

# Sulfonated Fluoroblock Copolymer Membranes for Direct Methanol Fuel Cell Applications

by

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## ABSTRACT

This investigation studied the transport properties of several fluorinated sulfonated membranes for direct methanol fuel cell applications. First, Nafion® membranes were processed with supercritical fluid (SCF) CO<sub>2</sub> and their resulting nanostructure was cross-linked with inorganic materials. Nafion® membranes were exposed to SCF CO<sub>2</sub> and a counter ion solution using two different approaches: first, it was processed with SCF CO<sub>2</sub>, and then exchanged using six different counter ions: Al<sup>+3</sup>, Fe<sup>+3</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup> and K<sup>+1</sup>. The second method performed the counter ion substitution first, followed by the SCF CO<sub>2</sub> processing. Results showed that the incorporation of counter ions into Nafion® influences the ionic domains uniquely for each cation or their combination studied, but also influences the crystallinity, the morphology, and the water swelling properties, which are very important in the transport of protons through the membrane. The processing order (SCF processing vs. counter ion substitution) shows that although the magnitude of the methanol permeability and proton conductivity are affected, the trends are primarily limited by the nature of the counter ion and not by the order of the process. Nafion® membranes were also processed with SCF CO<sub>2</sub> and then exchanged using a combination of three different counter ions: Fe<sup>+3</sup>, Ca<sup>+2</sup> and K<sup>+1</sup>. In addition, the transport properties of ionic membranes composed of a sulfonated poly(styrene-isobutylene-styrene) (SIBS SO<sub>3</sub>) with novel fluoropolymers based on poly(styrene) (PS), poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) (PHFBM), poly(4-fluorostyrene), poly(2,3,4,5,6-pentafluorostyrene) (P5FS) and poly(isobutylene) (PIB) were evaluated. Homopolymer, bi, tri and tetra fluoroblock copolymers were synthesized by Atom Transfer Radical Polymerization (ATRP); however, PIB was polymerized by cationic polymerization. Different initiators were employed: two fluoroinitiators, obtained from the esterification of 2-(perfluoroalkyl) ethanol or, octafluoro 4-4'-biphenol; the third initiator evaluated was 1-bromoethyl benzene. The esterified initiators have a significant impact on the thermal stability of PS, PHFBM and the diblock copolymers. The proton conductivity and methanol permeability of SIBS SO<sub>3</sub> blend membranes was limited by the nature of the initiator and the interaction of the polymer with the sulfonic group. The proton conductivity of SIBS SO<sub>3</sub> blend membrane was limited by the chemical and fluoropolymer composition, the blend morphology and the interaction of the fluoropolymer with the sulfonic group.

