membrane Science*, 2004, vol. 230, n°. 1-2, pp. 61-70.
21. SHAO K, ZHU J, ZHAO C, et al. Naphthalene-based poly(arylene ether ketone) copolymers containing sulfobutyl pendant groups for proton exchange membranes. *Journal of Polymer Science Part A: Polymer Chemistry*, 2009, vol. 47, n°. 21, pp. 5772-5783.
22. ZHANG Y, WAN Y, ZHAO C, et al. Novel side-chain-type sulfonated poly(arylene ether ketone) with pendant sulfoalkyl groups for direct methanol fuel cells. *Polymer*, 2009, vol. 50, n°. 19, pp. 4471-4478.
23. ZHANG Y, ZHANG G, WAN Y, et al. Synthesis and characterization of poly(arylene ether ketone)s bearing pendant sulfonic acid groups for proton exchange membrane materials. *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, vol. 48, n°. 24, pp. 5824-5832.
24. TSAI J-C and LIN C-K. Preparation of main-chain-type and side-chain-type sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell applications. *Journal of Power Sources*, 2011, vol. 196, n°. 22, pp. 9308-9316.
25. MATSUMURA S, HLIL A R, LEPILLER C, et al. Ionomers for Proton Exchange Membrane Fuel Cells with Sulfonic Acid Groups on the End Groups: Novel Branched Poly(ether-ketone)s. *Macromolecules*, 2008, vol. 41, pp. 281-284.
26. MATSUMURA S, HLIL A R, LEPILLER C, et al. Ionomers for Proton Exchange Membrane Fuel Cells with Sulfonic Acid Groups on the End Groups: Novel Linear Aromatic Poly(sulfide-ketone)s. *Macromolecules*, 2008, vol. 41, pp. 277-280.
27. WANG C, LI N, SHIN D W, et al. Fluorene-Based Poly(arylene ether sulfone)s Containing Clustered Flexible Pendant Sulfonic Acids as Proton Exchange Membranes. *Macromolecules*, 2011, vol. 44, n°. 18, pp. 7296-7306.
28. GHASSEMI H, SCHIRALDI D A, ZAWODZINSKI T A, et al. Poly(arylene ether)s with Pendant Perfluoroalkyl Sulfonic Acid Groups as Proton-Exchange Membrane Materials. *Macromolecular Chemistry and Physics*, 2011, vol. 212, n°. 7, pp. 673-678.
29. NAKABAYASHI K, HIGASHIHARA T, and UEDA M. Polymer Electrolyte Membranes Based on Poly(phenylene ether)s with Pendant Perfluoroalkyl Sulfonic Acids. *Macromolecules*, 2011, vol. 44, n°. 6, pp. 1603-1609.

30. MIYATAKE K, SHIMURA T, MIKAMI T, et al. Aromatic ionomers with superacid groups. *Chem Commun (Camb)*, 2009, n°. 42, pp. 6403-6405.
31. YOSHIMURA K and IWASAKI K. Aromatic Polymer with Pendant Perfluoroalkyl Sulfonic Acid for Fuel Cell Applications. *Macromolecules*, 2009, vol. 42, n°. 23, pp. 9302-9306.
32. NAKAGAWA T, NAKABAYASHI K, HIGASHIHARA T, et al. Polymer Electrolyte Membrane Based on Poly(ether sulfone) Containing Binaphthyl Units with Pendant Perfluoroalkyl Sulfonic Acids. *Journal of Polymer Science Part A Polymer Chemistry*, 2011, vol. 49, pp. 2997-3003.
33. MIKAMI T, MIYATAKE K, and WATANABE M. Poly(arylene ether)s Containing Superacid Groups as Proton Exchange Membranes. *ACS Appl Mater Interfaces*, 2010, vol. 2, n°. 6, pp. 1714-1721.
34. ZHANG Q, LIU B, HU W, et al. Poly(arylene ether) electrolyte membranes bearing aliphatic-chain-linked sulfophenyl pendant groups. *Journal of Membrane Science*, 2013, vol. 428, pp. 629-638.
35. PANG J, ZHANG H, LI X a, et al. Novel Wholly Aromatic Sulfonated Poly(arylene ether) Copolymers Containing Sulfonic Acid Groups on the Pendants for Proton Exchange Membrane Materials. *Macromolecules*, 2007, vol. 40, pp. 9435-9442.
36. JUTEMAR E P and JANNASCH P. Influence of the polymer backbone structure on the properties of aromatic ionomers with pendant sulfobenzoyl side chains for use as proton-exchange membranes. *ACS Appl Mater Interfaces*, 2010, vol. 2, n°. 12, pp. 3718-3725.
37. JUTEMAR E P, TAKAMUKU S, and JANNASCH P. Facile Synthesis and Polymerization of 2,6-Difluoro-2'-sulfobenzophenone for Aromatic Proton Conducting Ionomers with Pendant Sulfobenzoyl Groups. *Macromolecular Rapid Communications*, 2010, vol. 31, n°. 15, pp. 1348-1353.
38. ZHANG X, HU Z, PU Y, et al. Preparation and properties of novel sulfonated poly(p-phenylene-co-aryl ether ketone)s for polymer electrolyte fuel cell applications. *Journal of Power Sources*, 2012, vol. 216, pp. 261-268.
39. SUN F, WANG T, YANG S, et al. Synthesis and characterization of sulfonated polyimides bearing sulfonated aromatic pendant group for DMFC applications. *Polymer*, 2010, vol. 51, n°. 17, pp. 3887-3898.
40. PANG J, ZHANG H, LI X, et al. Low Water Swelling and High Proton Conducting Sulfonated Poly(arylene ether) with Pendant Sulfoalkyl Groups for Proton Exchange Membranes. *Macromolecular Rapid Communications*, 2007, vol. 28, n°. 24, pp. 2332-2338.
41. PANG J, ZHANG H, LI X, et al. Synthesis and characterization of sulfonated poly(arylene ether)s with sulfoalkyl pendant groups for proton exchange membranes. *Journal of Membrane Science*, 2008, vol. 318, n°. 1-2, pp. 271-279.
42. PANG J, ZHANG H, LI X, et al. Poly(arylene ether)s with pendant sulfoalkoxy groups prepared by direct copolymerization method for proton exchange membranes. *Journal of Power Sources*, 2008, vol. 184, n°. 1, pp. 1-8.
43. KRISHNAN P, ADVANI S G, and PRASAD A K. A functional monomer to synthesize sulfonated poly(ether ether ketone) with sulfonic acid group in the pendant side chain. *Journal of Applied Polymer Science*, 2012, vol. 123, n°. 6, pp. 3331-3336.

44. ZHANG Z, WU L, and XU T. Novel aromatic proton-exchange polyelectrolytes via polyacylation of pre-sulfonated monomers. *Journal of Materials Chemistry*, 2012, vol. 22, n°. 28, pp. 13996-14000.
45. YIN Y, FANG J, WATARI T, et al. Synthesis and properties of highly sulfonated proton conducting polyimides from bis(3-sulfopropoxy)benzidine diamines. *Journal of Materials Chemistry*, 2004, vol. 14, pp. 1062-1070.
46. NAKABAYASHI K, HIGASHIHARA T, and UEDA M. Highly Sulfonated Multiblock Copoly(ether sulfone)s for Fuel Cell Membranes. *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, n°. 48, pp. 2757-2764.
47. LEE H-S, BADAMI A S, ROY A, et al. Segmented sulfonated poly(arylene ether sulfone)-b-polyimide copolymers for proton exchange membrane fuel cells. I. Copolymer synthesis and fundamental properties. *Journal of Polymer Science Part A: Polymer Chemistry*, 2007, vol. 45, n°. 21, pp. 4879-4890.
48. ROY A, HICKNER M A, YU X, et al. Influence of chemical composition and sequence length on the transport properties of proton exchange membranes. *Journal of Polymer Science Part B: Polymer Physics*, 2006, vol. 44, n°. 16, pp. 2226-2239.
49. NAKABAYASHI K, MATSUMOTO K, HIGASHIHARA T, et al. Influence of adjusted hydrophilic-hydrophobic lengths in sulfonated multiblock copoly(ether sulfone) membranes for fuel cell application. *Journal of Polymer Science Part A: Polymer Chemistry*, 2008, vol. 46, n°. 22, pp. 7332-7341.
50. SHI Z a and HOLDCROFT S. Synthesis and Proton Conductivity of Partially Sulfonated Poly([vinylidene difluoride-co-hexafluoropropylene]-b-styrene) Block Copolymers. *Macromolecules*, 2005, vol. 38, pp. 4193-4201.
51. YANG Y, SHI Z a, and HOLDCROFT S. Synthesis of Sulfonated Polysulfone-block-PVDF Copolymers: Enhancement of Proton Conductivity in Low Ion Exchange Capacity Membranes. *Macromolecules*, 2004, vol. 37, pp. 1678-1681.
52. TAKAMUKU S and JANNASCH P. Multiblock Copolymers with Highly Sulfonated Blocks Containing Di- and Tetrasulfonated Arylene Sulfone Segments for Proton Exchange Membrane Fuel Cell Applications. *Advanced Energy Materials*, 2012, vol. 2, n°. 1, pp. 129-140.
53. LEE K H, CHU J Y, KIM A R, et al. Highly Sulfonated Poly(Arylene Biphenylsulfone Ketone) Block Copolymers Prepared via Post-Sulfonation for Proton Conducting Electrolyte Membranes. *Bulletin of the Korean Chemical Society*, 2013, vol. 34, n°. 6, pp. 1763-1770.
54. LEE H-S, ROY A, LANE O, et al. Hydrophilic–hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low-temperature coupling reactions for proton exchange membrane fuel cells. *Polymer*, 2008, vol. 49, n°. 3, pp. 715-723.
55. GHASSEMI H, MCGRATH J E, and ZAWODZINSKI T A. Multiblock sulfonated–fluorinated poly(arylene ether)s for a proton exchange membrane fuel cell. *Polymer*, 2006, vol. 47, n°. 11, pp. 4132-4139.
56. GUO M, LI X, LI L, et al. Novel postsulfonated poly(ether ether ketone)-block-poly(ether sulfone)s as proton exchange membranes for fuel cells: Design, preparation and properties. *Journal of Membrane Science*, 2011, vol. 380, n°. 1-2, pp. 171-180.

