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Karell Bosson, Pierre Marcasuzaa, Antoine Bousquet, Günter E.M. Tovar, Vladimir Atanasov, et al. para fluoro-thiol clicked diblock-copolymer self-assembly: Towards a new paradigm for highly proton-conductive membranes. *Journal of Membrane Science*, 2022, 659, pp.120796. 10.1016/j.memsci.2022.120796 . hal-03766516

**HAL Id: hal-03766516**

**<https://univ-pau.hal.science/hal-03766516>**

Submitted on 13 Dec 2022

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1 ***para* fluoro-thiol clicked diblock-copolymer self-assembly: Towards a new**  
2 **paradigm for highly proton-conductive membranes**

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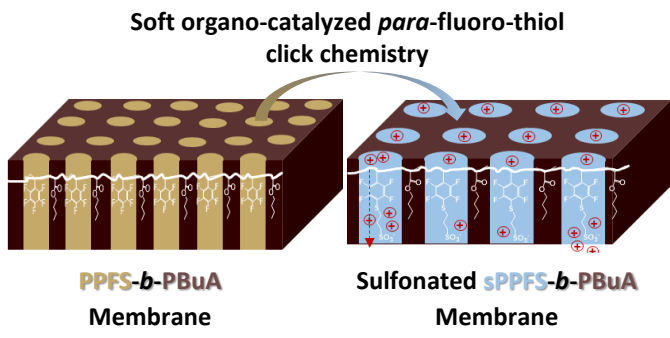
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1 **Graphical abstract**

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1 **Abstract**

2 Sulfonated sPPFS-*b*-PBuA diblock and statistical copolymers based on 2,3,4,5,6-  
3 pentafluorostyrene PFS and butyl acrylate BuA were elaborated for Proton Exchange  
4 Membrane Water Electrolyser (PEMWE) purposes. The block copolymers (BCP) were  
5 synthesized by Nitroxide Mediated Polymerization NMP, a controlled radical polymerization  
6 technique that yields a well-defined molar mass and a low dispersity material. These diblock-  
7 copolymers have the ability to self-assemble due to the immiscibility of the two  
8 macromolecular segments PPFS and PBuA. Statistical copolymers of the same chemical nature  
9 were synthesized by both controlled radical polymerization NMP in solution and by free radical  
10 polymerization FRP in emulsion as waterborne dispersed polymer with highest molar mass.  
11 The copolymers were sulfonated by a mild click-reaction, namely an organo-catalyzed  
12 nucleophilic substitution reaction with sodium 3-mercapto-1-propanesulfonate (SMPS) at low  
13 temperature. The morphology of the sulfonated diblock-copolymer BCP was studied by SAXS  
14 and AFM, revealing a nano-phase-segregated sulfonated membrane. The mechanical properties  
15 of the membranes were improved by ionic crosslinking with polybenzimidazole (PBI-OO).  
16 Finally, the conductive properties of the sulfonated BCPs and statistical copolymers were  
17 investigated as a function of parameters such as the morphology of the BCP, the molar mass,  
18 and the sulfonation degree of the materials.

19

20 **Keywords:** Nitroxide Mediated Polymerization NMP, Emulsion polymerization,  
21 Pentafluorostyrene, diblock-copolymers, Sulfonation, *Para* fluoro-thiol modification, Proton-  
22 conductive membrane

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## 1. Introduction

Over time, water electrolysis has emerged as the technique of choice for carbon-free hydrogen production. By using water and energy coming from renewable sources as its main feedstocks, water electrolyzers are expected to help reduce carbon dioxide emissions. Electrolyzers are divided in three types: alkaline electrolyzers (AEC), [1] proton exchange membrane (PEM) electrolyzers, [2] and solid oxide electrolysis (SOE) cells. [3] Although AEC represents the most developed electrolyser technology to date, PEM electrolyzers are regarded as most certainly considered superior due to their better energy efficiency, higher production rates, and compact electrolyser design. A PEM electrolyser is operated in acidic media, and the electrolyte is a thin proton-conducting polymer membrane. In a typical PEM electrolysis system, the electrodes are directly assembled on the membrane, also called Membrane Electrode Assembly (MEA). [2] At the anode, to which water is supplied, the oxidation reaction (Oxygen Evolution Reaction - OER) takes place with the decomposition of water into oxygen, protons, and electrons. At the cathode, the reduction reaction (Hydrogen Evolution Reaction - HER) takes place, recombining the electrons and protons into gaseous hydrogen. Most cathode materials for PEM electrolyzers are based on platinum, which has the best HER activity and is very stable in acidic media. Metal oxides such as  $\text{RuO}_2$  and  $\text{IrO}_2$  are usually used as anode materials.[4]

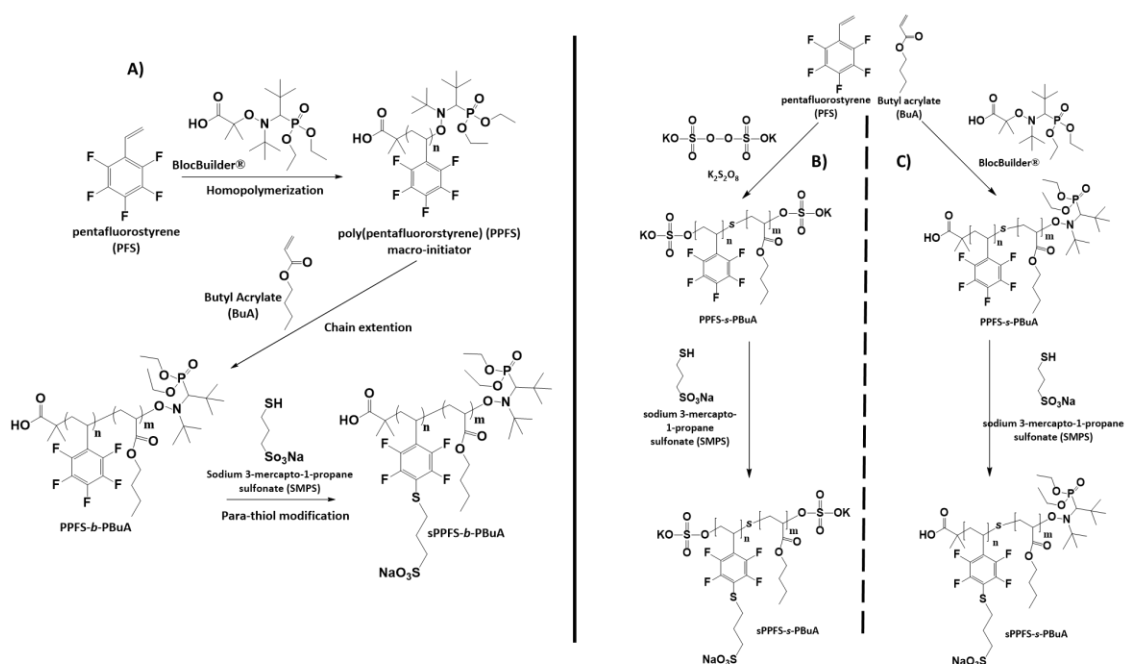
The proton-conducting membrane is the core component of the device. The membrane not only conducts protons, but also prevents the gas products coming from both electrodes from mixing. The thinner the membranes, the higher the transfer rate of protons between both electrodes. To be effective, the membrane must have a good chemical and mechanical stability, thermal and hydrolytic stability, and high proton conductivity. [5] Nafion<sup>®</sup> is currently the material of reference for these membranes. Nafion<sup>®</sup> membranes have been thoroughly investigated and shown to have very good proton-conducting properties as well as very good

1 chemical and mechanical properties. However, the synthesis of Nafion<sup>®</sup> requires several  
2 production steps, resulting in high production costs. With the aim of developing less expensive  
3 membranes with similar performances as Nafion<sup>®</sup>, different types of polymeric materials have  
4 been developed. [6] They consist of sulfonated fluorinated, partially fluorinated [7] or  
5 hydrocarbon polymers. [8] Sulfonated poly(ether ether ketone) (sPEEK) with high degree of  
6 sulfonation (IEC > 2 meq/g) has approached the conductivity of Nafion<sup>®</sup>. [9]

7         The mechanism of proton conduction in Nafion<sup>®</sup> has also been studied. Its good proton  
8 conductivity is attributed to the phase segregation that occurs when the hydrophilic acidic  
9 moieties are combined with the hydrophobic fluorocarbon chain. This results in the formation  
10 of hydrophilic channels in which the proton-conductivity occurs according to the water  
11 dynamics. [9, 10] For this reason, there has an increased interest in the synthesis of amphiphilic  
12 diblock-copolymers for the preparation of membranes. It has already been shown that the  
13 structural organization by diblock-copolymers positively affects the transport kinetics in the  
14 membrane. Examples such as sulfonated BCPs of poly(sulfone-*b*-vinylidene fluoride), and  
15 poly(styrene-*b*-isobutylene-*b*-styrene) (s-SIBS) have already been investigated. In these  
16 studies, it was found that the transport properties increased by an order of magnitude when  
17 diblock-copolymers were used compared to random copolymers, with the most influential  
18 parameter being the connections of the hydrophilic domains. [11, 12, 13]

19         In the present study, we investigated the structural and conductivity properties of new  
20 sulfonated poly(pentafluorotyrene-*b*-butyl acrylate) (sPPFS-*b*-PBuA) diblock copolymers.  
21 These copolymers were obtained from PPFS-*b*-PBuA diblock copolymers synthesized by  
22 nitroxide mediated polymerization (NMP) followed by a mild organo-catalyzed *para*-fluoro-  
23 thiol modification technique to introduce the sulfonated group on the PPFS block. [14] The  
24 initial and the sulfonated copolymers were characterized by <sup>1</sup>H NMR and <sup>19</sup>F NMR, DSC,  
25 AFM, SAXS, rheology and conductivity measurements. In addition, for a comparative study,

1 statistical copolymers of the PPFS/PBuA system were synthesized by emulsion polymerization  
 2 and also investigated (**Scheme 1**).



3  
 4 **Scheme 1.** Synthetic routes to sulfonated PPFS/PBuA diblock and statistical copolymers  
 5 (sPPFS-*b*-PBuA and sPPFS-*stat*-PBuA). (A) BCP synthesized by NMP controlled radical  
 6 polymerization, (B) Statistical copolymer synthesized by free radical polymerization in  
 7 emulsion and (C) Statistical copolymer synthesized by NMP controlled radical polymerization.