## Resumen

Esta investigación estudió las propiedades de transporte de membranas fluoradas y sulfonadas para aplicaciones de celdas de combustible de metanol. Nafion® se procesó con fluidos supercríticos y sometido a un intercambio con cationes usando dos diferentes procesos: primero la membrana se modificó con CO<sub>2</sub> supercrítico, y luego se realizó el intercambio iónico utilizando seis diferentes cationes: Al<sup>+3</sup>, Fe<sup>+3</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup> y K<sup>+1</sup>. El segundo método consistió en intercambiar el catión primero, seguido por el procesamiento con CO<sub>2</sub> supercrítico. Los resultados muestran que la incorporación de los cationes a Nafion® influyen el dominio iónico de una manera única por cada catión o su respectiva combinación, y también influyen la cristalinidad, morfología y la cantidad de agua absorbida, los cuales son parámetros importantes para el transporte de protones a través de la membrana. El orden del procesamiento (procesamiento con CO<sub>2</sub> supercrítico vs. sustitución de cationes) muestran que aunque se afectan la magnitud de la permeabilidad de metanol y la conductividad protónica, las propiedades de transporte son limitadas por la naturaleza del catión y no por el orden. Nafion® también fue procesada con CO<sub>2</sub> supercrítico, e intercambiados usando una combinación de tres diferentes cationes: Fe<sup>+3</sup>, Ca<sup>+2</sup> and K<sup>+1</sup>. Además se obtuvieron, las propiedades de transporte de membranas iónicas compuestas de poli(estireno-isobutileno-estireno) sulfonado (SIBS SO<sub>3</sub>H) con un fluoropolímero compuesto de poliestireno (PE), poli(2,2,3,4,4,4-hexafluorobutil metacrilato) (PHFBM), poli(4-fluoroestireno), poli(2,3,4,5,6-pentafluorostireno) (P5FS) y and poli(isobutileno) (PIB) se obtuvieron. Los polímeros se sintetizaron por medio de la técnica ATRP, pero el PIB se obtuvo por medio de la técnica de polimerización catiónica. Se utilizaron tres iniciadores: dos fluoroiniciadores obtenidos por medio de la esterificación de 2-(perfluoroalquil) etanol o, octafluoro 4-4'-bifenol, y 1-bromoetil benceno. Los iniciadores esterificados producen un impacto significativo sobre la estabilidad de PE, PHFBM y de los polímeros en bloque. Se encontró su conductividad protónica y la permeabilidad de metanol de las membranas estudiadas. Estas propiedades de transporte están limitadas por la naturaleza del iniciador y la interacción que tiene el polímero con el grupo sulfónico. La conductividad protónica de las membranas de SIBS SO<sub>3</sub>H es limitada por la naturaleza química y el contenido del fluoropolímero, la morfología de la membrana y la interacción del fluoropolímero con el grupo sulfónico.

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*With love to my parents*

*Mario Augusto Guerrero and Cruz Elizabeth Gutiérrez Franco*

*And my sisters Keila Mariana Guerrero Gutiérrez and Cruz Ivonne  
Guerrero Gutiérrez*

*“La rumba me está llamando.”*

*Nothing is impossible,*

*The word itself says*

*‘I’m possible’!*

**-Audrey Hepburn**

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## LIST OF SCHEMES

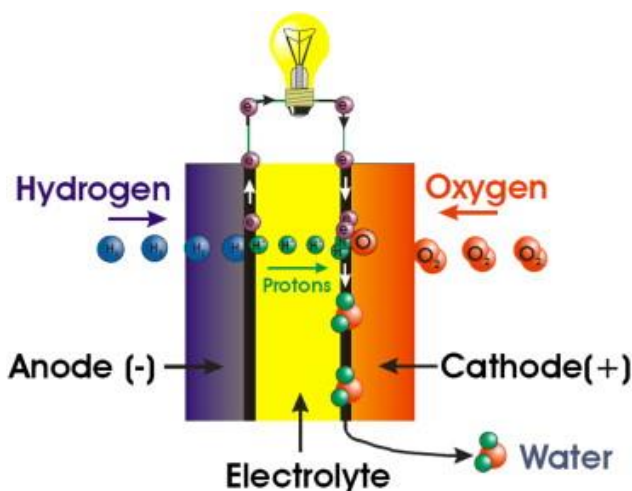
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# CHAPTER 1

## INTRODUCTION

### 1.1. FUEL CELLS

Fuel cells are a promising power source for portable applications. A fuel cell is an electrochemical device that converts the chemical energy released during the electrochemical reaction of the fuel and oxygen to electrical energy.<sup>1</sup> Hydrogen, methanol, and ethanol have been used as fuel in these devices<sup>2</sup>. Figure 1.1 shows a schematic design for the Proton Exchange Membrane (PEM) fuel cell using H<sub>2</sub> as a fuel.