57. GHASSEMI H, NDIP G, and MCGRATH J E. New multiblock copolymers of sulfonated poly(4'-phenyl-2,5-benzophenone) and poly(arylene ether sulfone) for proton exchange membranes. II. *Polymer*, 2004, vol. 45, n°. 17, pp. 5855-5862.
58. LI N, HWANG D S, LEE S Y, et al. Densely Sulfophenylated Segmented Copoly(arylene ether sulfone) Proton Exchange Membranes. *Macromolecules*, 2011, vol. 44, n°. 12, pp. 4901-4910.
59. BAE B, MIYATAKE K, and WATANABE M. Synthesis and properties of sulfonated block copolymers having fluorenyl groups for fuel-cell applications. *ACS Appl Mater Interfaces*, 2009, vol. 1, n°. 6, pp. 1279-86.
60. BAE B, MIYATAKE K, and WATANABE M. Sulfonated Poly(arylene ether sulfone ketone) Multiblock Copolymers with Highly Sulfonated Block. *Synthesis and Properties. Macromolecules*, 2010, vol. 43, n°. 6, pp. 2684-2691.
61. BAE B, YODA T, MIYATAKE K, et al. Proton-conductive aromatic ionomers containing highly sulfonated blocks for high-temperature-operable fuel cells. *Angewandte Chemie International Edition*, 2010, vol. 49, n°. 2, pp. 317-320.
62. BAE B, HOSHI T, MIYATAKE K, et al. Sulfonated Block Poly(arylene ether sulfone) Membranes for Fuel Cell Applications via Oligomeric Sulfonation. *Macromolecules*, 2011, vol. 44, n°. 10, pp. 3884-3892.
63. SEO D W, LIM Y D, LEE S H, et al. Preparation and characterization of block copolymers containing multi-sulfonated unit for proton exchange membrane fuel cell. *Electrochimica Acta*, 2012, vol. 86, pp. 352-359.
64. NA T, SHAO K, ZHU J, et al. Block sulfonated poly(arylene ether ketone) containing flexible side-chain groups for direct methanol fuel cells usage. *Journal of Membrane Science*, 2012, vol. 417-418, pp. 61-68.
65. BI H, CHEN S, CHEN X, et al. Poly(sulfonated phenylene)-block-Polyimide Copolymers for Fuel Cell Applications. *Macromol Rapid Commun*, 2009, vol. 30, n°. 21, pp. 1852-1856.
66. CHEN S, HARA R, CHEN K, et al. Poly(phenylene) block copolymers bearing tri-sulfonated aromatic pendant groups for polymer electrolyte fuel cell applications. *Journal of Materials Chemistry A*, 2013, vol. 1, n°. 28, pp. 8178-8189.
67. MIYATAKE K and WATANABE M. Emerging membrane materials for high temperature polymer electrolyte fuel cells: durable hydrocarbon ionomers. *Journal of Materials Chemistry*, 2006, vol. 16, n°. 46, pp. 4465-4467.
68. ASANO N, MIYATAKE K a, and WATANABE M. Hydrolytically Stable Polyimide Ionomer for Fuel Cell Applications. *Chemistry of Materials*, 2004, vol. 16, n°. 15, pp. 2841-2483.
69. ASANO N, AOKI M, SUZUKI S, et al. Aliphatic/Aromatic Polyimide Ionomers as a Proton Conductive Membrane for Fuel Cell Applications. *Journal American Chemical Society*, 2006, vol. 128, n°. 5, pp. 1762-1769.
70. ASANO N, MIYATAKE K, and WATANABE M. Sulfonated block polyimide copolymers as a proton-conductive membrane. *Journal of Polymer Science Part A: Polymer Chemistry*, 2006, vol. 44, n°. 8, pp. 2744-2748.
71. YAMAZAKI K, WANG G, TANAKA M, et al. Sulfonated block-graft copolyimide for high proton conductive and low gas permeable polymer electrolyte membrane. *Journal of Power Sources*, 2012, vol. 216, pp. 387-394.

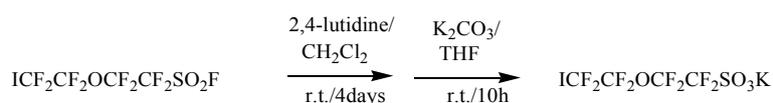
72. MCLOUGHLIN V C R a and THROWER J. A route to fluoroalkyl-substituted aromatic compounds *Tetrahedron*, 1969, pp. 5921.
73. KLEIDERER E C and ADAMS R. Preparation and Properties of 2,2',6,6'-Tetrafluoro-3,3'-dicarboxy-5,5'-dichlorodiphenyl. *Journal American Chemical Society*, 1933, vol. 55, pp. 4219-4225.
74. CHEN G J, CHEN L S a, and EAPEN K C. Perfluoroalkylations and perfluorooxaalkylations. Part 2. Coppermediated cross-coupling of secondary perfluorooxaalkyl iodides and aryl halides. *Journal of Fluoride Chemistry*, 1993, vol. 65, pp. 59-65.
75. GIL M, JI X, LI X, et al. Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications. *Journal of Membrane Science*, 2004, vol. 234, n°. 1-2, pp. 75-81.
76. TSANG E M W, ZHANG Z, YANG A C C, et al. Nanostructure, Morphology, and Properties of Fluorous Copolymers Bearing Ionic Grafts. *Macromolecules*, 2009, vol. 42, n°. 24, pp. 9467-9480.
77. IOJOIU C, GENOVA-DIMITROVA P, MARÉCHAL M, et al. Chemical and physicochemical characterizations of ionomers. *Electrochimica Acta*, 2006, vol. 51, n°. 23, pp. 4789-4801.
78. GAO Y, ROBERTSON G P, KIM D-S, et al. Comparison of PEM Properties of Copoly(aryl ether ether nitrile)s Containing Sulfonic Acid Bonded to Naphthalene in Structurally Different Ways†. *Macromolecules*, 2007, vol. 40, n°. 5, pp. 1512-1520.
79. KREUER K-D. Proton Conductivity: Materials and Applications. *Chemistry of Materials*, 1996, vol. 8, n°. 3, pp. 610-641.
80. SHIN D W, LEE S Y, KANG N R, et al. Durable Sulfonated Poly(arylene sulfide sulfone nitrile)s Containing Naphthalene Units for Direct Methanol Fuel Cells (DMFCs). *Macromolecules*, 2013, vol. 46, n°. 9, pp. 3452-3460.
81. KNAUSS D M a and EDSON J B. Poly(aryl ether sulfide)s by sulfide-activated nucleophilic aromatic substitution polymerization. *Polymer*, 2006, vol. 47, n°. 11, pp. 3996-4003.
82. SCHIEMANN G a and WINKELMÜLLER W. p-FLUOROBENZOIC ACID. *Organic Syntheses*, 1933, vol. 13, pp. 52.
83. STARKEY E B. p-DINITROBENZENE. *Organic Syntheses*, 1939, vol. 19, pp. 40.
84. DOYLE'Z M P a and BRYKER W J. Alkyl Nitrite-Metal Halide Deamination Reactions. Direct Synthesis of Arenediazonium Tetrafluoroborate Salts from Aromatic Amines, tert-Butyl Nitrite, and Boron Trifluoride Etherate in Anhydrous Media. *Journal Organic Chemistry*, 1979, vol. 44, n°. 9, pp. 1572-1574.
85. ANDRUS M B a and SONG C. Palladium-Imidazolium Carbene Catalyzed Aryl, Vinyl, and Alkyl Suzuki-Miyaura Cross Coupling. *ORGANIC LETTERS*, 2001, vol. 3, n°. 23, pp. 3761-3764.
86. CITTERIO A and ARNOLDI A. Synthesis of Aryliodides from Diazonium Tetrafluoroborate in Dimethylsulfoxide. *Synthetic Communications*, 1981, vol. 11, pp. 639-642.
87. KAITI S, HIMMELBERG W, P. J. , ALDELLATIF M, et al. Linear Poly(arylene ether)s with Pendant Phenylsulfonyl Groups: Nucleophilic Aromatic Substitution Activated from the Meta Position. *Macromolecules*, 2006, vol. 39, pp. 7909-7914.