8

## 9 2. Experimental section

### 10 2.1. Materials

11 Pentafluorostyrene (99%, Sigma-Aldrich), butyl acrylate (99%, Sigma-Aldrich),  
 12 BlocBuilder® (provided by Arkema), free-SG1 (83%, provided by Arkema),  
 13 dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), potassium persulfate/ $K_2S_2O_8$   
 14 (99%, Sigma-Aldrich), sodium dodecyl sulfate/SDS (99%, Sigma-Aldrich), sodium  
 15 phosphate/ $Na_2HPO_4$  (Merck), Sodium chloride/ $NaCl$  (99.5%, Sigma-Aldrich), DMSO (VWR),  
 16 sodium 3-mercapto-1-propanesulfonate (95%, Sigma-Aldrich), 1,8-Diazabicyclo[5.4.0]undec-  
 17 7-ene (DBU, 99%, Sigma, Aldrich), 2,2-(ethylenedioxy)diethanethiol (95%, Sigma-Aldrich),

1 PBI-OO (Fumatech), technical methanol (VWR), THF (VWR). Used without further  
2 purification.

## 3 **2.2. Copolymers synthesis**

### 4 *2.2.1. Synthesis of PPFS/PBuA diblock-copolymer*

5 The NMP of PFS was performed in bulk following a typical NMP procedure. [15]  
6 Pentafluorostyrene (41.2 mmol), BlocBuilder<sup>®</sup> (0.10 mmol) and free-SG1 (0.01 mmol) were  
7 added to a 25mL round bottom flask equipped with septum and a magnetic stirring bar. The  
8 mixture was placed into an ice bath and bubbled with nitrogen for 15 minutes and subsequently  
9 placed into an oil bath that was pre-heated at 115°C. The mixture was stirred for 5h at 115°C.  
10 At the end of the reaction time, the mixture was cooled down to RT and the polymer was  
11 precipitated in methanol. The solid precipitants were collected by filtration and the polymer  
12 was dried under vacuum at 60°C overnight. Purification of the polymer was performed by  
13 dissolution in THF and subsequent precipitation in methanol. The purification step was repeated  
14 twice and then final macro-initiator PPFS was obtained. The so obtained PPFS macro-initiator  
15 was then used for chain extension procedure with butyl acrylate (BuA) monomer. To do so, the  
16 PPFS macro-initiator (0.049 mmol) and some free-SG1 (0.0049mmol) were dissolved into  
17 DMF (1.5 mL) in a 25mL round bottom flask equipped with rubber seals and a magnetic stirring  
18 bar. Subsequently, BuA (26.9 mmol) was added to the mixture. Different ([BuA]/[PPFS]) ratios  
19 were calculated and used to target different self-assembly morphologies. The mixture was  
20 degassed with nitrogen at room temperature for 15 minutes before putting the flask in an oil  
21 bath pre-heated at 115°C. The mixture was stirred at 115°C for 9h. The BCP was recovered by  
22 precipitation of the mixture into methanol after cooling down to room temperature. The  
23 precipitation was followed by filtration and drying of the polymer under vacuum oven at 60°C  
24 overnight (conversion: 91%). The synthesis was previously reported by our group. [15]

### 25 *2.2.2. Synthesis of statistical PFS/BuA copolymer by NMP*



1 Statistical copolymerization of pentafluorostyrene (PFS) and butyl acrylate (BuA) was  
2 performed in DMF in a similar way than for the diblock-copolymer synthesis. PFS (33 mmol),  
3 BuA (21.5 mmol), BlocBuilder® (0.13 mmol) and some free-SG1 (0.013 mmol) were added to  
4 a 25mL round bottom flask equipped with rubber seals and a magnetic stirring bar. The mixture  
5 was placed into an ice bath, purged with nitrogen for 15 minutes and subsequently placed into  
6 an oil bath that was pre-heated at 115°C for 7 hours. The copolymer was recovered by  
7 precipitation of the mixture into methanol after cooling down to room temperature. The  
8 precipitation was followed by filtration and drying of the polymer in a vacuum oven at 60°C  
9 overnight. Purification of the polymer was performed by dissolution in THF and subsequent  
10 precipitation in methanol. The purification step was repeated twice. (Conversion BuA = 50%;  
11 conversion PFS = 66%)

### 12 2.2.3. Copolymerization PFS/BuA by free radical polymerization in emulsion

13 In a three-neck round bottom flask, water (200 g) was added and degassed with nitrogen  
14 for an hour at RT. Potassium persulfate ( $K_2S_2O_8$ , 1 mmol), sodium dodecyl sulfate (SDS, 6.9  
15 mmol) and sodium phosphate ( $Na_2HPO_4$ , 0.84 mmol) were added under nitrogen flow. The  
16 mixture was stirred at room temperature (RT) until all components were dissolved  
17 (approximately 30 min). The monomers PFS (151.5 mmol) and BuA (75.7 mmol) were pre-  
18 mixed by stirring and subsequently added to the flask under vigorous stirring. The temperature  
19 was raised as fast as possible with a preheated oil bath at 90°C. When the desired temperature  
20 of 90°C was reached in the mixture, the temperature controller was adjusted to keep the  
21 temperature constant at 90°C over time. The polymerization was stopped when the mixture  
22 became translucent, after 4 hours in our case. After completion of the reaction, the mixture was  
23 cooled down to RT and sodium chloride (NaCl) was added until full aggregation of the polymer  
24 particles. The polymer was then rinsed with water to remove the excess of salt and dried at  
25 100°C under vacuum for 24 hours. (conversion = 100%)

#### 2.2.4. Sulfonation by para-fluoro-thiol modification of the copolymers

The copolymer (containing 41.2 mmol PPFS units) was dissolved into DMF (5 mL) in a round bottom flask. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 43.3 mmol) was added to the mixture followed by the addition of sodium-3-mecapto-1-propanesulfonate (SMPS, 45.1 mmol). The mixture was stirred at room temperature overnight. After completion of the reaction, the solution was dialysed to remove the excess of the water-soluble components. For that, the polymer was mixed with distilled water (30 mL), poured in an adequate dialysis tube (MWCO 3 kDa), and dialysed in distilled water for 3 days. After dialysis, the solution in the tube was lyophilised for 2 days. (conversion = 100%)

### 2.3. Polymer crosslinking and membranes preparation

The crosslinking of the membranes was performed by both covalent and ionic crosslinking. To perform the covalent crosslinking, the polymers must be partially sulfonated to contain unsubstituted pentafluorostyrene units. The difunctional 2,2-(ethylenedioxy)diethanethiol molecule was used as a crosslinker agent. Different crosslinking ratios were studied. Here as an example is given the preparation of a membrane containing 12 mol% crosslinker. In a separate flask, 0.26 mmol of 2,2-(ethylenedioxy)diethanethiol was mixed with 0.26 mmol DBU in 3 ml DMSO. In another flask, a 10 wt% solution of copolymer was formed by dissolving the partially sulfonated copolymer in DMSO. Both solutions were then mixed and casted in a silicon mold. The mold was placed in the convection oven at 80°C for 2 hours followed by an increase of temperature to 120°C overnight.

The ionic crosslinking was performed using Polybenzimidazole (PBI-OO). In a separate flask, PBI-OO was dissolved in DMSO (2 wt%). In another flask, a 10 wt% solution of copolymer was made by dissolving the sulfonated copolymer in DMSO. Both solutions were then mixed and casted in a silicon mold. The mold was placed in the convection oven at 80°C for 2 hours followed by an increase of temperature to 120°C overnight. The dried membranes

1 were then immersed into a 5% HCl solution overnight, rinsed several times with deionised  
2 water and dried at 50°C under vacuum. [16]

3 For the preparation of a membrane without crosslinking, the procedure was repeated  
4 without addition of 2,2-(ethylenedioxy)diethanethiol or PBI-OO/ DBU mixture.

## 5 **2.4. Characterization techniques**

### 6 *2.4.1. Nuclear Magnetic Resonance $^1H$ NMR & $^{19}F$ NMR*

7 NMR spectra were recorded on a Bruker DPX-400 spectrometer using deuterated  
8 solvents obtained from Sigma-Aldrich ( $CDCl_3$  and  $DMSO-d_6$ ). The spectra were recorded at  
9 room temperature.

### 10 *2.4.2. Size Exclusion Chromatography (SEC)*

11 The molar mass of the copolymers was determined by SEC. The set up consisted of a  
12 pump (LC-20A, Shimadzu), an autosampler (Sil- 20AHT), a differential refractometer (Optilab  
13 Rex, Wyatt), a light scattering detector (Dawn Heleos II, Wyatt), a viscosimeter (Viscoton,  
14 Wyatt), and three columns in series (Styragel HR2, HR4 and HR6 with pore sizes ranging from  
15 102 to 106 Å). The polymers were dissolved in THF at a concentration of 3 g/L. Prior to  
16 injection, the samples were filtered through 0.45 µm nylon filter. The chromatography was  
17 performed at 30°C at a flow rate of 1ml/min.

### 18 *2.4.3. Differential Scanning Calorimetry DSC*

19 Polymer sample (1-10 mg) was placed into aluminium capsules that are closed  
20 hermetically. The capsule was then placed into the DSC device (DSC Q100 from TA  
21 instruments) that was set to heating and cooling rates of 20°C/min under nitrogen atmosphere  
22 at a flow of 50 mL/min. The characterization was performed at the temperature range of -80°C  
23 to 180°C.

### 24 *2.4.4. Atomic force microscopy AFM*

1 AFM was performed on a Multimode 8 Atomic Force Microscope (Bruker) and  
2 recorded in PeakForce QNMmode. For the BCPs, the polymer film was obtained by spin-  
3 coating of a diluted polymer solution on a silicon wafer. The solution was obtained by  
4 dissolution of the polymers in a mixture of toluene : propylene glycol methyl ether acetate  
5 (PGMEA) = 75 : 25, (2 wt%). The sample was first characterized by AFM directly after spin-  
6 coating and drying and then after annealing at 140°C for 30 minutes and subsequent quenching  
7 at RT. As the sulfonated BCPs were no longer soluble in the toluene/PGMEA mixture, they  
8 were solubilized in DMSO (2 wt%). The polymer solution was then drop casted on the silicon  
9 wafer and dried in the oven at 50°C overnight.

#### 10 2.4.5. *Small-angle X-ray scattering SAXS*

11 SAXS experiments were performed with a high-resolution X-ray Spectrometer Xeuss  
12 2.0 from Xenox. The spectrometer operates with a radiation wavelength of  $\lambda = 1.54 \text{ \AA}$  (Copper  
13  $K_{\alpha}$  radiation). Scattering patterns were collected using a PILATUS 300K Dectris detector with  
14 a sample-to-detector distance of 1637 mm. The collected data were analysed using Primus  
15 software. The film preparation for the SAXS experiment was done in a similar way than for the  
16 AFM characterization. The polymers were solubilized in their adequate solvents (2wt%) and  
17 drop casted on a Kapton film. The films were annealed prior to analysis. For the BCP, the  
18 annealing was done at 140°C for 30 minutes, and for the sulfonated BCP at 50°C overnight.

#### 19 2.4.6. *Rheology*

20 Rheology was performed on an Anton Paar rheometer equipped with a SER (Sentmanat  
21 Elongational Rheometer) universal testing platform. The SER platform consisted of two  
22 counter rotating drums stretching the sample until breaking point. The drums each had a  
23 diameter of 10.3 mm. A rectangular section was collected from the membranes and positioned  
24 on the drums. The films were stack to the drums at elevated temperature. The drums were set  
25 to a rotating speed of  $0.1 \text{ s}^{-1}$ , and the chosen rotational angle was 360°.

#### 2.4.7. Ion Exchange Capacity

Ion Exchange Capacity (IEC) of the membranes were measured by titration method. A dry piece of membrane (in H-form) was immersed in 50 mL of saturated NaCl solution under stirring for 24 h. Solution was titrated with 0.1N NaOH solution to the equivalence point of bromothymol blue indicator (pH = 7). The IEC was calculated according to the equation: [IEC (meq/g) = (V<sub>NaOH</sub> × C<sub>NaOH</sub>)/W<sub>d</sub>], where W<sub>d</sub> is the dry weight (mg) of the sample and V<sub>NaOH</sub> and C<sub>NaOH</sub> are the volume (mL) and molar concentration of NaOH solution, respectively.