**Figure 1.1.** Schematic design of the PEM fuel cell with H<sub>2</sub> gas.<sup>2</sup>

The oxidation reaction occurs in the anode. The hydrogen passes through a gas diffusion layer with a catalyst, therefore the hydrogen reacts producing hydrogen ions and the electrons are released. The oxidation reaction is as follows:



The reduction reaction occurs in the cathode. The hydrogen ion reacts with oxygen to produce water. The reduction reaction is the following:

Cathode electrode:  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

The overall reaction in the cell:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

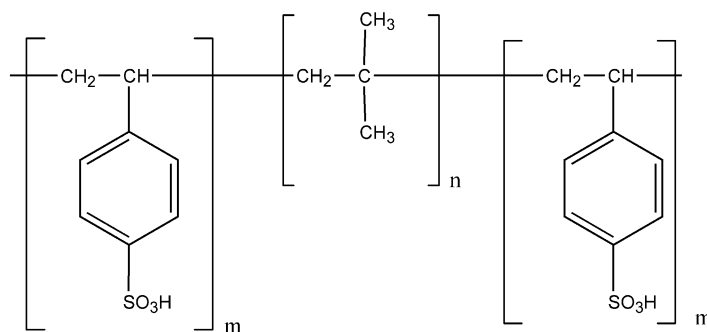
Electrochemical reaction for the direct methanol fuel cell (DMFC):

Anode electrode:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{e}^- + \text{CO}_2$

Cathode electrode:  $3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$

The overall reaction in the cell:  $\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

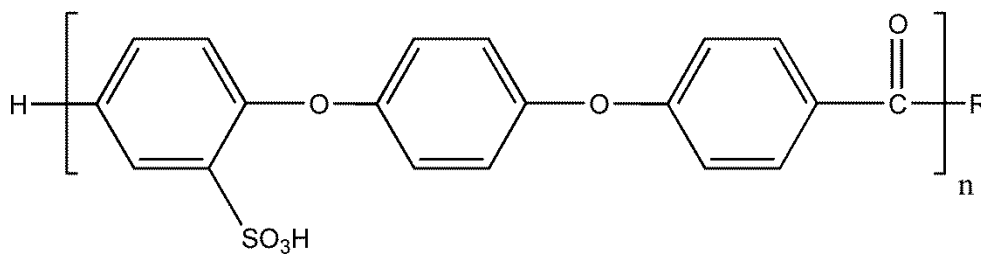
A principal component for this technology is the proton exchange membrane (PEM), whose function is to allow the transport of protons from the anode to the cathode while blocking the passage of the fuel.<sup>2</sup> Many different types of PEMs have been developed and exchanged with acidic organic/inorganic chemicals for this application. Sulfonated poly(styrene-isobutylene-styrene) has been synthesized and characterized for fuel cells applications.<sup>3,4</sup> In this study, a maximum percentage of sulfonation level was determined. The sulfonation level allows the maximum proton conductivity while maintaining low methanol permeability.<sup>4</sup> Sulfonated poly(styrene-isobutylene-styrene) exchanged with different cations reduced the methanol permeability. Figure 1.2 shows the chemical structure for sulfonated poly(styrene-isobutylene-styrene) (SIBS).



**Figure 1.2.** Chemical structure for sulfonated poly(styrene-isobutylene-styrene) (SIBS).<sup>5</sup>

Sulfonated poly(styrene–isobutylene–styrene) (SIBS) has a highly ordered sequence of ionic and non-ionic blocks which self-assemble into a three-phase nanostructured morphology in the solid state. Studies suggest that sulfonated SIBS with ion content less than 0.5 mequiv g<sup>-1</sup> shows a hexagonally packed cylinder morphology. This membrane with a ion content between 0.5 and 1 mequiv g<sup>-1</sup> exhibited in the SAXS profiles, reflections at this vector positions:  $q_1$ ,  $2q_1$ ,  $3q_1$ ,  $4q_1$ ,  $5q_1$  and  $6q_1$  that correspond to a laminar morphology; however as the ion content increased above 1 mequiv g<sup>-1</sup>, the membrane exhibited a non-periodic morphology at higher ion content<sup>5</sup>.