88. CHAIKOVSKII V K, FILIMONOV V D, SKOROKHODOV V I, et al. Superactivity and dual reactivity of the system N-iodosuccinimide-H₂SO₄ in the iodination of deactivated arenes. *Russian Journal of Organic Chemistry*, 2007, vol. 43, n°. 9, pp. 1278-1281.
89. UEDA M and SATO M. Synthesis of aromatic poly(ether ketones). *Macromolecules*, 1987, vol. 20, n°. 11, pp. 2675-2678.
90. ROY A, YU X, DUNN S, et al. Influence of microstructure and chemical composition on proton exchange membrane properties of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers. *Journal of Membrane Science*, 2009, vol. 327, n°. 1-2, pp. 118-124.
91. BADAMI A S, ROY A, LEE H-S, et al. Morphological investigations of disulfonated poly(arylene ether sulfone)-b-naphthalene dianhydride-based polyimide multiblock copolymers as potential high temperature proton exchange membranes. *Journal of Membrane Science*, 2009, vol. 328, n°. 1-2, pp. 156-164.

EXPERIMENTAL SECTION

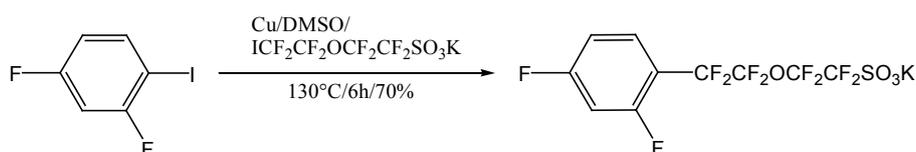
I. Monomer Synthesis

I.1. Synthesis of PSA-K



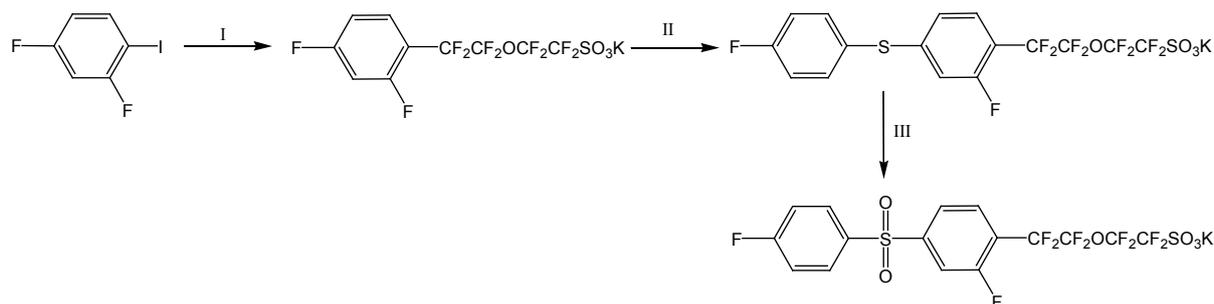
To a solution of 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride (PSA-F) (5.0 g, 11.5 mmol) in dichloromethane (1.7 mL) were added water (1.7 mL), 2,4-lutidine (1.61 g, 14.9 mmol) and a 1 M solution of tetra-*n*-butylammonium fluoride in THF (0.03 mL). The reaction mixture was stirred vigorously at room temperature for 4 days. After this time the mixture was extracted with dichloromethane. The organic phase was dried under sodium sulphate, filtered off and then solvent was removed under reduced pressure. The residue was diluted with THF (3 mL) and potassium carbonate (0.94 g, 6.8 mmol) was added, followed by stirring at room temperature for 10 hours. The remaining solid was filtrated off, and then the filtrate was concentrated to yield a solid. The solid was recrystallized from a mixture of THF/toluene (1/1) to obtain pure PSA-K. The product was dried at 100°C under vacuum during 24 hours. The white solid product was obtained in 90% yield.

I.2. Synthesis of FPSAB-K



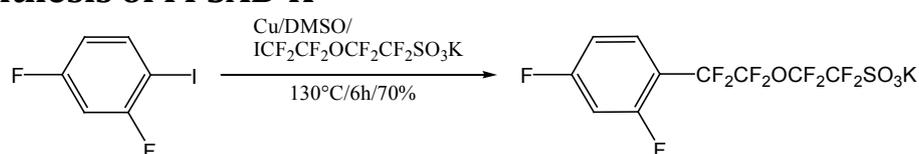
To a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was introduced 1 g (4.08 mmol) of 2,4-difluoro-1-iodobenzene, 2.23 g (12.2 mmol) of copper bronze, 0.064 g (0.41 mmol) of bipyridine and 5 ml of DMSO. The solution was heated at 80°C for approximately 30 min. 0.94 g (2.04 mmol) of PSA-K was then added to the reaction mixture and then temperature was increased to 130°C. Monitored by ^{19}F NMR, the reaction was completed after 5 hours. The cold solution was poured to a beaker containing 50 mL deionised water. A precipitate was formed. Then, the solution was filtered through celite on a Buchner funnel to afford a clear light green solution. This solution was extracted with ethyl acetate (3x50mL). The organic phase was then washed by acid solution, (HCl 2N, 3x50mL) then washed with a sodium bicarbonate solution, and finally washed with deionized water (3x50 mL). After drying the solution over Na_2SO_4 , the solvent was evaporated under vacuum. On the other hand, the precipitate obtained by pouring the reaction mixture into water, was placed in a Soxhlet apparatus in order to extract the small fraction of final product adsorbed. A treatment with ethyl acetate was run for 48 hours. The resulting organic phase was then washed of the same manner as afore mentioned. The crude product obtained by this extraction and isolated after evaporation of the ethyl acetate was added to the first fraction of isolated crude product and then purified by using percolation method. Silica gel (Silicagel 60 (40-63 μm) was placed in Buchner funnel and then the crude product was added on the top. By-products were eliminated using a large amount of eluent (petroleum ether/ethyl acetate, v/v, 80/20). The expected product stayed on the top of the silica gel which was then eluted with acetone. After evaporation of the solvent under vacuum, the isolated product was dried under vacuum during 24 hours and then placed in a desiccators with P_2O_5 as desiccant. The dark-brown solid FPSAB-K product was obtained in 70% yield.

I.3. Synthesis of 3,4'-FPSAPS-K



Scheme I.3.1. Synthesis of potassium 3,4'-FPSAPS-K.

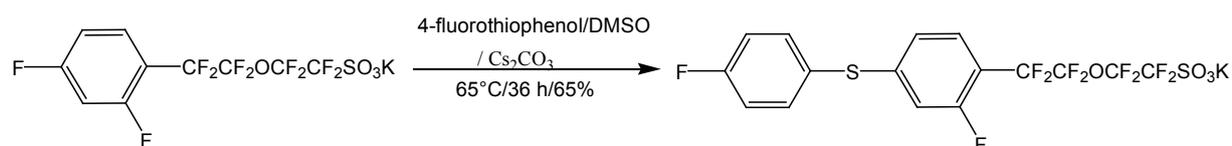
I.3.1. Synthesis of FPSAB-K



I Stage

The first stage was carried out in according to the synthetic procedure of FPSAB-K.

I.3.2. Synthesis of 1-1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2(potassiumoxysulfonyl)ethoxy]ethyl-3,4'-diphenylsulfid (3,4'-FPSADPS-K)

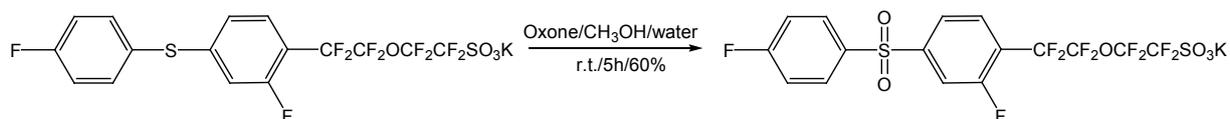


II Stage

In a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was introduced with 4-fluorothiophenol (0.64 g, 4.9 mmol), FPSAB-K (2.0 g, 4.46 mmol), Cs_2CO_3 (2.18 g, 6.69 mmol) and DMSO (8 mL). The reaction was heated at 65°C during 16 h. After this time if the reaction wasn't finished, to the solution 4-fluorothiophenol (0.3 eq., 0.17 g, 1.33 mmol) was added. The reaction was monitored by ^{19}F NMR analysis. The solution was diluted with water and extracted with ethyl acetate 3x. The organic phase was cleaned 3x with water, dried over sodium sulphate, filtrated and concentrated by using

rota evaporator. The crude product was purified by flash chromatography on silica gel column (C18) using methanol/water (v/v, 55/45) mixture as eluent. Then the methanol was evaporated and water phase extracted 3 x with ethyl acetate. The organic phase was dried over Na₂SO₄, filtered and the solvent evaporated under vacuum immediately. The product was dried. The yellow solid 3,4'-FPSADPS-K was obtained in 65-70% yield.