#### 2.4.8. Water uptake measurement

Water uptake was determined by comparing the weight of the membrane in its dry state and in its hydrated state. To do so, the membrane was weighted in dry state and immersed in deionised water for 24h at room temperature. The water uptake was calculated using the following formula:

$$\text{Water uptake (\%)} = \frac{w_{hydrated} - w_{dry}}{w_{dry}} \times 100$$

#### 2.4.9. Electrochemical Impedance Spectroscopy

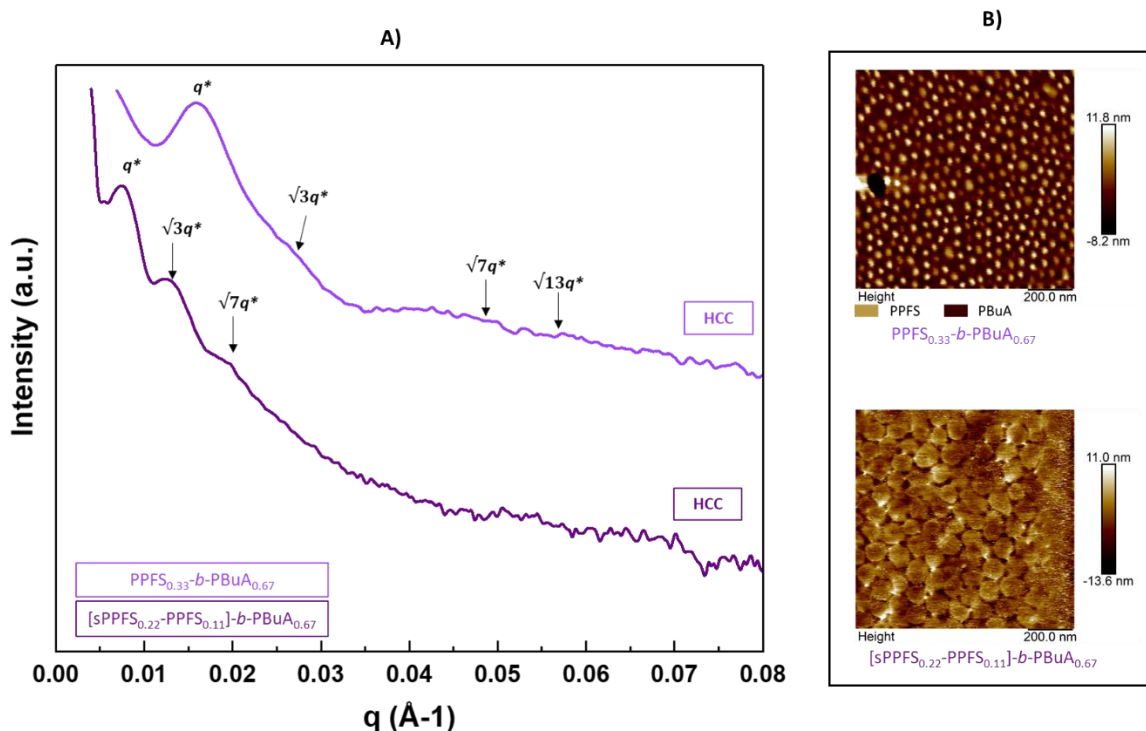
The electric resistance of the membranes was determined via impedance spectroscopy (IM6 Impedance measurement system, Zahner elektrik) in a Teflon cell with gold-plated copper electrodes having the following electrode area: 0.25 cm<sup>2</sup>. The impedance, where the phase angle between current and voltage was zero, was taken as the (ohmic) ion-exchange membrane resistance. The measurement was performed in 0.5 N H<sub>2</sub>SO<sub>4</sub>. The membrane was placed between two Nafion<sup>®</sup> 117 membranes and pressed in a stack between the two electrodes at T = 25 °C. By this method, the resistances at the interphase membrane/electrode are eliminated by first measuring all three membranes, followed by measurement of the two Nafion<sup>®</sup> membranes alone, and subtracting of the impedance of the Nafion<sup>®</sup> membranes from the impedance of all three membranes.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of diblock and statistical copolymers

Poly(pentafluorostyrene)-*b*-poly(butyl acrylate) (PPFS-*b*-PBuA) diblock-copolymer (BCP) was previously synthesized by NMP controlled radical polymerization. To summarize, the BCP was synthesized by NMP using the commercially available alkoxyamine BlocBuilder® as an initiator and control agent. By varying the monomer to initiator ratio and adjusting the reaction times, we were able to synthesize diblock-copolymers BCPs with different molar compositions. BCPs morphologies such as hexagonally closed-packed cylinders (HCC) or lamellas (LAM) were obtained by BCP self-assembly as revealed by AFM and SAXS. [15]

It has been proven that favorable nano-structuration in the copolymer improves the proton-conduction in the membrane. [17] For that reason, we aimed to prepare proton-conducting membranes that self-organized into *out-of-the-plane cylinders* of PPFS in a PBuA matrix, *i.e.* perforating nano-channels through the film. Indeed, a polymer structured in such a way after sulfonation would result in a membrane that would dispose of sulfonated conductive channels with diameter of few dozens of nanometers. In order to achieve this goal, PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub> with a molar mass of 40 000 g/mol was used for the experiments. Its molar composition and molar mass were calculated from <sup>1</sup>H NMR and SEC characterizations, and its structure observed by AFM and SAXS (**Figure 1**). PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub> reveals to be composed of nano-domains of PPFS structured in hexagonally-closed-packed cylinders (HCC), with a pitch of 45 nm determined by SAXS. At the same time, PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub> displayed two glass transition temperatures at -40°C and one at 104°C corresponding to PBuA and PPFS *T<sub>g</sub>*, respectively (**Figure SI 1**).



1  
 2 **Figure 1.** (A) SAXS patterns of (PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub>)<sub>40K</sub> BCP before and after partial  
 3 sulfonation (DS = 68%, see Table 2); (B) Peak Force mode AFM height images showing  
 4 morphology transition before and after sulfonation of the BCP.

5 Statistical copolymers of PPFS/PBuA were synthesized by both NMP and free radical  
 6 polymerization (FRP). NMP was performed in solution in DMF using the alkoxyamine  
 7 BlocBuilder® as a control agent, and the FRP in emulsion using peroxodisulfate as the initiator.  
 8 The copolymers were characterized by <sup>1</sup>H NMR, SEC, and DSC.

9 On a typical <sup>1</sup>H NMR spectrum of PPFS/PBuA copolymers, the chemical shifts of the  
 10 backbone protons (-CH and -CH<sub>2</sub>) are located between 1.8 and 2.9 ppm. Protons of PBuA side  
 11 chains (-CH<sub>3</sub> and -CH<sub>2</sub>) are located between 1 and 1.8 ppm and -OCH<sub>2</sub> protons of the PBuA  
 12 side chain are located at 4 ppm (**Figure SI 2, Figure SI 3, Figure SI 4**). From the attribution  
 13 and integration of the proton signals, the molar composition of both PPFS and PBuA was  
 14 determined (**Table 1**). The statistical copolymer (PPFS<sub>0.87</sub>-*stat*-PBuA<sub>0.13</sub>)<sub>19K</sub> obtained by NMP  
 15 was composed of 87 mol% of PPFS in contrast to the 80 mol% of PPFS (PPFS<sub>0.80</sub>-*stat*-

1 P BuA<sub>0.20</sub>)<sub>140K</sub> which were obtained by FRP. (PPFS<sub>0.87</sub>-*stat*-P BuA<sub>0.13</sub>)<sub>19K</sub> synthesized by NMP  
2 presents a dispersity  $\mathcal{D}$  of 1.16, whereas the one made by the FRP method  $\mathcal{D} = 15.2$  (**Figure SI**  
3 **5**). The glass transition temperature  $T_g$  of the copolymers was determined by DSC giving a  $T_g$   
4 around 64 and 89°C for the copolymers by NMP and FRP, respectively. The increase in  $T_g$   
5 could be explained by the high molar mass of the (PPFS<sub>0.80</sub>-*stat*-P BuA<sub>0.20</sub>)<sub>140K</sub> copolymer  
6 obtained by FRP method in emulsion process (**Table 1**).



**Table 1.** Summary of the experimental conditions and macromolecular characterizations of the PPFS/PBuA diblock and statistical copolymers.

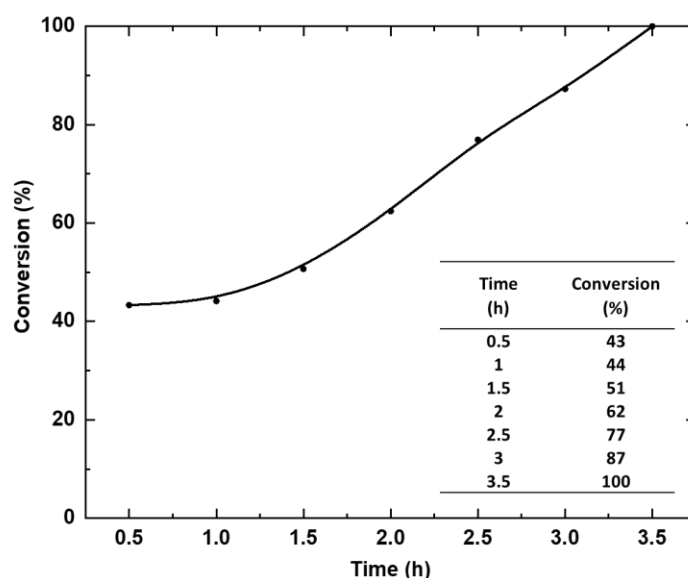
<b>Polymer</b> <b>(synthetic method)</b>	<b>[M]/[I]</b>	<b>Temp</b> <b>(°C)</b>	<b>Time</b> <b>(h)</b>	<b>M<sub>n</sub><sup>a</sup></b> <b>(kg/mol)</b>	<b>M<sub>w</sub><sup>a</sup></b> <b>(kg/mol)</b>	<b>Đ<sup>a</sup></b>	<b>Molar</b> <b>%PPFS<sup>b</sup></b> <b>(%)</b>	<b>Molar</b> <b>%PBuA<sup>b</sup></b> <b>(%)</b>	<b>T<sub>g</sub><sup>c</sup></b> <b>(°C)</b>
PPFS <sub>0.33</sub> - <i>b</i> -PBuA <sub>0.67</sub> (NMP/ solution)	550*	115	22	40	76	1.88	33	67	-40/104
PPFS <sub>0.87</sub> - <i>stat</i> -PMA <sub>0.13</sub> (NMP / solution)	370	115	7	19	22	1.16	87	13	64
PPFS <sub>0.80</sub> - <i>stat</i> -PBuA <sub>0.20</sub> (FRP / emulsion)	230	90	6	140	2 000	15.2	80	20	89

\* [BuA]/[PPFS macro-initiator]; <sup>a</sup> Determined by SEC by equivalent PS. <sup>b</sup> Determined by <sup>1</sup>H NMR (300 MHz, room temperature, CDCl<sub>3</sub>). <sup>c</sup> Determined by DSC.

### 3.2. Sulfonation by *para*-fluoro-thiol modification of the copolymers

Here, the *para*-fluoro-thiol modification was selected as an efficient soft substitution of *para*-fluorine atom in perfluorinated phenyl ring. The substitution was performed with a functional thiol, *i.e.* sodium-3-mecapto-1-propanesulfonate (SMPS) in a one-step synthesis in the presence of a base 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). The high capability of the *para*-F of the perfluorinated phenyl ring to thiols has features of a click-reaction: quick, and at mild conditions (RT). Moreover, the versatility and the commercial availability of thiol compounds make them attractive for such reactions. [14]

Firstly, the kinetic of the *para*-fluoro-thiol modification with the sulfonate compound was studied. To do so, the substitution reaction was performed on PPFS homopolymer and the reaction progress was controlled by  $^{19}\text{F}$  NMR. In fact, the reaction mixture which consisted of PPFS homopolymer with a molar mass of 12 500 g/mol and dispersity  $D$  of 1.07, DMF, DBU (1.05 eq), and SMPS (1.1 eq) were introduced in an NMR tube and placed into the NMR rotor.  $^{19}\text{F}$  NMR spectrum of the blend was recorded at room temperature over 24 hours (**Figure 2**). It turned out that the full substitution of the *para*-F of PPFS by SMPS was obtained after only 3.5 hours of reaction. This experiment proved that in mild conditions, the *para*-fluoro-thiol modification is very efficient and only few hours are needed for a full sulfonation.



1 **Figure 2.** *Para*-fluoro-thiol modification of PPFS homopolymer by SMPS over time. The  
 2 conversions were determined by  $^{19}\text{F}$  NMR.