Other non-fluorinated ionic polymers, like sulfonated aromatic poly(etheretherketone)<sup>6</sup>, sulfonated poly(arylenethioether sulfones), poly(arylene ether sulfone)<sup>7</sup> have been studied as proton exchange membranes (PEMs) for direct methanol fuel cell (DMFC) applications. Figure 1.3 exhibits another example of a non-fluorinated sulfonated membrane: sulfonated aromatic poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (SPEEK).

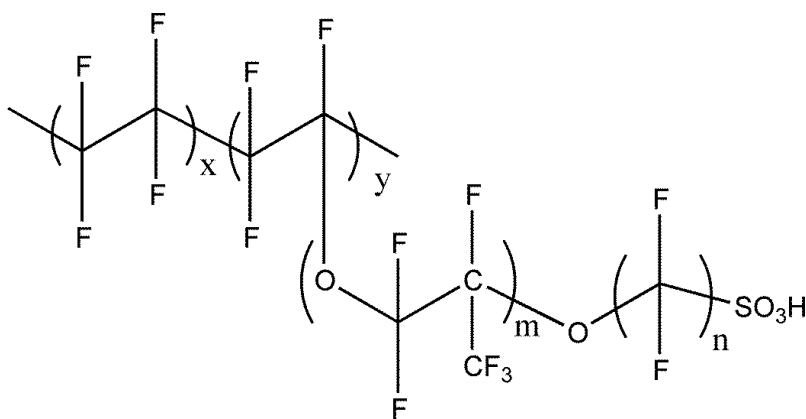


**Figure 1.3.** Chemical structure for sulfonated poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (SPEEK).

Fluorinated polymers are used in numerous and diverse functional materials because they possess high thermal stability, enhanced chemical resistance, and low surface energy compared to their non-fluorinated analogs.<sup>8</sup> Applications for these polymers include: proton conducting materials<sup>9</sup>, stabilizers for emulsion polymerization<sup>10</sup>, additives in oil recovery and water treatment<sup>11</sup>, surfactants<sup>12</sup>, lubricants<sup>13</sup>, and ion conducting materials among others. Polyelectrolyte-fluoropolymer blend membranes processed with different degrees of

tetrabutylammonium hydroxide (TBA-OH) were characterized and studied as proton exchanged membranes (PEM) for fuel cell applications.<sup>14</sup>

Unfortunately, even today, most of these PEMs have either low proton conductivity ( $\sigma$ ) or high methanol permeability limiting their performance in DMFC. Nafion® is a sulfonated fluoropolymer, which is commonly used in DMFC applications. This membrane consists of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by a sulfonated ionic group.<sup>15</sup> Figure 1.4 exhibits the chemical structure of Nafion® membranes.



Nafion®117  $m \geq 1$ ,  $n = 2$ ,  $x = 5-14$ ,  $y = 1000$

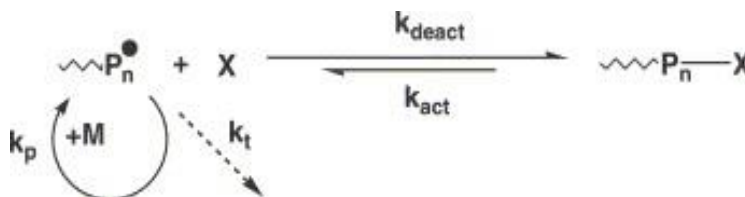
**Figure 1.4.** Chemical structure of Nafion® membrane.

Nafion® remains the standard in DMFC applications, because it has high proton conductivity and excellent thermal and mechanical properties; unfortunately, it also has a higher than desired methanol permeability leading to the well-known methanol cross-over limitation.<sup>16</sup> Numerous additional investigations have evaluated the incorporation of additives to Nafion® to improve its transport properties.<sup>17-19</sup> Unfortunately, limited success has been obtained due to the chemical nature of the perfluoroblocks, which often leads to additional phase segregation.<sup>20</sup> Limited studies have evaluated novel fluoropolymers with sulfonic blocks to create ionic synergism and improve selectivity.<sup>14,21,22</sup> This investigation directly focuses on the synthesis and characterization

of unique novel fluoropolymers with sulfonic elastomeric blends to create unique ionic polymer membranes.