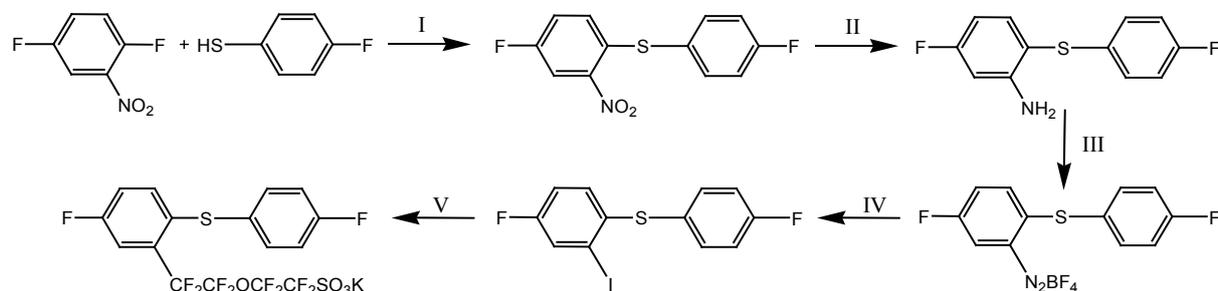
I.3.3. Synthesis of 3,4'-FPSAPS-K



III Stage

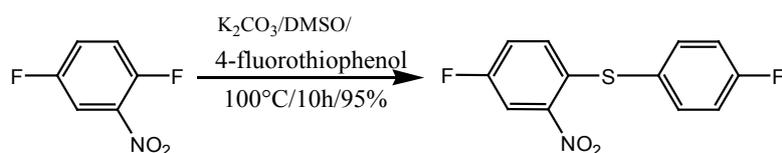
The product from II stage (2.0 g, 3.59 mmol) was dissolved in methanol (7 mL). Oxone (4.42 g, 7.18 mmol) was added in water (4 mL) and stirred at room temperature for 5 h. The reaction was monitored by ¹⁹F NMR. 1 N HCl was used to dissolve the salts and ethyl acetate was added to extract the products. The organic extract was washed with 1N HCl 3x and brine, dried over sodium sulphate, filtrated and the solvent was removed under reduced pressure to obtain the crude product. The residue was recrystallized in mixture of toluene and THF (v/v, 1/1). Then the crude product was purified by flash chromatography on silica gel column (C18) using methanol/water (v/v, 55/45) mixture as an eluent. After that methanol was evaporated and water phase extracted 3 x with ethyl acetate. The organic phase dried over Na₂SO₄, filtered and the solvent evaporated under vacuum immediately. The pure product was dried under vacuum. The white solid 3,4'-FPSAPS-K was obtained in 50-60% yield.

I.4. Synthesis of FPSAPS-K



Schema I.4.1. Synthesis of FPSAPS-K.

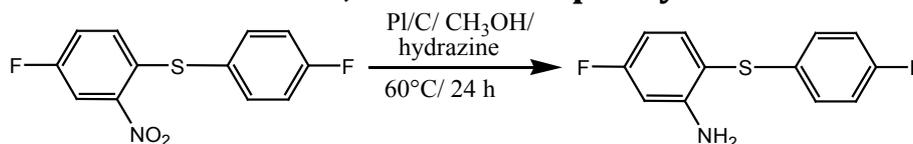
I.4.1. Synthesis of 4,4'-difluoro-2-nitrodiphenylsulfide



I Stage

In a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was introduced with 4-fluorothiophenol (1.0 g, 7.6 mmol), 1,4-difluoro-2-nitrobenzene (1.25 g, 7.6 mmol), potassium carbonate (1.12 g, 8.0 mmol) and DMSO (6.0 mL). The solution was heated at 100°C during approximately 15 hours. The completion of reaction was followed with TLC (Silica gel 60F₂₅₄), using 80/20 (v/v) hexane/ethyl acetate mixture as eluent. Then solution was cold down and poured to a beaker with 50 mL deionised water. The residue was extracted with chloroform (3x50 mL). The organic phase was washed (3x50mL) by deionised water, dried over Na₂SO₄ and filtrated. The solvent was evaporated and then product was dried. The pure yellow solid 4,4'-difluoro-2-nitrodiphenylsulfid was obtained (yield=95%).

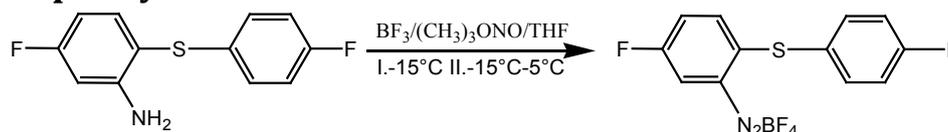
I.4.2. Synthesis of 2-amino-4,4'-difluorodiphenylsulfide



II Stage

In a 250 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was charged with 4,4'-fluoro-2-nitrobisphenylsulfid (1.0 g, 3.74 mmol), methanol (5 mL), 10% palladium-charcoal (0.2 g) and methanol (10mL). Then to the solution hydrazine hydrate (0.93 g, 18.7 mmol) was dropping very slowly under ambient temperature. Then the reaction was heated to 60°C for 10 hours. The completion of reaction was followed with TLC (Silica gel 60F₂₅₄), using 80/20 (v/v) hexane/ethyl acetate mixture as eluent. Then solution was cooled down. On the Buchner funnel was applied silica gel (Silicagel 60 (40-63μm)), and then on the top the residue. To remove the product was used large amount of methanol. The solvent was evaporated, and the product dried. The yellow, solid 2-amino-4, 4'-dichlorobisphenylsulfid was obtained (75-80% yield).

I.4.3. Synthesis of 2-diazonium tetrafluoroborate- 4,4'-difluorobiphenylsulfide

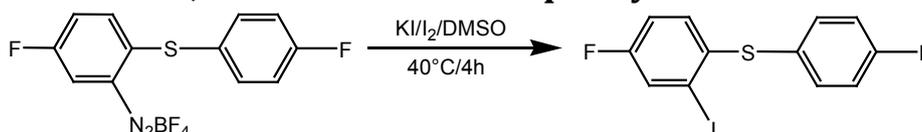


III Stage

To boron trifluoride diethyle etherate (1.79 g, 1.26 mmol) contained in a 250 mL round-bottom flask fitted with an addition funnel, was added 2-amino-4,4'-difluorobiphenylsulfid (2.0 g, 8.43mmol) in a minimal volume of anhydrous THF. Prior to addition of the amine, the boron trifluoride etherate was cooled to -15°C in an ice-acetone bath. *Tert*-butyl nitrite (0.89g, 7.77mmol) in THF was added drop by drop to the rapidly stirred reaction solution over a 10 min period. Following complete addition, the temperature of the reaction solution was maintained at -15°C for 10 min and then allowed to warm to 5°C in ice-water bath over 20 min period. A crystalline precipitate usually formed during the addition of *tert*-butyl

nitrite, and following the 20 min period at 5°C precipitation was complete. Heptane was then added to the reaction solution, and then solid was suction filtered, washed with cold ether, and dried. The yellow solid 2-diazonium tetrafluoroborate- 4,4'-difluorobiphenylsulfid was obtained.

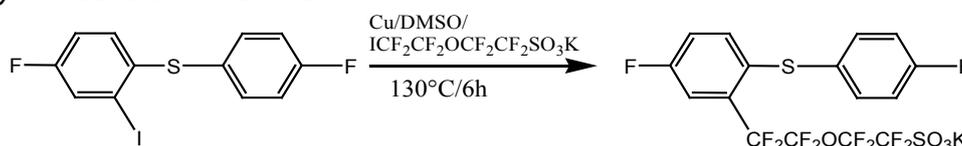
I.4.4. Synthesis of 4,4'-difluoro-2-iododiphenylsulfide



IV Stage

Into solution of KI (1.26g, 7.53 mmol) and I_2 (1.04 g, 4.11 mmol) in DMSO was dropping a 0.65 M solution of diazonium tetrafluoroborat (2-diazonium tetrafluoroborate- 4,4'-difluorobiphenylsulfid (2.3 g, 6.84 mmol) in DMSO (11mL) during 30 min at 15°C. After 30 min the mixture was warmed to 40°C. The completion of reaction was followed with TLC (Silica gel 60F₂₅₄), using 80/20 (v/v) hexane/ethyl acetate mixture as eluent. The reaction was stopped after 5 h and cooled down. The residue was extracted with ethyl acetate (3x50 mL) then the organic phase was extracted with 5 % solution of the sodium thiosulfate, washed (3x50mL) by deionised water, dried over Na_2SO_4 and filtrated. The solvent was evaporated. On the Buchner funnel was applied silica gel (Silicagel 60 (40-63 μm)) and on the top the residue. To remove the product was used large amount of heptane. Subsequently, solvent was evaporated under vacuum, and then the product was dried. The crude transparent liquid 4, 4'-difluoro-2-iodobiphenylsulfid was obtained.