3 Using the gathered information on the *para*-substitution with the sulfonate compound,  
 4 the copolymers were fully or partially sulfonated according to the molar ratios of PFS monomer  
 5 units and SMPS (**Figure 3 I**). Even if the full conversion is reached at 3.5h, the reactions were  
 6 left for 24 or 48h to make sure that all the polymer reacted with the thiol moiety. Because of its  
 7 high molar mass,  $(\text{PPFS}_{0.80}\text{-}i\text{-PBuA}_{0.20})_{140\text{K}}$  synthesized by FRP did not dissolve in DMF at  
 8 room temperature. Therefore, the temperature was raised to  $50^\circ\text{C}$  and the reaction proceeded  
 9 for 24h. All the sulfonated copolymers were purified by dialysis in water. They were  
 10 characterized by  $^{19}\text{F}$  NMR and DSC (**Table 2**).

11

12 **Table 2.** Summary of the *para*-fluoro-thiol modification conditions and characterizations of the  
 13 PPFS/PBuA diblock and statistical copolymers.

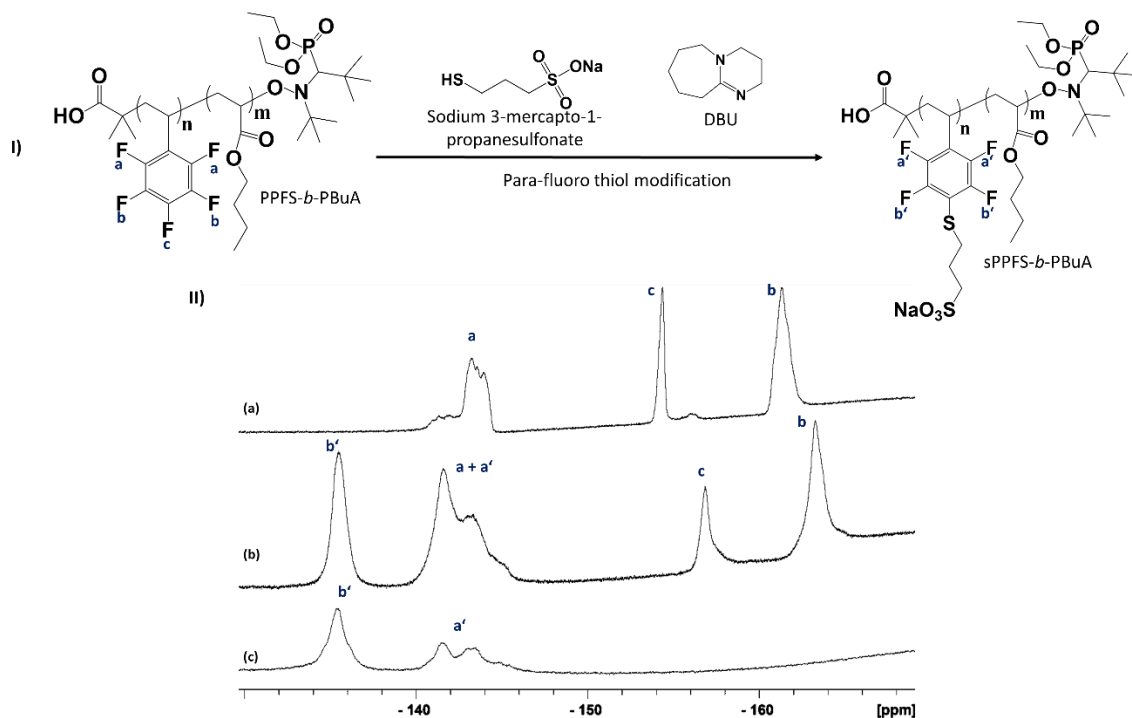
Polymer (synthesis method)	Thiol Sulfonate salt /PFS unit (eq)	Temp ( $^\circ\text{C}$ )	Time (h)	DS <sup>a</sup> (%)	T <sub>g</sub> <sup>b</sup> ( $^\circ\text{C}$ )
$(\text{PPFS}_{0.33}\text{-}i\text{-PBuA}_{0.67})_{40\text{K}}$	$\approx 0.70$	25	24	68	- 42/60
(NMP / solution)	$\approx 1$	25	24	100	-40/15
$(\text{PPFS}_{0.87}\text{-}i\text{-PBuA}_{0.13})_{19\text{K}}$	$\approx 0.5$	25	48	57	32
(NMP / solution)					
$(\text{PPFS}_{0.80}\text{-}i\text{-PBuA}_{0.20})_{140\text{K}}$	$\approx 1$	50	24	100	61
(FRP / emulsion)					

14 <sup>a</sup> Degree of sulfonation (DS) determined by  $^{19}\text{F}$  NMR. <sup>b</sup> Glass transition temperature (T<sub>g</sub>) determined by DSC after  
 15 sulfonation.

16

17 The  $^{19}\text{F}$  NMR spectra of the non-modified polymers displays 3 signals for the fluorine  
 18 at each position of the aromatic ring:  $\delta 2\text{F}_{ortho}$  -143 ppm;  $\delta 2\text{F}_{meta}$  -161 ppm;  $\delta 1\text{F}_{para}$  -154 ppm

1 **(Figure 3 II (a))**. After full modification, there was no more fluorine in *para* position, and the  
 2 signal of fluorine in *meta* positions is up-field shifted due to the presence of the sulphur in *para*  
 3 position ( $\delta 2F_{ortho} = -141$  ppm:  $\delta 2F_{meta} = -134$  ppm) **(Figure 3 II (c))**. The  $^{19}\text{F}$  NMR spectra of  
 4 the partially fluorinated copolymer displays the signals of all the fluorine of both the initial  
 5 copolymer and the sulfonated one **(Figure 3 II (b))**.



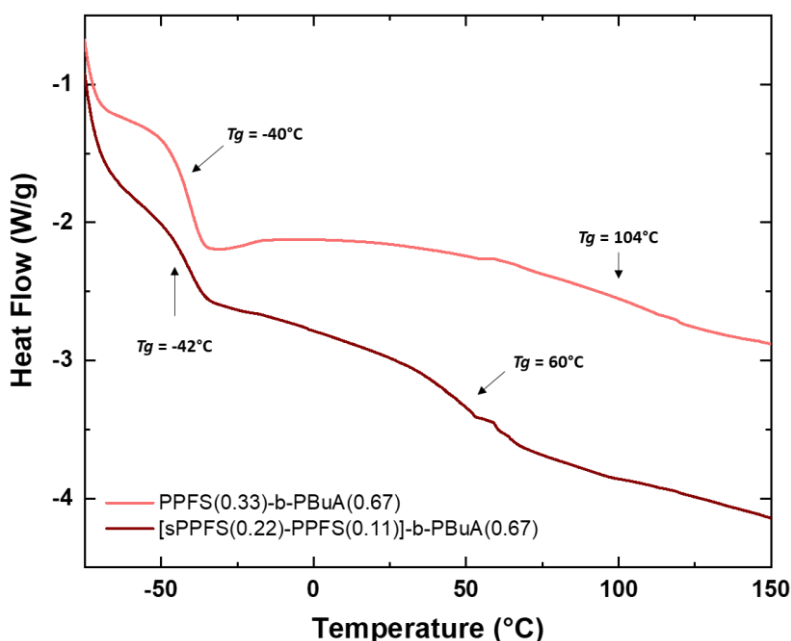
6  
 7 **Figure 3.** (I) Sulfonation reaction of PPFS-*b*-PBuA with SMPS. (II)  $^{19}\text{F}$  NMR spectra of (a)  
 8  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  in  $\text{CDCl}_3$ , (b) Partially sulfonated  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  in  
 9  $\text{DMSO-d}_6$ , DS = 68% and (c) Fully sulfonated  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  in  $\text{DMSO-d}_6$ , DS =  
 10 100%.

11

### 12 3.3. Thermal properties of the diblock-copolymers

13 The diblock-copolymer was characterized by DSC before and after full and partial  
 14 sulfonation **(Table 2)**. A decrease in  $T_g$  is observed after sulfonation. Indeed, for the BCPs, the  
 15 glass transition temperature of the sulfonated PPFS (sPPFS) moiety decreased from  $100^\circ\text{C}$  to  
 16  $60^\circ\text{C}$  **(Figure 4)**. It is worth noting that introducing a sulfonic group in the polymer chain has

1 been reported in the literature to increase of the  $T_g$  of the polymer. [18, 19] This increase has  
2 been attributed to the decrease of flexibility introduced in the chain by adding  $-\text{SO}_3\text{H}$  groups,  
3 which is increasing the number of interacting species (e.g. h-bonding, ionic interactions).  
4 However, the compound used herein for sulfonation (sodium-3-mercapto-1-propanesulfonate,  
5 SMPS) presents a sulfonic moiety linked to a flexible alkane chain. The use of a short spacer ( $-\text{C}_3\text{H}_6-$ )  
6 between the backbone and the sulfonic acid functional group introduces some mobility  
7 to the polymer, and hence contributes to the decrease of the  $T_g$ .



8  
9 **Figure 4.** DSC thermograms of  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  and partially sulfonated  $(\text{PPFS}_{0.33}\text{-}b\text{-}$   
10  $\text{PBuA}_{0.67})_{40\text{K}}$  (DS = 68%) BCPs showing the glass transition temperatures conservation for  
11 PBuA at  $-40^\circ\text{C}$  and evolution of the PPFS ones from 104 to  $60^\circ\text{C}$ .

12 Although it is clearly proven that the sulfonation of PPFS with SMPS is possible under  
13 mild conditions for both the homopolymer and the diblock copolymers. The fully sulfonated  
14  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  PPFS block displayed a  $T_g$  lower than the ambient temperature ( $T_g =$   
15  $15^\circ\text{C}$ ). This drastic decrease from the original  $T_g$  of PPFS ( $T_g = 104^\circ\text{C}$ ) is not ideal for  
16 membrane purposes. For that reason, the partially sulfonated BCP ( $T_g = 60^\circ\text{C}$ ) was used for  
17 further experiments.

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### 3.4. Morphological studies of the sulfonated diblock-copolymer

As stated previously, having an organised sulfonated material was proven to be beneficial for the membrane conductivity. Using amphiphilic diblock-copolymers as membrane materials have increased the transport kinetics of protons. [11] Thus, continuous nano-domains of sPPFS through the membrane should provide an efficient transfer of protons from one side of the membrane to the other, *i.e.* nano-channels. In a previous study, it was proven both by AFM and SAXS that (PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub>)<sub>40K</sub> BCP displayed an HCC structuration of PPFS nano-domains in a PBuA matrix. [15] After sulfonation, the morphology of the partially sulfonated BCP was studied by AFM and SAXS (**Figure 1**). For this purpose, polymers were dissolved in DMSO (2 wt%) and drop casted on silicon wafer for AFM characterization and on Kapton film for the SAXS experiment. The films were then annealed in oven at 50°C overnight.

AFM images showed an increase in size of nano-domains from 45 nm (PPFS) to 96 nm (sPPFS) after sulfonation. This may be due to a volume increase of the PPFS block caused by the addition of the sodium-3-mecapto-1-propanesulfonate moieties ( $M_{\text{PPFS unit}} = 194.1$  g/mol;  $M_{\text{sPPFS unit}} = 351.98$  g/mol). Indeed, the morphological features of the self-assembled BCP are dictated by the volume fraction and specific chain/segment interactions of both blocks in the BCP among other factors. The SAXS measurements on the annealed film revealed an HCC structuration of the BCP after sulfonation, with a first order peak at  $q^* = 7.5 \cdot 10^{-2} \text{ nm}^{-1}$  and a cylinder-to-cylinder distance of 96 nm ( $d = 4\pi / \sqrt{3}q^*$ ). The following peaks at  $\sqrt{3}q^*$  and  $\sqrt{7}q^*$  are representative of the HCC structure (**Figure 1**). From those results, we can assume that the sulfonated BCP is able to self-assemble with nano-domains of *out-of-the-plane* cylinders of sPPFS in a PBuA matrix.