## 1.2. Controlled Radical Polymerization (CRP)

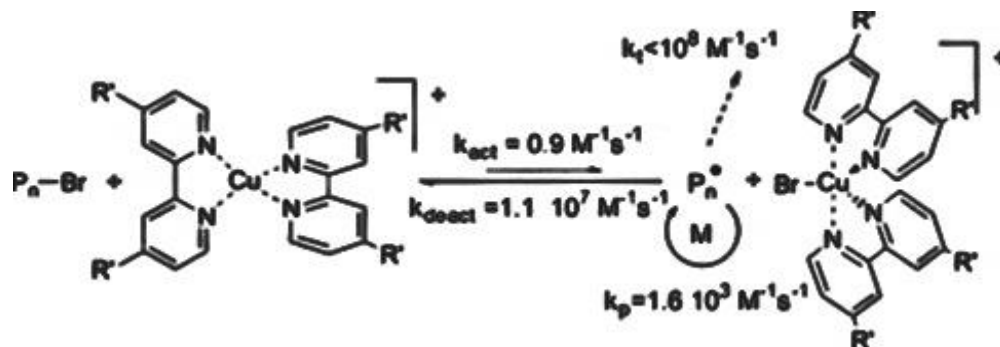
Controlled radical polymerization (CRP) is a polymerization technique that allows the synthesis of advanced well-defined polymers with specific structures and lower polydispersities.<sup>23</sup> Scheme 1.1 shows the basic mechanism for controlled radical polymerization. Controlled radical polymerization uses thermodynamic equilibrium between growing radical and various types of dormant species.<sup>24</sup> These intermolecular interactions can be exploited to create polymers with a specific nanostructure, a uniform dimension and different functionalities.



Source: Matyjaszewski, K. *Macromolecules*. **2012**, 45, 4015–4039.

**Scheme 1.1:** Controlled radical polymerization mechanism.<sup>23</sup>

Atom transfer radical polymerization (ATRP) is a CRP technique that uses an alkyl halide as the initiator, a transition metal in the lower oxidation state and a ligand to synthesize different fluoropolymers such as, perfluoroalkyl ethyl methacrylate and fluoropolymers with polyether blocks.<sup>25</sup> Initiators for ATRP must have a halogen (Br or Cl) and a functional group that can stabilize the formed radical. Scheme 1.2 shows the ATRP mechanism. ATRP components are a transition metal (e.g. CuBr), a complex ligand (nitrogen-based) and an initiator (alkyl halide).<sup>24</sup> The complex ligand forms a covalent or ionic bond with the transition metal. The thermodynamic equilibrium between the growing radical and the dormant species controls the polymerization.<sup>24</sup>



Source: Braunecker, W.A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, 32, 93–146.

### Scheme 1.2: Mechanism for ATRP.<sup>24</sup>

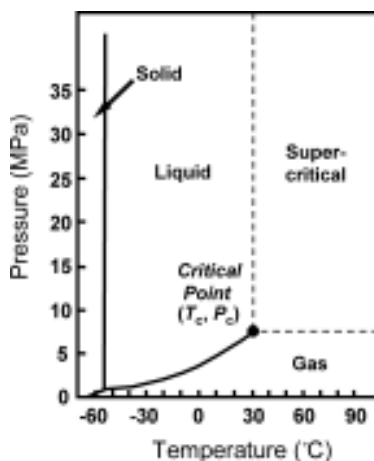
Different fluoropolymers were synthesized under this technique. Homopolymer and diblock copolymers containing 4-fluorostyrene and methyl acrylate were prepared by ATRP. A (1-bromoethyl)benzene/CuBr/N,N,N', N'', N''-pentamethyldiethylenetriamine system was used.<sup>26</sup> Poly(2,3,4,5,6-Pentafluorostyrene) and block copolymers with styrene were synthesized under ATRP conditions. In this case, a (1-bromoethyl)benzene/CuBr/2,2'-Bipyridyl system was used to obtain the diblock copolymers.<sup>27</sup>