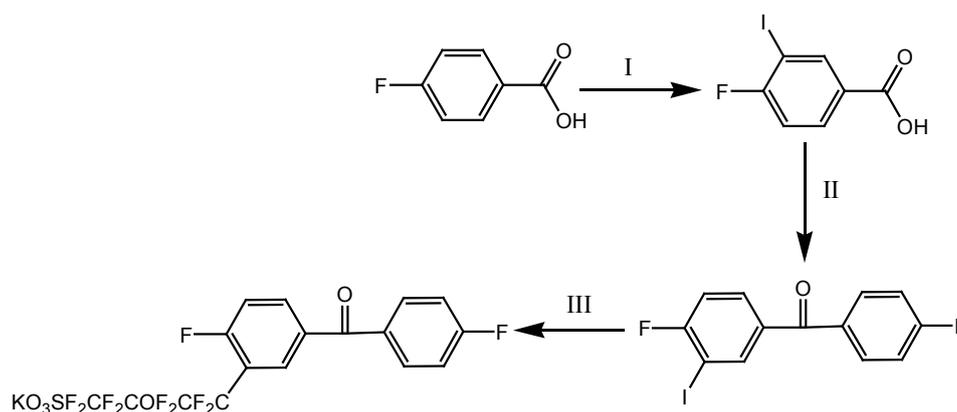
I.4.5. Synthesis of FPSAPS-K



V Stage

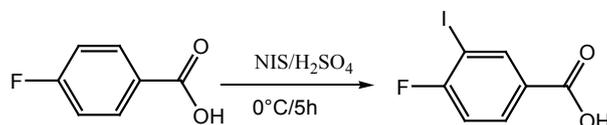
In a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was charged with 4,4'-difluoro-2-iodobiphenylsulfonyl (DFIDPS) (without prior purification), (0.5 g, 1.43 mmol), copper bronze (1.3 g, 7.18mmol), bipyridine (0.037 g, 2. 39 mmol) and DMSO (3 mL). The solution was heated at 80°C during approximately 30 min and then PSA-K (0.55 g, 1.19 mmol) was added to a reaction solution. Then the temperature was increased to 130°C. The completion of the coupling reaction was followed by ¹⁹F NMR. After 7 hours the reaction was stopped. Purification was performed as followed the synthetic procedure of the product FPSAB-K. The brown solid FPSAPS-K was obtained (Total yield=65%).

I.5. Synthesis of FPSABP-K



Scheme I.5.1. Synthesis of FPSABP-K.

I.5.1. Synthesis of 4-fluoro-3-iodobenzoic acid

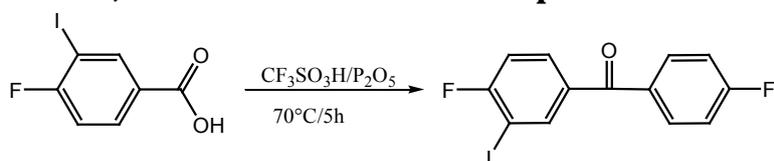


I Stage

Sulfuric acid (10mL) was cooled to 0-5°C and then N-iodosuccinimide (1.04 g, 4.34 mmol) was added. The mixture was stirred for 20-30 min until it became homogeneous. To affect monoiodination, fluorobenzoic acid (0.5 g, 3.49 mmol) was added gradually at 0°C. The

reaction was monitored with ^{19}F NMR. The mixture was vigorously stirred for 5 h. When the reaction was complete, the solution was poured into 100 mL of ice-water mixture. The residue was extracted with ethyl acetate (3x50 mL) and then an organic phase was washed with 5 % solution of the sodium thiosulfate, and then by deionised water (3x50mL), dried over Na_2SO_4 and filtrated off. The solvent was evaporated and after that product was dried over vacuum. The crude product was purified by sublimation at 70°C . The white powder 4-fluoro-3-iodobenzoic acid was obtained.

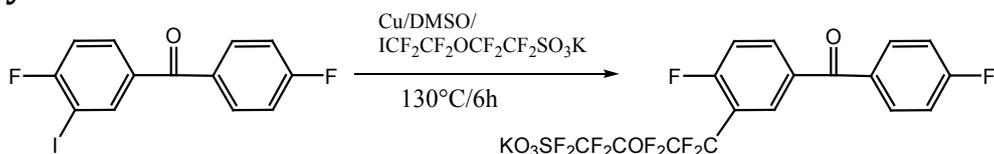
I.5.2. Synthesis of 4,4'-difluoro-3-iodobenzophenone



II Stage

Eaton's reagent (triflic acid (1.25 g) and P_2O_5 (0.125g)) was prepared. A 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was charged with 4-fluoro-3-iodobenzoic acid (0.5g, 1.87 mmol), 4-fluorobenzene (0.91 g, 9.39 mmol) and Eaton's reagent. Subsequently, temperature was increased progressively to 70°C . The reaction was monitored with TLC (Silica gel 60F₂₅₄), using 80/20 (v/v) hexane/ethyl acetate mixture as eluent. After 4 hours, the reaction was stopped and cooled down. The solution was quenched with water-ice, basified up to $\text{pH}=10$ and extracted by ethyl acetate (3x50mL). Then the organic phase was washed with water (3x50mL) and then dried over sodium sulphate, filtrated and concentrated by using rota evaporator. The substance was recrystallized twice in methanol, filtered and washed with cold methanol, and then dried under vacuum. (The second purification method for this product can be used sublimation, at 70°C under reduced pressure).

I.5.3. Synthesis of FPSABP-K

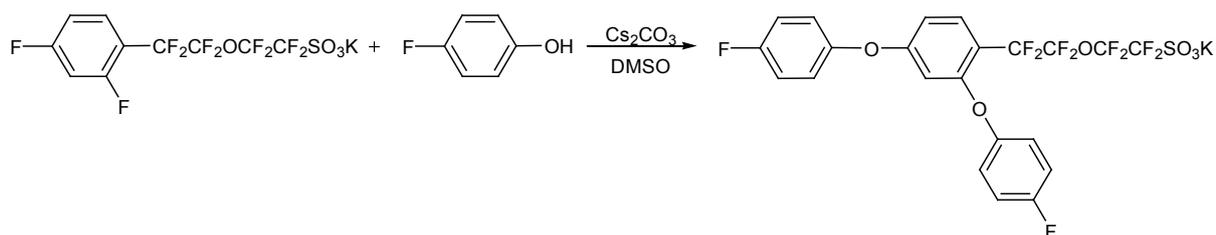


III Stage

A 250 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar was charged with 4,4'-difluoro-3-iodobenzophenone (6.5 g, 18.89 mmol), copper bronze (13.24 g, 72.65 mmol), bipyridine (0.45 g, 2.9 mmol) and DMSO (30 mL). The solution was heating to 80°C during 30 min then solid PSA-K (6.7 g, 14.53 mmol) was added. Subsequently, the temperature was increased to 130°C. The reaction was stopped after 6 h. The purification was performed as followed the synthetic procedure of the product FPSAB-K. The brown solid FPSABP-K was obtained (total 70% yield).

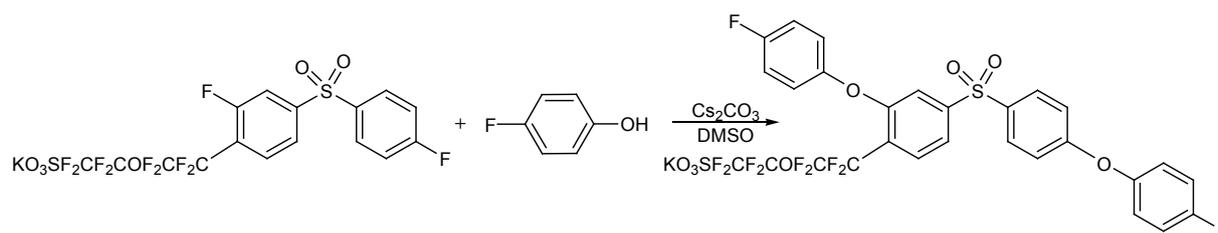
II. Model compound synthesis

II.1. From FPSAB-K monomer



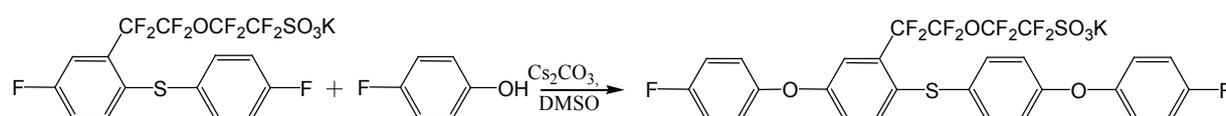
FPSAB-K (0.5185 g, 1.15 mmol), fluorophenol (0.2617 g, 2.31 mmol), Cs₂CO₃ (0.8391 g, 2.54 mmol) and DMSO (2.2 mL) were placed into a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar. The first sample was taken at room temperature, then the reaction was heated progressively to 140°C. During the reaction samples were taken: at 80°C, 140°C, and then each 2x10 min, 2x15 min, 30 min and 1 hour.