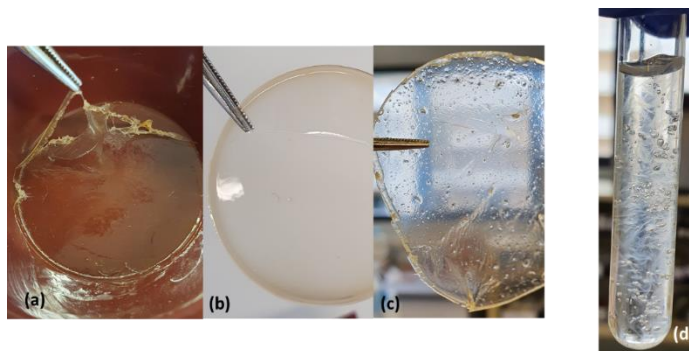
### 3.5. Membrane elaboration and properties

1 Membranes were prepared using the sulfonated copolymers and DMSO as a solvent.  
2 The challenge here is to define the conditions for achieving mechanically stable membranes.  
3 The choice of solvent was made considering the solubility of the sulfonated copolymers and its  
4 evaporation rate ( $bp_{\text{DMSO}} = 189^{\circ}\text{C}$ ).

### 5 3.5.1. Membrane elaboration process without crosslinking

6 DMSO solutions (10 wt%, and 2wt% in the case of  $(\text{PPFS}_{0.80}\text{-}s\text{-PBuA}_{0.20})_{140\text{K}}$ ) of the  
7 fully or partially sulfonated copolymers were prepared.  $(\text{PPFS}_{0.80}\text{-}s\text{-PBuA}_{0.20})_{140\text{K}}$  made by FRP  
8 in emulsion was used at 2 wt% solution due to its high molar mass. For all the copolymers, the  
9 solutions were stirred until complete solubilization of the copolymers. They were then casted  
10 in a silicon mold and placed in the convection oven at  $80^{\circ}\text{C}$  for 2 hours and then at  $120^{\circ}\text{C}$   
11 overnight.

12 The partially sulfonated  $(s\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  BCP resulted in a very sticky  
13 membrane and was therefore difficult to unmold without tearing the membrane apart (**Figure**  
14 **5 (a)**). The sulfonated statistical copolymers by NMP and FRP in emulsion,  $(\text{PPFS}_{0.87}\text{-}s\text{-}$   
15  $\text{PBuA}_{0.13})_{19\text{K}}$  and  $(\text{PPFS}_{0.80}\text{-}s\text{-PBuA}_{0.20})_{140\text{K}}$  respectively, resulted in free-standing membranes  
16 (**Figure 5 (b) & (c)**). However, all the membranes swelled a lot and then solubilize when  
17 immersed in water, which is an issue for PEMWE applications (**Figure 5 d**).



18  
19 **Figure 5.** Pristine membranes from sulfonated  $(\text{PPFS}_{0.33}\text{-}b\text{-PBuA}_{0.67})_{40\text{K}}$  (a);  $(\text{PPFS}_{0.87}\text{-}s\text{-}$   
20  $\text{PBuA}_{0.13})_{19\text{K}}$  (b);  $(\text{PPFS}_{0.80}\text{-}s\text{-PBuA}_{0.20})_{140\text{K}}$  (c); Swollen sulfonated  $(\text{PPFS}_{0.87}\text{-}s\text{-PBuA}_{0.13})_{19\text{K}}$   
21 membrane in water (d).

1 Crosslinking reactions were foreseen in order to enhance the mechanical properties of  
2 the membranes and to decrease their swelling during subsequent use. Two different types of *in-*  
3 *situ* crosslinking were investigated. Either covalent crosslinking was performed *via para-*  
4 fluoro-thiol modification on the PPFS units using the dithiol 2,2-(ethylenedioxy)diethanethiol,  
5 or ionic crosslinking by mixing the sulfonated anionic copolymers with polybenzimidazole  
6 (PBI-OO). [16] Preliminary tests using the (PPFS<sub>0.87</sub>-*s*-PBuA<sub>0.13</sub>)<sub>19K</sub> with a degree of  
7 sulfonation DS = 57%, *i.e.* ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-*s*-PBuA<sub>0.13</sub>) were performed to optimise the  
8 amount of crosslinker. In fact, a subtle balance must be found to enhance the mechanical  
9 properties and reduce the swelling capacity of the membrane.

### 10 3.5.2. Covalent crosslinking

11 To crosslink the PPFS/PBuA copolymers, *para*-fluoro-thiol modification was  
12 performed as it has already proven to be an efficient reaction process for the sulfonation of the  
13 copolymers. A crosslinker, 2,2-(ethylenedioxy)diethanethiol with two reactive functional thiol  
14 groups was introduced to allow the creation of bridges between the polymer chains [20] using  
15 DBU in DMSO at room temperature (**Figure 6 A**).

16 Different compositions were tested by calculating a molar ratio [2,2-  
17 (ethylenedioxy)diethanethiol] / [PFS units] of 3, 6 and 12 mol% with a polymer content of 10  
18 wt% in DMSO. The crosslinked membranes were then characterized by DSC and elongational  
19 rheology. From the DSC thermograms, we notice a slight increase of  $T_g$  with the increase of  
20 the mol% of added crosslinker (**Figure 6 B**). Indeed, as the mol% of crosslinker increases, the  
21 more crosslinking occurs and the more energy the polymer needs to reach the rubbery state.

22 Elongational rheology experiments were performed on the covalently crosslinked  
23 membranes. To do so, a rectangular piece of the membrane was placed at 100°C on two counter-  
24 rotating drums at 0.1 s<sup>-1</sup> at a 360° angle rotation. Temperature was applied for the film to stick  
25 to the drums (**Figure SI 6**). [21, 22]



1           When looking at the rheology curves of all the samples, we noticed that the membranes  
2 without added covalent crosslinker and with 3 mol% of added covalent crosslinker behaved the  
3 same way to the stress applied. Indeed, the increase of viscosity is followed by a decrease of  
4 the extensional viscosity associated to the rupture of the film (**Figure 6 C**). On the contrary, an  
5 upward deviation of the viscosity curves is observed for the copolymer with 6 mol% of added  
6 covalent crosslinker, this deviation is more noticeable with 12 mol%. This behaviour is called  
7 strain-hardening and is characteristic of the occurrence of a chemical crosslinking. [22, 23]

8           In fact, when the polymer is crosslinked, there is a creation of chemical intermolecular  
9 bonds between the polymer chains. This results in the creation of polymer nodes and in the  
10 change of the polymer's properties. Due to the presence of those nodes, the polymers' viscosity  
11 increases until rupture of the chains when applying a strain to the material. From the rheology  
12 results, we notice that the covalent crosslinking of sulfonated (PPFS<sub>0.87-S</sub>-PBuA<sub>0.13</sub>)<sub>19K</sub> was  
13 effective at 6 and 12 mol% of added covalent crosslinker. There is a correlation between the  
14 DSC and rheology results. They both show that to covalently crosslink the copolymers  
15 efficiently, the amount of 2,2-(ethylenedioxy)diethanethiol to be added to the mixture should  
16 be above 12 mol%.

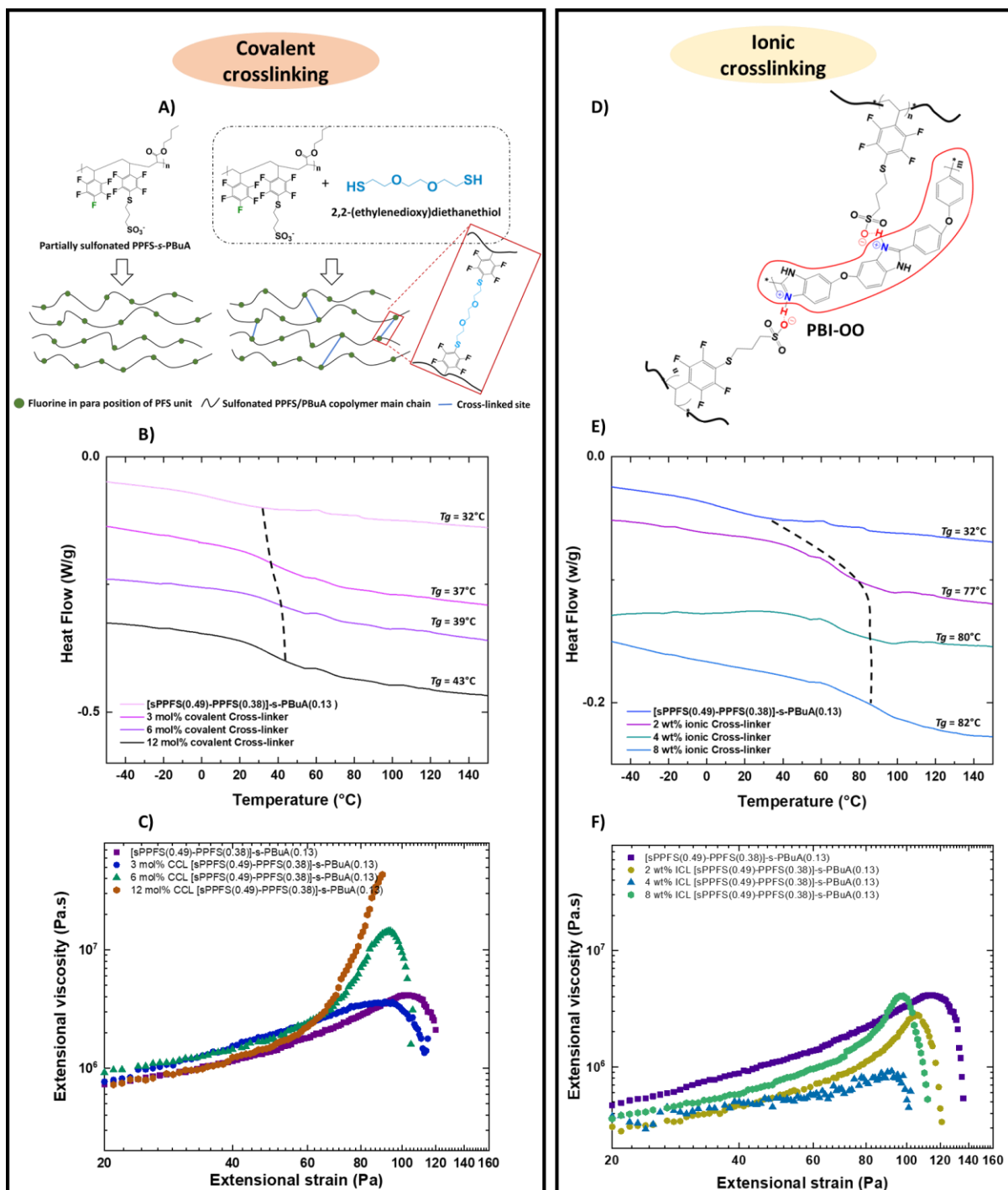
### 17           3.5.3. *Ionic crosslinking.*

18           Similarly, ionic crosslinking was performed on partially sulfonated (PPFS<sub>0.87-S</sub>-  
19 PBuA<sub>0.13</sub>)<sub>19K</sub>. To perform ionic crosslinking, one needs ionically charged crosslinker and  
20 polymer to create ion-pair interactions between them. Polybenzimidazole (PBI-OO) was used  
21 as a polymer base (**Figure 6 D**). It presents good thermal and mechanical stabilities, with an  
22 initial weight loss observed by TGA at temperatures above 600°C. [24]

23           Different PBI-OO crosslinking weight ratios were tested (2, 4 and 8 wt%). The  
24 membranes were made by solubilization in DMSO with a copolymer content of 10 wt%. The  
25 final dried membranes were immersed into an acid solution to promote the ionic crosslinking

1 interactions. The  $T_g$  of the membrane was increased from 32°C to 82°C at the highest wt% of  
2 added crosslinker (8 wt%) (**Figure 6 E**). An influence of the crosslinking with PBI-OO on the  
3  $T_g$  is noticeable from 2 wt% of added crosslinker with a  $T_g$  increasing from 32 to 77°C.