CRP can also be used to synthesize polymers with controlled topologies, such as, star polymers, branched, hyper branched, network and cyclic type structures.<sup>24</sup> Chemical modification on terminal groups of fluoroalcohols,<sup>28,29</sup> and polymers like poly(ethylene glycol) (PEG)<sup>30</sup> have been synthesized to obtain novel ATRP initiators and control the final polymer's topology. Jankova and Hvilsted<sup>31</sup> chemically modified dipentaerythritol using an esterification reaction to obtain an ATRP initiator. A hexa-arm star diblock copolymer of styrene and 2,3,4,5,6-pentafluorostyrene was synthesized.

### 1.3. Supercritical Fluid (SCF) processing with CO<sub>2</sub>

A pure substance is said to be in a supercritical state, when the pressure and the temperature exceed certain critical values. For CO<sub>2</sub>, the critical temperature and critical pressure are 31°C and 7.4 MPa respectively. A supercritical fluid (SCF) exhibits liquid-like density, but gas-like transport

properties of diffusivity and viscosity. Figure 1.5 shows the pressure-temperature diagram for CO<sub>2</sub>. In supercritical condition, there is no distinct liquid phase nor vapor phase, only a single supercritical phase coexists.<sup>32</sup>



**Figure 1.5.** Pressure-temperature diagram for CO<sub>2</sub>.<sup>32</sup>

A limited number of studies have evaluated the effect of SCF CO<sub>2</sub> processing on polymer membranes. Akin and Temelli<sup>33</sup> processed two commercial polyamide membranes using SCF CO<sub>2</sub>. They found out that there was a reorganization of the polymeric network induced by the processing time and depressurization.<sup>33</sup> Su et al.<sup>34</sup> prepared perfluorosulfonic acid membranes and then treated them with SCF CO<sub>2</sub>. Their membranes showed a change in the size of the ion cluster and the relative crystallinity, which led to a reduction in the methanol permeability.<sup>34</sup> Gribov et al.<sup>35</sup> incorporated zeolite (Fe-silicalite-1) to Nafion®-115 assisted by SCF CO<sub>2</sub>. Their membranes had lower methanol permeability than non-processed Nafion®-115.<sup>35</sup> Pulido-Ayazo and Suleiman<sup>36</sup> modified the morphology of Nafion®-117 using SCF CO<sub>2</sub> with different co-solvents. A significant reduction in the methanol permeability was observed with a smaller loss of proton conductivity.

#### 1.4. Justification and Dissertation Overview

Unique properties arise from incorporating sulfonic acid (anionic groups) into polymers via sulfonation, such as increased strength, hydrophilicity, and proton conductivity.<sup>5</sup> These features have led to an exploration of a variety of applications for sulfonated polymers, such as batteries,

sensors, displays, ion-exchange resins, and fuel cells. Fuel cells are emerging as an alternative for clean power generation.

This investigation studied the synthesis and transport properties of different novel fluoroblock copolymers for blend membranes and the morphological modification of Nafion® induced by SCF CO<sub>2</sub> and then exchanged with different counter ions. First, the transport properties of Nafion® membranes processed with supercritical fluid (SCF) CO<sub>2</sub> and their resulting nanostructure after cross-linking with inorganic materials was studied in Chapter 2. Nafion® membranes were exposed to SCF CO<sub>2</sub> and a counter ion solution using two different approaches: first it was processed with SCF CO<sub>2</sub>, and then exchanged using six different cations: Al<sup>+3</sup>, Fe<sup>+3</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup> and K<sup>+1</sup>. The second method performed the cation substitution first, followed by the SCF CO<sub>2</sub> processing.