II.2. From 3,4'-FPSAPS-K monomer



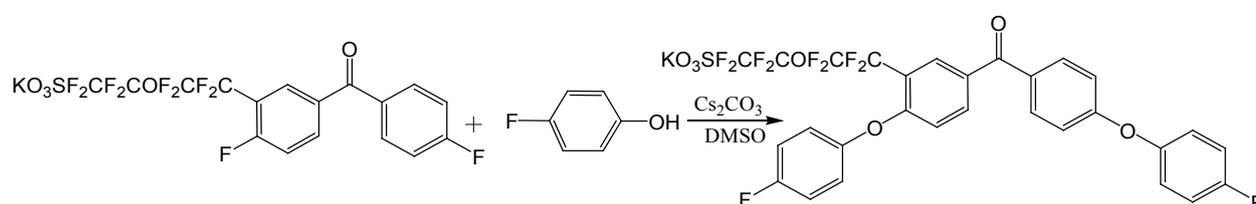
3,4'-FPSAPS-K (0.5163 g, 0.87mmol), fluorophenol (0.1985 g, 1.75 mmol), Cs₂CO₃ (0.715 g, 2.19 mmol) and DMSO (2 mL) were placed into a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar. Follow the synthetic procedure of the section II.1.

II.3. From FPSAPS-K monomer



FPSAPS-K (0.89613 g, 1.61 mmol), 4-fluorophenol (0.364357g, 3.22mmol), Cs₂CO₃ (1.31 g, 4.02 mmol) and DMSO (2.7 ml) were added into a 50 mL three necked flask equipped with a reflux condenser, a nitrogen inlet and a magnetic bar. Follow the synthetic procedure of the section II.1.

II.4. From FPSABP-K monomer



FPSABP-K (0.34 g, 0.62mmol), fluorophenol (0.14 g, 1.2 mmol), Cs₂CO₃ (0.5 g, 1.55 mmol) and DMSO (1.5 mL) were placed into a 50 mL three necked flask equipped with a reflux

condenser, a nitrogen inlet and a magnetic bar. Follow the synthetic procedure of the section II.1.

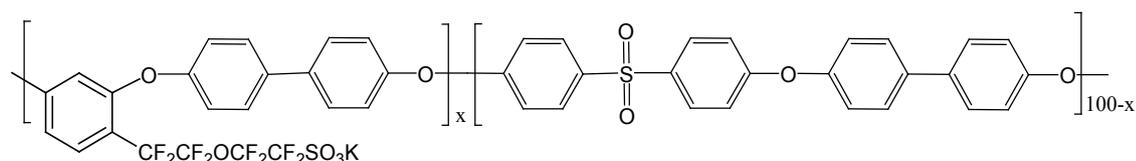
III. Polymer synthesis

MATERIALS			
4,4'-biphenol (BP)	A	3,4'-FPSAPS-K	I
4,4'-dichlorodiphenyl sulfone (CIPS)	B	4,4'-difluorodiphenyl sulfone (FPS)	J
FPSAPS-K	C	DMAc	K
cesium carbonate	D	FPSAB-K	L
DMSO	E	calcium carbonate	M
2,6-difluorobenzonitrile (FBN)	F		
hydroquinone (HQ)	G		
FPSABP-K	H		

A typical procedure is described as follows: 4,4'-biphenol **A**, 4,4'-difluorodiphenyl sulfone **J**, FPSAPS-K **C**, cesium carbonate **D** and DMSO **E** were charged into a 50 mL 3-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer. The mixture was heated at 160°C and stirred for 32 hours. The reaction medium was then poured into deionized water to precipitate the polymer. The polymer was filtered, stirred in 1 L of deionized water for overnight, filtered again, and washed with deionized water and methanol. The polymer was dried at 150°C under vacuum for 24 h.

III.1. Synthesis of sulfonated poly(arylene ether)s polymers (SPAES)

SPAES-S



SPA-E-N

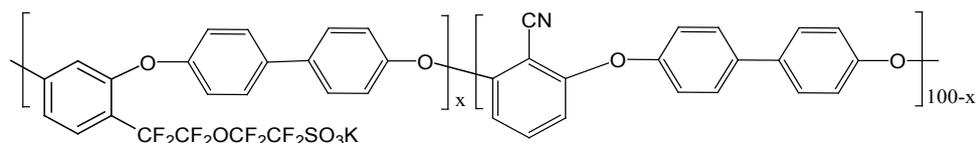


Table III.1.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAES-S polymers.

Materials		A	B	L	F	D	E	M
SPA-E-S IEC=1.1	[g]	1.5674	1.0973	1.9472	-	6.6507	12	1.22
	[mmol]	8.16	3.82	4.34	-	20.41	-	12.2
SPA-E-N IEC=1.1	[g]	1.6098	-	1.6803	0.66504	6.8373	8	1.25
	[mmol]	8.39	-	3.75	4.64	20.9	-	12.6

III.2. Synthesis of sulfonated poly(arylene ether sulfone)s (SPAESulfone)

A typical procedure of the synthesis of SPAESulfone was performed according to the polymerization synthetic procedure in section III. However, polymerization of SPAEK was performed at 140 °C.

III.2.1. Synthesis of SPAESulfone-N

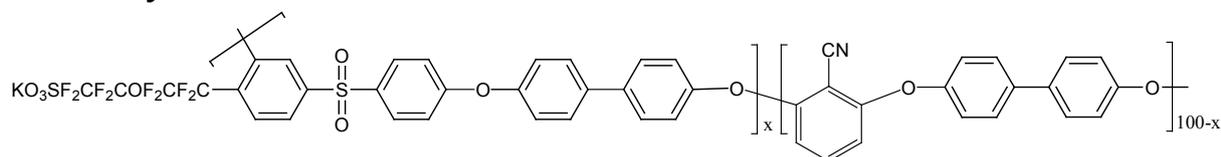


Table III.2.1.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAESulfon-N polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.44
A	[g]	0.5699	0.3786	0.6309
	[mmol]	3.02	2.01	2.46
F	[g]	0.1855	0.0586	-
	[mmol]	1.29	0.41	-
I	[g]	1.0216	0.9441	1.9738
	[mmol]	1.73	1.6	3.35
D	[g]	2.46	1.63	2.73
	[mmol]	7.57	5.03	8.38
E	[mL]	3.75	3	5.5

III.2.2 .Synthesis of SPAESulfone-S

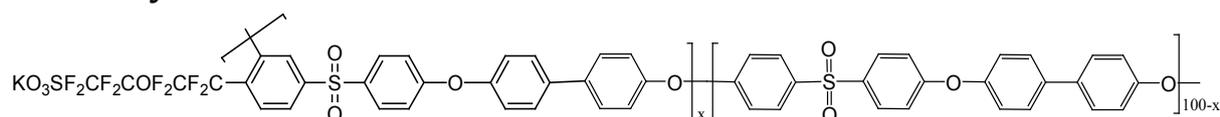


Table III.2.2.1 The amounts of reacting substances are in dependence of ion exchange capacity for SPAESulfone-S polymers.

Materials		A	J	I	D	E
IEC=1.1	[g]	0.8527	0.3919	1.7067	3.618	6.6 mL
	[mmol]	4.44	1.54	2.9	1.11	

III.3. Synthesis of sulfonated poly(arylene ether sulfide)s polymers (SPAES)

III.3.1. Synthesis of SPAES-S

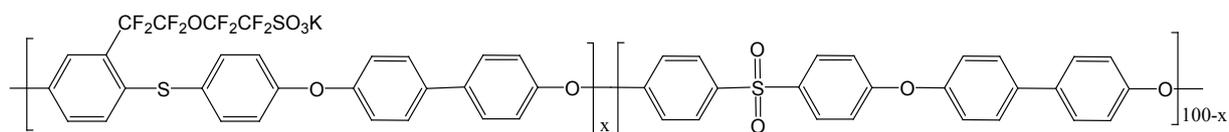


Table III.3.1.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAES-S polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5
A	[g]	1.2785	0.4362	0.381
	[mmol]	6.79	2.32	2.02
J	[g]	0.73978	0.1378	0.0029
	[mmol]	2.57	4.8	0.01
C	[g]	2.3488	1.0234	1.1217
	[mmol]	4.22	1.84	2.01
D	[g]	5.5366	1.889	1.6486
	[mmol]	16.99	5.79	5.06
E	[mL]	12	4	4

III.3.2. Synthesis of SPAES-N

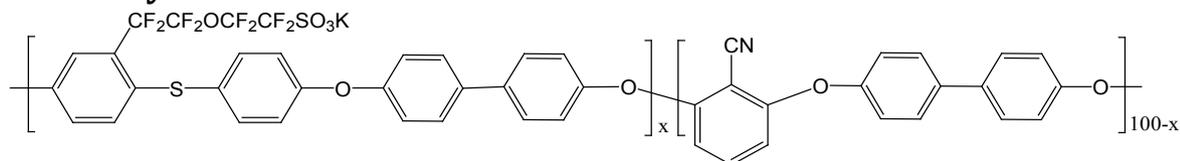


Table III.3.2.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAES-N polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5
A	[g]	0.7257	0.558	0.4485
	[mmol]	3.85	2.96	2.38
F	[g]	0.2556	0.114	0.0024

	[mmol]	1.78	0.79	0.016
C	[g]	1.1550	1.2084	1.3175
	[mmol]	2.07	2.17	2.36
D	[g]	3.1428	2.4166	1.942
	[mmol]	9.64	7.41	5.96
E	[mL]	6	5.5	4.5

III.4. Synthesis of sulfonated poly(arylene ether ketone)s (SPAEK)

A typical procedure of the synthesis of SPAEK was performed according to the polymerization synthetic procedure in section III. However, polymerization of SPAEK was performed at 140 °C.