4         The rheology curves displayed a steady increase of the extensional viscosity of all the  
5 samples until rupture to strain regardless of the wt% of added ionic crosslinker (**Figure 6 F**).  
6 This observation suggests the occurrence of strain-hardening of the membranes as it was the  
7 case for the covalent crosslinking. This behaviour occurs regardless of the added amounts of  
8 ionic crosslinker. In this sense, only 2 wt% of PBI-OO are necessary to ionically crosslink the  
9 partially sulfonated (PPFS<sub>0.87-S</sub>-PBuA<sub>0.13</sub>)<sub>19K</sub> copolymer.



1  
 2 **Figure 6.** (A) Molecular structures of partially sulfonated PPFS-*s*-PBuA membrane and its  
 3 crosslinked homologue with 2,2-(ethylenedioxy)diethanethiol. (B) DSC thermograms of  
 4 sulfonated (PPFS<sub>0.87</sub>-*s*-PBuA<sub>0.13</sub>)<sub>19K</sub> membrane and the membrane with added covalent  
 5 crosslinkers. (C) Extensional viscosity *versus* extensional strain at 100°C of partially sulfonated  
 6 (PPFS<sub>0.87</sub>-*s*-PBuA<sub>0.13</sub>)<sub>19K</sub> ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-*s*-PBuA<sub>0.13</sub>) membrane with 0, 2, 6 & 12 mol%  
 7 of 2,2-(ethylenedioxy)diethanethiol as covalent crosslinker (CCL). (D) Representation of the

1 crosslinked site of the copolymer with PBI-OO. (E) DSC graphs of sulfonated (PPFS<sub>0.87-S-</sub>  
2 PBuA<sub>0.13</sub>)<sub>19K</sub> membrane and the membrane with added ionic crosslinkers. (F) Extensional  
3 viscosity *versus* strain of partially sulfonated (PPFS<sub>0.87-S-PBuA<sub>0.13</sub></sub>)<sub>19K</sub> ([sPPFS<sub>0.49-PPFS<sub>0.38</sub></sub>]-S-  
4 PBuA<sub>0.13</sub>) with added of 0, 2, 4 & 8 wt% of PBI-OO ionic crosslinker (ICL).

### 5 **3.6. Water uptake, Ion Exchange capacity and conductivity of the membranes**

#### 6 *3.6.1. Water uptake*

7 Beside the proton-conductivity and ion exchange capacity, water uptake is a critical  
8 factor in determining the performance of a membrane. Indeed, the proton-conductivity is  
9 dictated by the water content and diffusion in the membrane. Nevertheless, too much absorbed  
10 water can negatively impact the mechanical properties of the membranes leading to a loss of  
11 their mechanical integrity. In fact, the water uptake parameter is dependent on the degree of  
12 sulfonation of the polymer as the presence of too many ion groups (IEC > 2-2.5 meq/g) causes  
13 an extreme swelling of the membranes. Water will act as a plasticizer and lower the  $T_g$  of the  
14 membranes. [25] Water uptake of the crosslinked partially sulfonated (PPFS<sub>0.87-S-PBuA<sub>0.13</sub></sub>)<sub>19K</sub>  
15 membranes was determined by comparing the weights of the dry and hydrated membranes.  
16 Following the detailed procedure in the experimental section, crosslinked membranes were  
17 placed in a vial containing deionised water for 24 hours (**Figure SI 7 I & II**). As already  
18 mentioned in the previous section, non-crosslinked membranes of PPFS/PBuA were  
19 excessively swollen and were disrupted after 24 hours in water. Covalently crosslinked  
20 membranes having 3 and 6 mol% crosslinker behaved the same way as the pristine membranes.  
21 They swelled a lot and then were disrupted in water which render the water uptake  
22 determination impossible. In the case of 12 mol% of added crosslinker, the membranes were  
23 very swollen, with a water uptake exceeding 1000 wt%, and a hydration number of 563, they  
24 were losing their mechanical integrity. On the other hand, the ionically crosslinked membranes  
25 were all stable in water with water uptake values around 45wt%, and hydration number of 23-

1 25, (**Table 3**) comparable to the Nafion<sup>®</sup>117 ones with a water uptake of  $\approx 30\text{wt}\%$  and a  
 2 hydration number of 18. [26]

3 **Table 3.** Water uptake values of crosslinked partially sulfonated ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-  
 4 PBuA<sub>0.13</sub>)<sub>19K</sub>.

Type of crosslinking	Crosslinker (%)	Water uptake (wt%)	$\lambda^*$ [H <sub>2</sub> O/SO <sub>3</sub> H]
CCL	3 mol%	-	-
	6 mol%	-	-
	12 mol%	1076	563
ICL	2 wt%	44	23
	4 wt%	48	25.2
	8 wt%	45	23.6

5 \*Hydration number: number of water molecules per sulfonic acid functional group,  $\lambda = \text{Water uptake} / (\text{IEC}_{\text{exp}} \times$   
 6  $100 \times \text{MW}_{\text{water}})$  [27]

7 All the copolymers ionically crosslinked with PBI-OO gave a similar water uptake  
 8 around 45 wt%. The covalent crosslinking reaction of the partially sulfonated ([sPPFS<sub>0.49</sub>-  
 9 PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>)<sub>19K</sub> copolymer was successfully demonstrated by rheology. However, the  
 10 water uptake of these membranes was above 1000%, which is more than 30 times higher than  
 11 Nafion<sup>®</sup>'s. On top of this, the covalently crosslinked membranes appeared to be too fragile as  
 12 PEM for application in water electrolysis. On the contrary, ionic crosslinking with the PBI-OO  
 13 performed better in terms of mechanical properties and stability in water, regardless of the  
 14 added PBI-OO amounts. For that reason, ionic crosslinking by blending the copolymers with  
 15 PBI-OO was selected as the most suitable crosslinking technique to finally tailor the  
 16 membranes. As the percentage of added ionic crosslinker didn't have severe impact on the  
 17 properties of the membrane (2, 4 or 8 wt%), the chosen amount was 2 wt%. Indeed, using the  
 18 lowest amount of crosslinker possible will allow to have more anionic groups available for the

1 proton conduction. All the following characterizations were performed on the PBI-OO (2wt%)  
2 crosslinked sulfonated membranes.

### 3 3.6.2. Proton conductivity

4 Factors influencing the conductivity are mainly the morphology (ion-channel  
5 structuring) of the membrane, the water uptake (content of water), and the degree of sulfonation  
6 (DS) of the polymers characterized by the IEC (**Figure SI 8**). ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-  
7 PBuA<sub>0.13</sub>)<sub>19K</sub> showed IEC = 1.06 meq/g, higher than the reference that we are using Nafion<sup>®</sup>117  
8 (IEC = 0.93 meq/g) (**Table 4**). A similar IEC was obtained for the other two copolymers  
9 (sPPFS<sub>0.80</sub>-s-PBuA<sub>0.20</sub>)<sub>140K</sub> and ([sPPFS<sub>0.22</sub>-PPFS<sub>0.11</sub>]-b-PBuA<sub>0.67</sub>)<sub>40K</sub>, showing 0.3 meq/g and  
10 0.35 meq/g, respectively. The lower IEC of the sulfonated ([sPPFS<sub>0.22</sub>-PPFS<sub>0.11</sub>]-b-PBuA<sub>0.67</sub>)<sub>40K</sub>  
11 is explained by the low amounts of sPPFS that is 3 times less than ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-  
12 PBuA<sub>0.13</sub>)<sub>19K</sub>. The low IEC of sulfonated (sPPFS<sub>0.80</sub>-s-PBuA<sub>0.20</sub>)<sub>140K</sub> could be linked to high  
13 molar mass of the polymer making it difficult to access the sulfonated groups in the bulk of the  
14 2wt% crosslinked membrane during the 24h at room temperature.

15 The conductivity of the membranes was determined by Electrochemical Impedance  
16 Spectroscopy (EIS). The membrane made with the BCP ([sPPFS<sub>0.22</sub>-PPFS<sub>0.11</sub>]-b-PBuA<sub>0.67</sub>)<sub>40K</sub>,  
17 gave the best proton-conductivity from all studied membranes ( $\sigma = 179$  mS/cm) (**Table 4**). The  
18 membrane made with ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>)<sub>19K</sub> had a conductivity of 94 mS/cm and  
19 (sPPFS<sub>0.80</sub>-s-PBuA<sub>0.20</sub>)<sub>140K</sub> had the lowest conductivity of all three membranes,  $\sigma = 16$  mS/cm.  
20 The BCP was expected to conduct the best due to its higher IEC value, even if it has the lowest  
21 amount of sPPFS (22 mol%). This could be explained by the influence of the morphology of  
22 the diblock-copolymer and then its self-assembly behaviour on the conductive performances of  
23 the materials. The low conductivity value of sulfonated (sPPFS<sub>0.80</sub>-s-PBuA<sub>0.20</sub>)<sub>140K</sub> compared  
24 to the other membranes could not be explained at this stage, and further work is needed to  
25 improve the membrane formulation. Compared to the conductivity of the reference Nafion<sup>®</sup>117

1 with  $\sigma = 12$  mS/cm, we were able to achieve a similar conductivity for (sPPFS<sub>0.80</sub>-s-  
 2 PBuA<sub>0.20</sub>)<sub>140K</sub> and greater conductivities for ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>)<sub>19K</sub> and  
 3 ([sPPFS<sub>0.22</sub>-PPFS<sub>0.11</sub>]-b-PBuA<sub>0.67</sub>)<sub>40K</sub> using the PPFS/PBuA copolymer system.

4

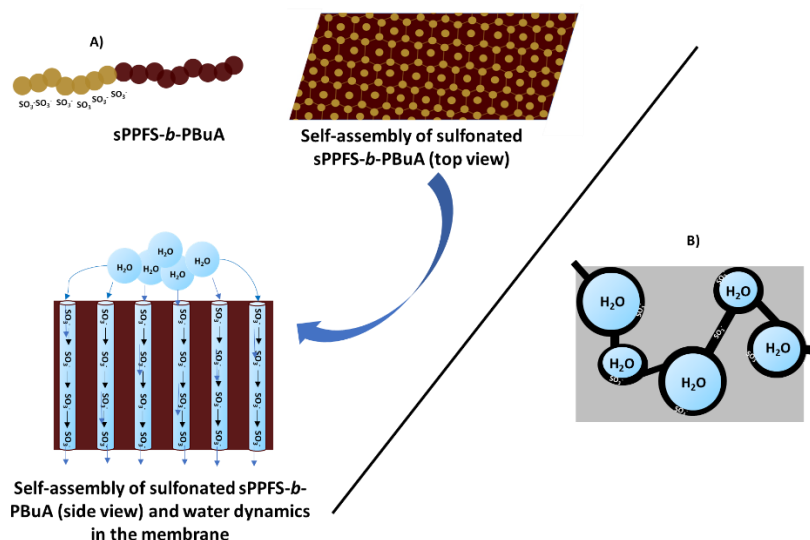
5 **Table 4.** IEC and conductivity of the sulfonated PPFS/PBuA crosslinked proton conductive  
 6 membranes.