Chapter 3 focuses in evaluating the effect of SCF CO<sub>2</sub> and the cross-linking Nafion® membranes with the combination of three different counter ions (Fe<sup>+3</sup>, Ca<sup>+2</sup> and K<sup>+1</sup>); transport properties were critically evaluated.

Chapter 4, the focus is the synthesis and characterization of an ionic membrane composed of sulfonated poly(styrene-isobutylene-styrene) (SIBS SO<sub>3</sub>H) with a novel sulfonated trifluoroblock copolymer. The fluoroblock copolymer of Zonyl®-b-poly(4-fluorostyrene)-b-poly(styrene)-b-poly(isobutylene) [P4FS-b-PS-b-PIB] as synthesized using atom transfer radical polymerization (ATRP) and cationic polymerization.

Chapter 5 studies the transport properties of ionic membranes composed of a sulfonated poly(styrene-isobutylene-styrene) (SIBS SO<sub>3</sub>H) with three different novel fluoropolymers based on poly(styrene) (PS). In addition, the impact of the initiator on the thermal stability of the different homopolymers and block copolymers as studied. These fluoroblock copolymers were synthesized by ATRP using three different initiators; two fluoroinitiators were obtained from the esterification of 2-(perfluoroalkyl) ethanol or, octafluoro 4-4'-biphenol.

Finally, Chapter 6 studies the transport and morphological changes of ionic blend membranes composed of sulfonated copolymers with four different fluoroblock copolymers. Two novel fluoroblock copolymers composed of poly(styrene)-b-poly(2,3,4,5,6-pentafluorostyrene)-b-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) [PS-b-P5FS-b-PHFBM] and poly(4-fluorostyrene)-

b-poly(styrene)-b-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) [P4FS-b-PS-b-PHFBM] were synthesized using ATRP. Additionally, a difluoroblock copolymer composed of PS-b-PHFBM and a homopolymer composed of PHFBM were also used. These polymers were synthesized by ATRP and free radical polymerization respectively.

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## CHAPTER 2

### Supercritical CO<sub>2</sub> Processing and Counter Ion Substitution of Nafion® Membranes.

#### 2.1. ABSTRACT

Nafion® was exposed to supercritical (SCF) CO<sub>2</sub> and a counter ion solution using two different approaches. In the first one, Nafion® was processed with SCF CO<sub>2</sub>, and then exchanged using six different counter ions: Al<sup>+3</sup>, Fe<sup>+3</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup> and K<sup>+1</sup>. In the second approach, the counter ion substitution was done first, and it was followed by the SCF CO<sub>2</sub> processing. The resulting composite membranes were characterized using several techniques: thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), small angle X-Ray scattering (SAXS) and X-Ray diffraction (XRD). These techniques were used to identify the changes in the chemical and thermal properties of the membranes, as well as to evaluate changes in the resulting morphologies and crystallinities. Proton conductivity and methanol permeability were measured to understand how the different approaches promoted or inhibited the transport of certain substances through the membrane. Significant differences in their thermal, physical and transport properties were observed when Nafion® was first processed with SCF CO<sub>2</sub> and exchanged with the counter ions.

## 2.2. INTRODUCTION

Non-fluorinated polymers, like sulfonated poly(styrene-isobutylene-styrene),<sup>1</sup> sulfonated aromatic poly(etheretherketone),<sup>2</sup> sulfonated polyarylenethioether sulfones, poly(arylene ether sulfone)<sup>3</sup> and fluorinated polymers like poly(arylene ether benzonitrile) containing hexafluoroisopropylidene diphenol<sup>4</sup> have been studied as proton exchange membranes (PEMs) for direct methanol fuel cells (DMFC). Unfortunately, even today, most of these PEMs have either low proton conductivity ( $\sigma$ ) or high methanol permeability limiting their performance in DMFC. Nafion® is a sulfonated fluoropolymer that is commonly used in DMFC. This membrane consists of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by a sulfonate ionic group.<sup>5</sup> Nafion® remains the standard in DMFC, because it has very high proton conductivity and excellent thermal and mechanical properties; unfortunately, it also has higher than desired methanol permeability leading to the well-known methanol cross-over limitation.<sup>6</sup>