III.4.1. Synthesis of SPAEK-N

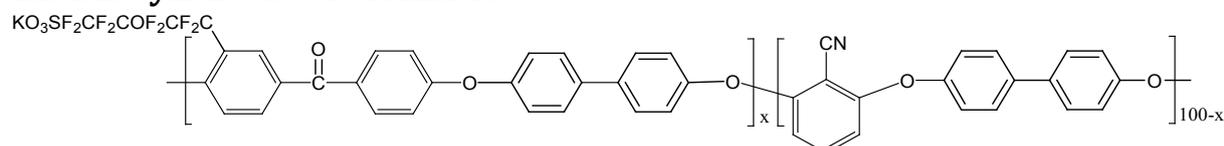


Table III.4.1.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAEK-N polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5
A	[g]	0.7352	0.5382	0.4422
	[mmol]	3.91	2.86	2.35
F	[g]	0.26122	0.1133	0.0071
	[mmol]	1.82	0.79	0.04

H	[g]	1.153	1.1451	1.2715
	[mmol]	2.08	2.07	2.3
D	[g]	3.64	2.3323	1.9153
	[mmol]	11.19	7.15	5.87
E	[mL]	7	5	5

III.4.2. Synthesis of s-PAEK-NQ

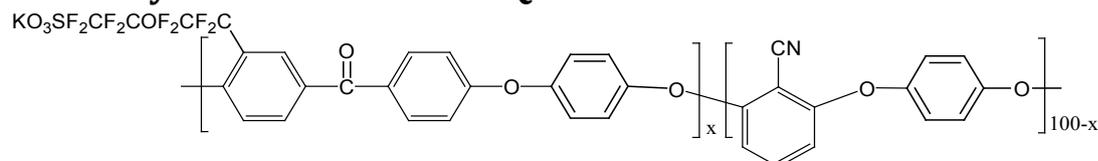


Table III.4.2.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAEK-N polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5	IEC=1.7
G	[g]	0.54284	0.5509	0.3434	0.1795
	[mmol]	4.92	5.0	3.11	1.85
F	[g]	0.4296	0.3365	0.1261	-
	[mmol]	2.99	2.34	0.88	-
H	[g]	1.0674	1.4675	1.2371	0.9006
	[mmol]	1.93	2.65	2.23	1.63
D	[g]	4.01	4.075	2.54	1.33
	[mmol]	12.32	12.5	7.79	4.07
E	[mL]	4.5	6.5	4.75	3

III.4.3. Synthesis of SPAEK-SQ

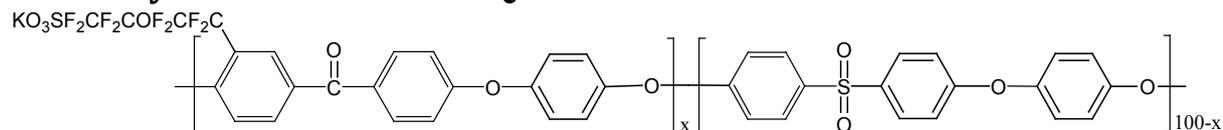


Table III.4.3.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAEK-SQ polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5
G	[g]	0.9568	0.7057	0.5881
	[mmol]	8.68	6.41	5.34
J	[g]	1.1046	0.5915	0.2743
	[mmol]	4.34	2.32	1.07
H	[g]	2.3999	2.2553	2.3546
	[mmol]	4.34	4.08	4.26
D	[g]	7.078	4.59	3.82
	[mmol]	21.72	14.1	11.75
E	[mL]	12	9.5	8.5

III.4.4. Synthesis of SPAEK-S

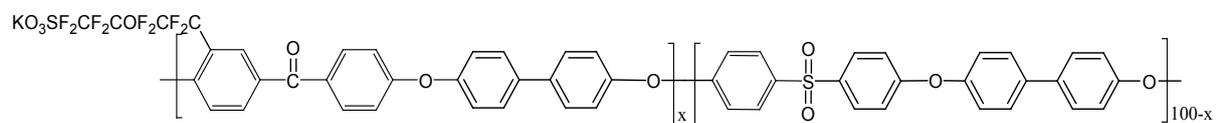


Table III.4.4.1. The amounts of reacting substances are in dependence of ion exchange capacity for SPAEK-S polymers.

Materials		IEC=1.1	IEC=1.3	IEC=1.5
A	[g]	1.2106	1.0529	0.7817
	[mmol]	6.43	5.59	4.15
J	[g]	0.7078	0.4436	0.02506
	[mmol]	2.46	1.54	0.08
H	[g]	2.19367	2.2388	2.2475
	[mmol]	3.97	4.05	4.06
D	[g]	5.24	4.012	2.97
	[mmol]	16.09	12.31	9.14
E	[mL]	11	9	8

III.5. Synthesis of multiblock sulfonated poly(arylene ether ketone)s

A typical procedure is as follows: A three-neck 250 mL round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet/outlet was charged with FPSABP-K **A**, hydroquinone (HQ) **B**, cesium carbonate **C**, DMAc **D**. The reaction was carried out at 140°C for 5 h. The reaction was slightly viscous. Then the mixture was cooled down to room temperature. Then to the flask were added, bisphenol A (BPA) **E**, decafluorodiphenyl (DFDP) **F** (or 4,4'-difluorodiphenyl sulfone (FP) **I**), potassium carbonate **G** and DMAc **H**. The mixture was heated at 80°C during 2-3 hrs. At the end of this period, the reaction solution was diluted with DMAc. The solution was precipitated into distilled water, cut, filtered and then kept in a large beaker with excess of water to remove any trace amount of DMAc and salt. After few hours the polymer was filtered, washed with a big quantity of water and methanol. Then the copolymer was purified in a Soxhlet extractor with methanol for 48h. The product was dried at 150 °C in a vacuum oven for 24 hours.

III.5.1. Synthesis of B-SPAEEK-F

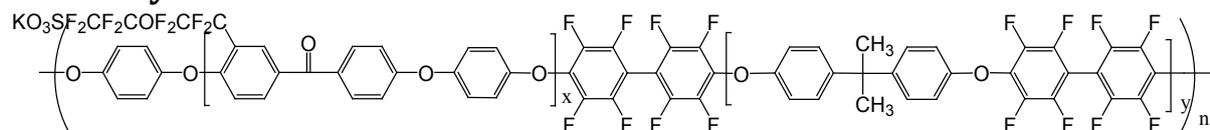


Table III.5.1.1. The amounts of reacting substances for highly fluorinated sulfonated block copolymers.

M_{nAB}		8000	6000	4000
A	[g]	2.0418	2.3341	2.0354
	[mmol]	3.69	4.22	3.68
B	[g]	0.4404	0.5172	0.4763
	[mmol]	4.0	4.69	4.32
C	[g]	2.8672	3.3618	3.1007
	[mmol]	8.8	10.3	9.51
H	[mL]	5.5	6	6

Table III.5.1.2. The amounts of reacting substances for nonsulfonated block copolymers.

		$M_{nAB}8000$	$M_{nAB}6000$	$M_{nAB}4000$
M_{nCD}		4000	4000	4000
E	[g]	0.4517	0.6945	0.9441
	[mmol]	1.97	3.07	4.18
F	[g]	0.7702	1.1962	1.6262
	[mmol]	2.28	3.54	4.82
G	[g]	0.6012	0.9329	1.27
	[mmol]	4.35	6.75	9.19
H	[mL]	2.5	5	5

III.5.2. Synthesis of BSPAEK-S

A typical procedure of the synthesis of B-SPAEEK-S copolymers was performed according to the polymerization synthetic procedure in section III.5. However, the second stage of polymerization was carried out at 90°C for 3 h.