Polymer	DS (%)	sPPFS (mol%)	IEC	IEC	Membrane thickness ( $\mu\text{m}$ )	Conductivity (mS/cm)
			Theoretical (meq/g)	Experimental (meq/g)		
(PPFS <sub>0.33</sub> -b-PBuA <sub>0.67</sub> ) <sub>40K</sub> (NMP / solution)	68	22	0.66	0.35	16	179
(PPFS <sub>0.87</sub> -s-PBuA <sub>0.13</sub> ) <sub>19K</sub> (NMP / solution)	57	49	2.15	1.06	86	94
(PPFS <sub>0.80</sub> -s-PBuA <sub>0.20</sub> ) <sub>140K</sub> (FRP / Emulsion)	100	80	2.76	0.3	6	16

7

8 These results reveal the importance of the material nano-structuration in the proton  
 9 conduction. Indeed, with sulfonated (PPFS<sub>0.33</sub>-b-PBuA<sub>0.67</sub>)<sub>40K</sub>, AFM analysis demonstrated the  
 10 formation of *out-of-the-plane* cylinders with a diameter of 100 nm. If such nanostructures are  
 11 percolating across the membrane, water will be attracted and conducted to the hydrophilic  
 12 sPPFS nano-domains structured in HCC. The protons will follow the water dynamic that in our  
 13 case consists of following a straight path from one end of the membrane to the other, improving  
 14 the overall transfer of protons compared to a random organization of the material (**Scheme 2**).  
 15 [28]

16



1  
 2 **Scheme 2.** Representation of sPPFS-*b*-PbuA self-assembled at the nanometre scale in  
 3 Hexagonally Compacted Cylinders (HCC) of sPPFS in a PBuA matrix, top view and side view  
 4 with the representation of water dynamics (A); Representation of the cluster network occurring  
 5 in Nafion<sup>®</sup> for the proton-conduction (B).

6

#### 7 **4. Conclusion**

8 The influence of the microstructure of PPFS/PBuA copolymers for proton-conducting  
 9 membrane for PEMWE applications was investigated. For this purpose, a diblock-copolymer  
 10 self-assembled in HCC structure was synthesized by NMP controlled radical polymerization.  
 11 In addition, statistical copolymers of PPFS/PBuA were synthesized in two ways: (i) NMP in  
 12 solution (DMF) and (ii) free radical polymerization in emulsion. The latter method resulted in  
 13 an aqueous formulation with a higher molar mass copolymer. The copolymers were then fully  
 14 or partially sulfonated by the efficient technique of soft *para*-fluoro-thiol modification using  
 15 sodium-3-mecapto-1-propanesulfonate according to a click-reaction. Partial sulfonation was  
 16 carried out to achieve a high IEC and to produce water insoluble polymers and preserve some  
 17 hydrophobicity. Full sulfonation was performed on the copolymer with the higher molar mass,  
 18 as it is the most mechanically stable. In addition, the membranes were ionically crosslinked  
 19 using at least 2 wt% of PBI-OO. In this way, stable films were prepared, highlighting high IEC



1 = 1.06 meq/g and conductivity  $\sigma = 179$  mS/cm. The ionic crosslinking improved the mechanical  
2 stability of the membranes in water and reduced the water uptake to about 45%. The  
3 conductivity of the membranes was measured by EIS in 0.5N H<sub>2</sub>SO<sub>4</sub>, with BCP showing the  
4 best conductivity with  $\sigma = 179$  mS/cm, which is more than 10 times higher than the reference  
5 Nafion<sup>®</sup> 117.

6 The use of amphiphilic diblock-copolymers modified by an elegant *para*-fluoro-thiol  
7 reaction under mild conditions, allowing self-assembly in 100 nm diameter *out-of-the-plane*  
8 cylinders, paves the way to design efficient proton-conducting nano-channels across the  
9 membranes. This new concept offers the opportunity to rethink the Nafion<sup>®</sup> paradigm for proton  
10 transport and water dynamic in polymeric membrane but also be transposed to other thiol  
11 functional molecules for applied energy materials.

12

### 13 **Acknowledgements**

14 The eSCALED project has received funding from the European Union's Horizon 2020  
15 research and innovation program under grant agreement No. 765376.

16 PM thanks E2S UPPA Hub ENSUITE for his fellowships.

17 The authors would like to thank Ahmed Bentaleb of the Centre de Recherche Paul Pascal  
18 (CRPP) for the SAXS experiments; Inna Kharitiniva and Galina Schumski from ICVT  
19 University of Stuttgart for the IEC measurements and calculations and impedance  
20 measurements.

21

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- 17
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1 **Supporting information**

2 **Elegant *para*-fluoro-thiol clicked diblock-copolymer self-assembly: Paving**  
3 **the way towards a new paradigm for proton-conductive membranes**

4

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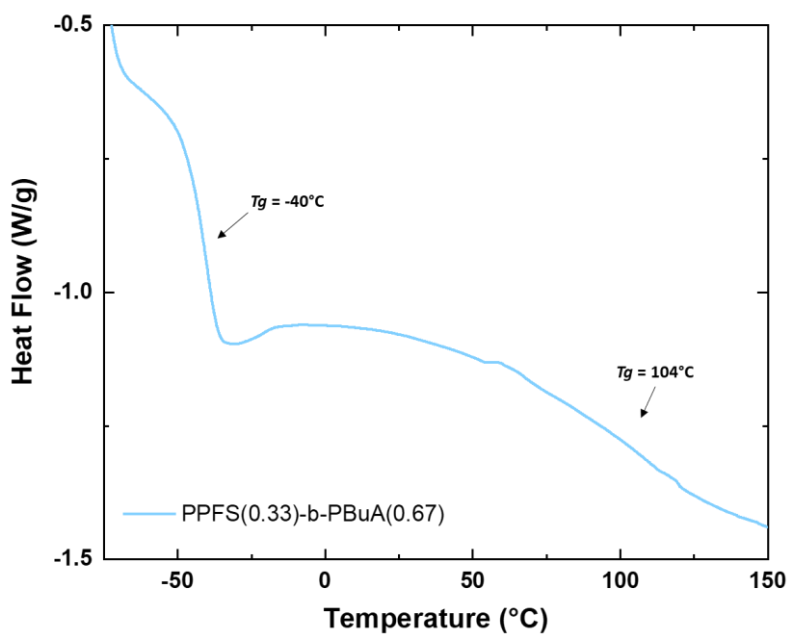
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20 <sup>1</sup>H NMR, SEC, and DSC of the copolymers

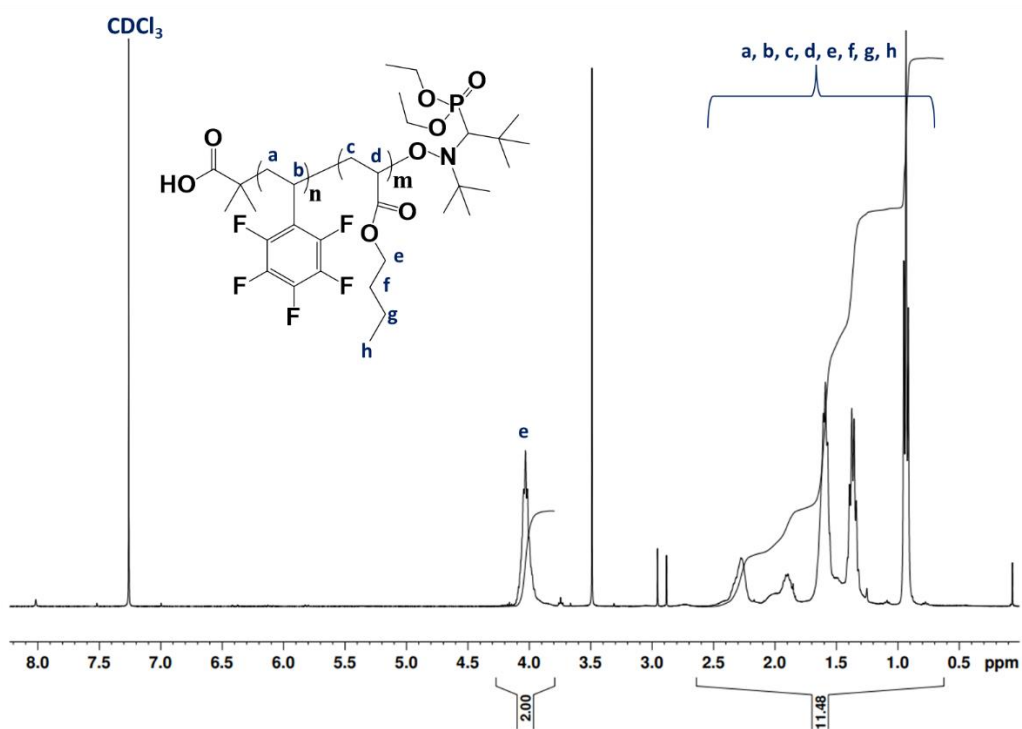
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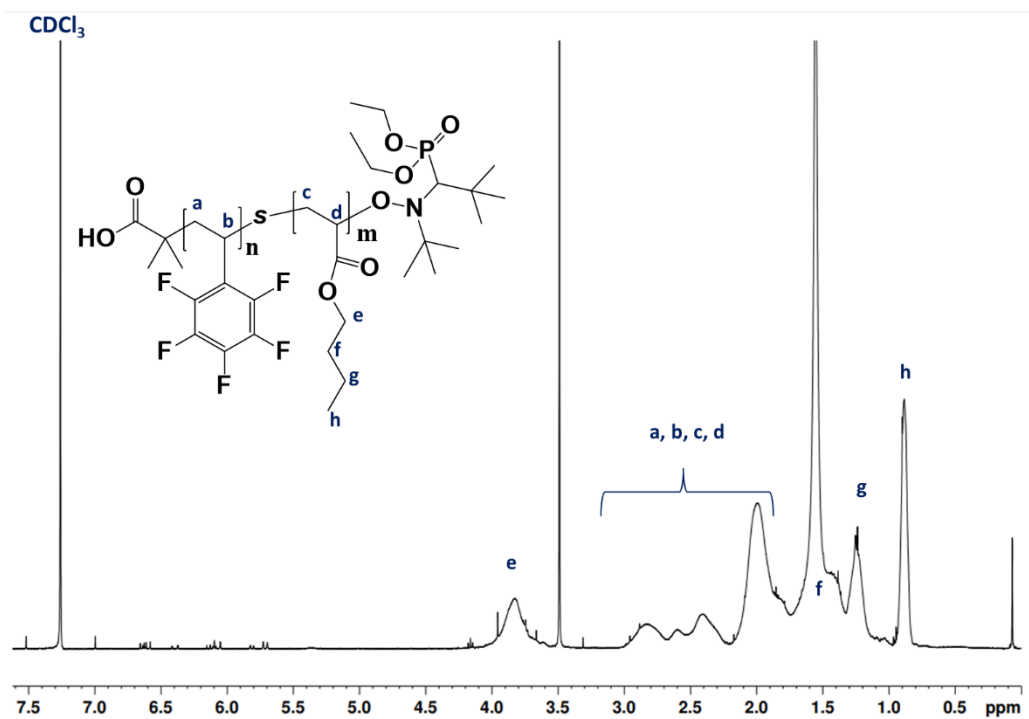
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2 **Figure SI 1.** DSC of (PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub>)<sub>40K</sub> diblock-copolymer.



3

4 **Figure SI 2.** Structure and <sup>1</sup>H NMR spectrum (300 MHz, room temperature, CDCl<sub>3</sub>) of  
 5 (PPFS<sub>0.33</sub>-*b*-PBuA<sub>0.67</sub>)<sub>40K</sub> synthesized by NMP controlled radical polymerization. The spectrum  
 6 shows the absence of residual monomer.