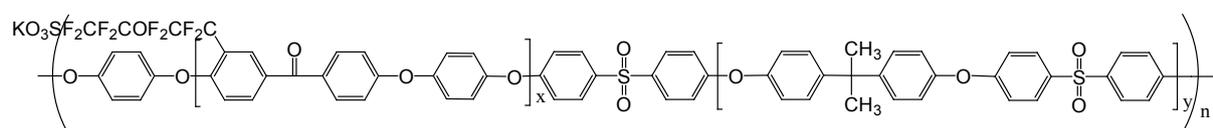


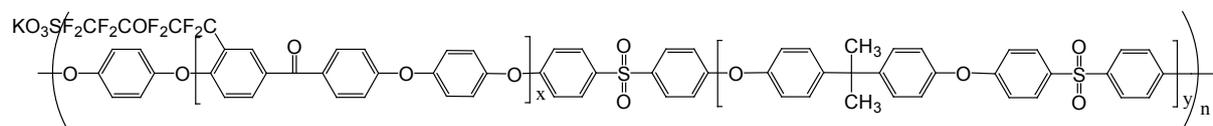
Table III.5.2.1. The amounts of reacting substances for sulfonated block copolymers.

M_{nAB}		8000	6000	4000
A	[g]	2.8048	2.4028	2.3738
	[mmol]	5.07	4.35	4.29
B	[g]	0.6050	0.5324	0.5555
	[mmol]	5.49	4.86	5.04
C	[g]	3.9352	3.4657	3.6162
	[mmol]	12.07	10.6	11.1
D	[mL]	8	6	6

Table III.5.2.2. The amounts of reacting substances for nonsulfonated block copolymers.

		$M_{nAB}8000$	$M_{nAB}6000$	$M_{nAB}4000$
M_{nCD}		4000	4000	4000
E	[g]	0.7547	0.8782	1.3525
	[mmol]	3.3	3.85	5.92
I	[g]	0.9466	1.1015	1.6964
	[mmol]	3.72	4.33	6.67
G	[g]	0.9121	1.1696	1.8014
	[mmol]	6.6	8.46	13.03
H	[mL]	3.3	4.5	6

III.6. Synthesis of statSPA EK



A three-neck 250 mL round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet/outlet was charged with FPSABP-K (2.2762 g, 4.12 mmol), HQ (0.5043 g, 4.58 mmol), FPS (1.0434 g, 4.1 mmol), BA (0.8329 g, 3.64 mmol), cesium carbonate (5.8921 g, 18.08 mmol) and DMSO (10 mL). The mixture was heated at 90°C during 6 h. At the end of this period, the reaction solution was diluted with more DMSO. The solution was precipitated into distilled water, cut, filtered and then kept in a large beaker with excess of water to remove any trace amount of DMSO and salt. After few hours the polymer was filtered, washed with a big quantity of water and methanol. The product was dried at 150 °C in a vacuum oven for 24 hours

IV. Characterization Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H, ¹⁹F and ¹³C NMR were used to obtain the chemical composition of the monomers and polymers synthesized. NMR spectra were recorded in DMSO-*d*₆ using a Bruker Avance III Spectrometer operating at 400 MHz.

High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) was utilized to aid the determination of monomer purity. HPLC grade acetonitrile was used as mobile phase. The injected sample volume was 10 μL and the flow rate of the mobile phase was 1 mL/min, UV detector (254 nm).

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) was performed using TA instruments, TGA Q50. The samples were heated at a rate of 10°C/min under a nitrogen atmosphere. The sample weight loss was measured as a function of temperature. The thermal stability of the poly(arylene ether)s was generally reported as the temperature at which 5% weight loss was observed.

Differential Scanning Calorimetry (DSC)

DSC was used to ascertain the thermal transition temperature of the synthesized sulfonated polymers. DSC analysis were performed on METTLERT TOLEDO instrument, model 822^e under argon at a heating rate of 10°C/min.

Thin Layer Chromatography (TLC)

Thin layer chromatography is a valuable technique providing information on the completion of a reaction and the purity of synthesized monomers.

Solubility Test

The solubility of various synthesized polymers was determined using several commercial solvents. The dried polymers were mixed with a number of appropriate solvents including chloroform, toluene, THF, NMP, DMSO, DMAc, to give a concentration of 10 wt./vol. %. Then, the mixture was let it at room temperature for 4-5 hours. Solubility was assessed by visual observation.

Solvent-cast films

Sulfonated poly(arylene ether)s films were prepared by casting solution of polymer dissolved in NMP, DMAc or DMSO. Prior to casting onto a glass substrate, polymer solutions were centrifuged and then filtered to remove particles using special filters having porosities of 5.0 and 0.45 µm. The filtrate was spread onto a glass plate and placed on plate under argon atmosphere to remove the solvent. Temperature of plate was gradually ramped up to provide heating according to the following schedule: r.t. to 50°C overnight, at 80°C for 1 hour, 120°C for 1 hour, 150°C for 1 hour and 180°C for 2 hours. Films were peeled from the

glass plate by immersing them in water. Then, the obtained membranes were immersed in 4 M H₂SO₄ for 24 h at 50°C. The membranes were then washed with deionized water several times and dried under vacuum at 70°C for 24 h.

Aqueous Titration

The ion exchange capacity (IEC) was determined by titration. Approximately 70-100mg of dried membrane was immersed in water at 70°C for 2 hours. Then the film was placed into solution of NaCl (2 N) at r.t. for 48 hours. The HCl released ion-exchange was measured by titration with a 0.02M NaOH aqueous solution using an Auto Potentiometer Titrator (TitraLab TIM880).

Non-Aqueous Titration

Non-aqueous potentiometric titrations were employed to determine milli-equivalent weight of sulfonated groups in sulfonated polymers. 70-100 mg of dried membrane was dissolved in diethylenglycol monomethyl ether (DGME) and then titrated with 0.05 N NaOH in DGME in the presence of bromothymol blue.

Water Uptake

The polymer film was dried at 70°C for 24 h and then immersed in water for 4 h at indicated temperature. Then the membrane was taken out and quickly weighted on a microbalance. The water uptake measurements were conducted at 30°C, 50°C, 70°C and 90°C. Water uptake of the membrane was determined by the weight difference of the weight between dry and hydrated membrane.

Conductivity Measurement

The in-plane proton conductivity measurements were performed by electrochemical impedance spectroscopy over a frequency range 10-10⁶ Hz using a system based on a GAMRY Instruments, Ref 600. A 40x10 mm membrane sample was mounted in a conductivity cell which was then placed in a thermo and humidity controlled chamber. The samples were equilibrated for 10 min at indicated RH. An impedance spectrum was

recorded from 10MHz to 10Hz. All measurements were performed at different temperatures up to 90°C and at 50, 70 and 95% of relative humidity.

Transmission Electron Microscopy Analysis (TEM)

In order to clearly evidence the size and shape of the hydrophilic-hydrophobic domains TEM analysis was performed. Before, test, the polymers were first converted into Pb^{2+} forms by immersing the polymers in 1 M $Pb(NO_3)_2$ solutions for 48 h to improve the contrast obtained by TEM. After this time membranes were rinsed with deionized water. The polymers were then microtomed and then casted onto copper grids. The prepare samples were analyzed by TEM, with a Philips CM120 microscope operating at 80 kV.

Atomic Force Microscopic (AFM) Observation

Tapping mode AFM observations were performed with a Digital Instrument, MultiMode 8 Brucker with contact mode, tapping and PeakForce QNM at ambient temperature.



FOLIO ADMINISTRATIF

THESE DE L'UNIVERSITE DE LYON OPEREE AU SEIN DE L'INSA LYON

NOM : Swiecicka Fichou

DATE de SOUTENANCE : 15 novembre 2016

Prénoms : Joanna

TITRE : Synthèse de polymères à chaînes latérales perfluoroalkyles sulfonées pour la conception de membranes conductrices protoniques

NATURE : Doctorat

Numéro d'ordre : 2016LYSEI116

Ecole doctorale : Matériaux de Lyon

Spécialité : matériaux

RESUME :

Dans le cadre de ces travaux, l'objectif fixé était de développer des polymères aromatiques possédant des propriétés de conduction protonique. Pour y parvenir des motifs de type acide sulfonique ont été introduits le long des chaînes macromoléculaires. La méthodologie de synthèse de ces polymères qui a été choisie, consistait à polymériser des précurseurs contenant dans leur structure un motif perfluoroalkyle sulfoné. Quatre précurseurs originaux ont ainsi été initialement synthétisés. Différents polymères aromatiques ont été préparés à partir de ces précurseurs en faisant varier le taux de séquences perfluoroalkyles sulfonées. Ces polymères ont ensuite été mis en oeuvre sous la forme de membranes denses selon un procédé de coulée évaporation. A partir de ces membranes, des études de gonflement à l'eau et de conductivité ionique ont été réalisées.

MOTS-CLÉS : Polymères aromatiques sulfonés, polycondensation, conductivité ionique, membranes

Laboratoire de recherche : IMP UMR5223

Directeur de thèse: Etienne Fleury

Président de jury : Jean-Yves Sanchez

Composition du jury : Cristina Iojoiu, Jean-Jacques Robin, Véronique Bounor Legaré, Jean-Yves Sanchez, Régis Mercier, Etienne Fleury