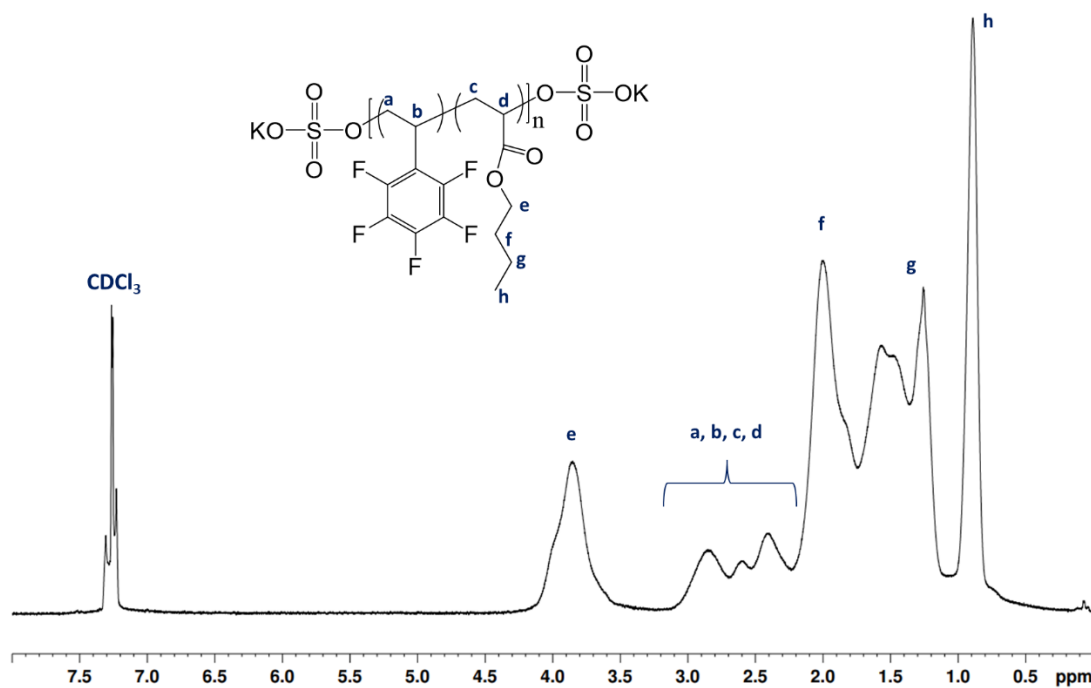
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 2 **Figure SI 3.** Structure and  $^1\text{H}$  NMR spectrum (300 MHz, room temperature,  $\text{CDCl}_3$ ) of  
 3  $(\text{PPFS}_{0.87}\text{-}s\text{-PBuA}_{0.13})_{19\text{K}}$  synthesized by NMP controlled radical polymerization. The spectrum  
 4 shows the absence of residual monomer.

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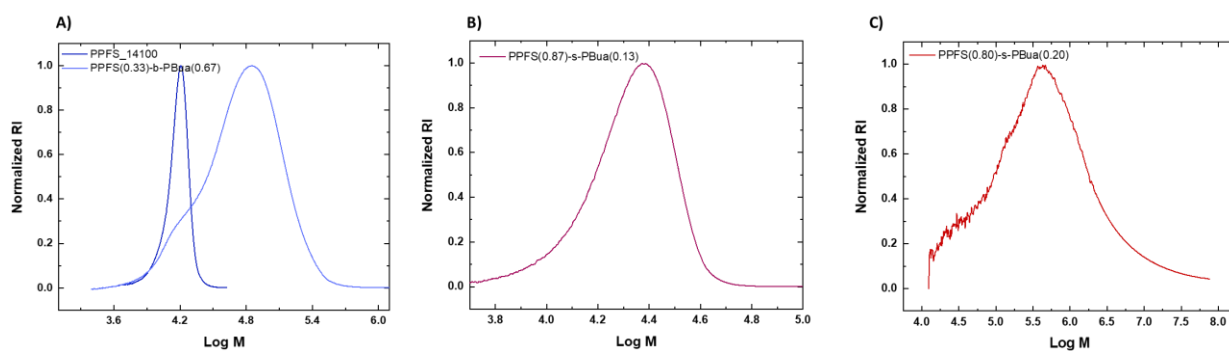
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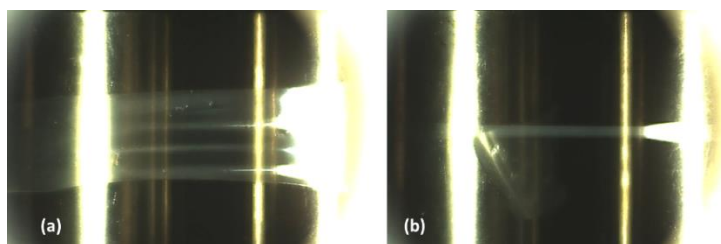


1  
 2 **Figure SI 4.** Structure and  $^1\text{H}$  NMR spectrum (300 MHz, room temperature,  $\text{CDCl}_3$ ) of purified  
 3  $(\text{PPFS}_{0.80}\text{-s-PBuA}_{0.20})_{140\text{K}}$  synthesized by free radical polymerization in emulsion. The spectrum  
 4 shows the absence of residual monomer.



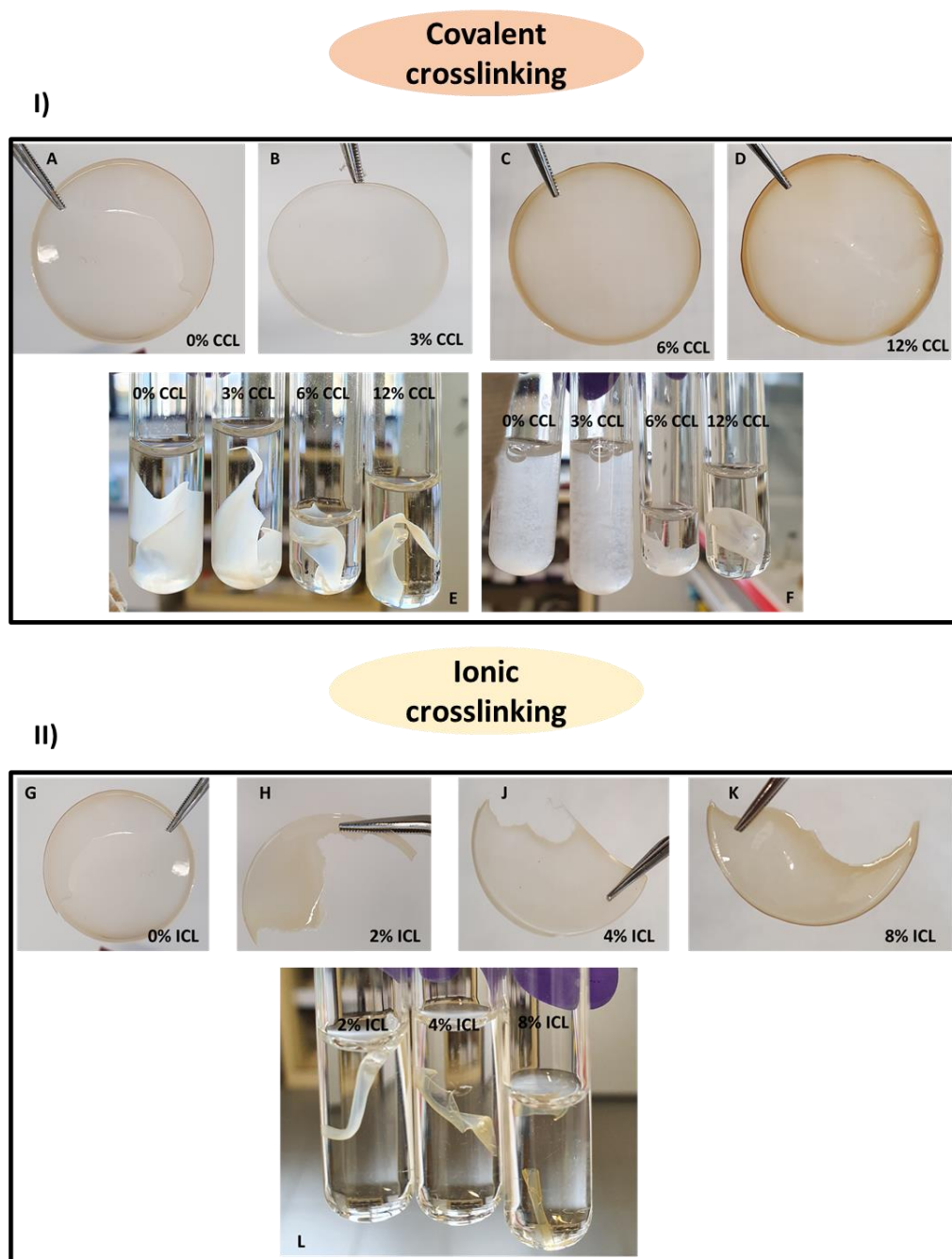
5  
 6 **Figure SI 5.** SEC chromatograms of macro-initiator ( $\text{PPFS}_{14100}$ ) ( $M_n = 14\ 100$  g/mol,  $D = 1.07$ )  
 7 and  $(\text{PPFS}_{0.33}\text{-b-PBuA}_{0.67})_{40\text{K}}$  ( $M_n = 40\ 100$  g/mol,  $D = 1.88$ ) chain extension from  $\text{PPFS}_{14100}$   
 8 (A);  $(\text{PPFS}_{0.87}\text{-s-PBuA}_{0.13})_{19\text{K}}$  ( $M_n = 19\ 100$  g/mol,  $D = 1.16$ ) (B);  $(\text{PPFS}_{0.80}\text{-s-PBuA}_{0.20})_{140\text{K}}$   
 9 ( $M_n = 140\ 200$  g/mol,  $D = 15.2$ ) (C).

10



1

2 **Figure SI 6.** Film on the setup before test (a) and just before rupture (b).

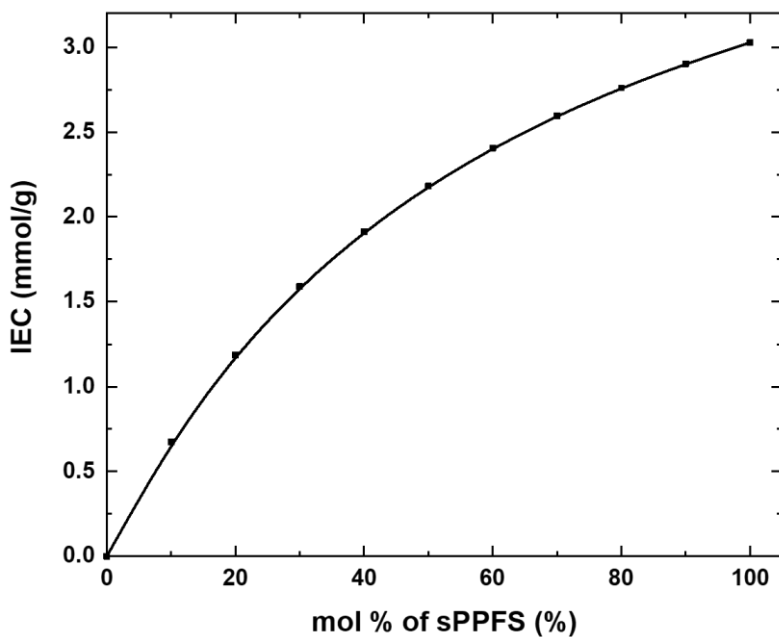


3

4 **Figure SI 7.** (I) Membranes of (A) partially sulfonated (PPFS<sub>0.87-s</sub>-PBuA<sub>0.13</sub>)<sub>19K</sub> ([sPPFS<sub>0.49-</sub>  
 5 PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 0 mol% of added covalent crosslinker (CCL);

- 1 (B) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 3 mol% of added CCL;  
 2 (C) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 6 mol% of added CCL;  
 3 (D) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 12 mol% of added CCL;  
 4 Behaviour of the membranes in deionised water (E) at t = 0h and (F) at t = 24h  
 5 (II) Membranes of (G) partially sulfonated (PPFS<sub>0.87</sub>-s-PBuA<sub>0.13</sub>)<sub>19K</sub> ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-  
 6 PBuA<sub>0.13</sub>) with 0 mol% of added ionic crosslinker (ICL);  
 7 (H) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 2 wt% of added ICL;  
 8 (J) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 4 wt% of added ICL;  
 9 (K) ([sPPFS<sub>0.49</sub>-PPFS<sub>0.38</sub>]-s-PBuA<sub>0.13</sub>) with 8 mol% of added ICL;  
 10 (L) Behaviour of the membranes in deionised water at t =24h.

11  
 12



13  
 14 **Figure SI 8.** Theoretical IEC as function of the molar composition of sPPFS for a PPFS/PBuA  
 15 copolymer system.

16