Different studies have investigated the incorporation of acidic inorganic-organic fillers to Nafion® with the objective of lowering Nafion® membranes methanol permeability; however, some of these composite Nafion® membranes showed a decrease in the proton conductivity similar to the reduction in methanol permeability.<sup>6-8</sup>

Supercritical fluid (SCF) processing with CO<sub>2</sub> has been another alternative used to modify the morphology of fluoroelastomers. SCF CO<sub>2</sub> possesses gas-like mass transport properties (*e.g.* high diffusivity and low viscosity) and liquid-like densities to easily penetrate the membrane, while aligning functional groups according to physico-chemical affinities. NMR studies suggest specific interactions between <sup>19</sup>F isotope and supercritical CO<sub>2</sub> which may support the high solubility of many fluorocarbon polymers in SCF CO<sub>2</sub>.<sup>9</sup>

A limited number of studies have evaluated the effect of SCF CO<sub>2</sub> processing on polymer membranes. Akin and Temelli<sup>10</sup> processed two commercial polyamide membranes using SCF CO<sub>2</sub>. They found out that there was a reorganization of the polymeric network induced by the

processing time and depressurization. Su et al.<sup>11</sup> prepared perfluorosulfonic acid membranes and then treated them with SCF CO<sub>2</sub>. Their membranes showed a change in the size of the ion cluster and the relative crystallinity, which led to a reduction in the methanol permeability. Gribov et al.<sup>12</sup> incorporated zeolite (Fe-silicalite-1) to Nafion®-115 assisted by SCF CO<sub>2</sub>. Their membranes had lower methanol permeability than non-processed Nafion®-115. Pulido-Ayazo and Suleiman<sup>13</sup> modified the morphology of Nafion®-117 using SCF CO<sub>2</sub> with different co-solvents. A significant reduction in the methanol permeability was observed with a smaller loss of proton conductivity.

Two major factors influence the transport properties throughout polymer membranes, morphology and physicochemical interactions. SCF CO<sub>2</sub> processing seems to have a strong influence on the morphology of perfluorosulfonic membranes. Therefore, the goal of this investigation was to evaluate if the changes in the morphology of Nafion® when exposed to SCF CO<sub>2</sub> and different metallic cations affected their transport, thermal and physical properties and to determine if the order of the processing affected these properties. The selection of counter ions included the evaluation of different size and electronegativity within the same group (*e.g.* Ca<sup>+2</sup>, and Ba<sup>+2</sup>) and counter ions of different number of valence electrons within the same period (*e.g.*, K<sup>+1</sup>, Ca<sup>+2</sup>, Fe<sup>+3</sup>, and Cu<sup>+2</sup>). In addition, Al<sup>+3</sup> was evaluated since a previous study showed changes in the thermogravimetric properties of Nafion®,<sup>14</sup> but lacked the evaluation of transport properties. The SCF processed membranes were then characterized for methanol permeability, proton conductivity and water swelling; the results were explained with some additional materials characterization techniques (*e.g.*, FT-IR, TGA, DSC, SAXS and XRD).

## **2.3. EXPERIMENTAL**

### **2.3.1. Materials**

Ultra high purity CO<sub>2</sub> (99.998% purity) was acquired from Linde Gas Puerto Rico, Inc. Nafion® 117 was obtained from Ion Power, Inc. Other chemicals used include: potassium chloride -KCl-, (Sigma-Aldrich, anhydrous powder, 99.99%), calcium chloride, anhydrous -CaCl<sub>2</sub>-, (Acros Organic, anhydrous powder, 96%), barium chloride -BaCl<sub>2</sub>-, (Fisher Scientific, anhydrous powder, 99.99%),

cooper chloride - $\text{CuCl}_2$ - (Sigma–Aldrich, anhydrous powder, 99.99%), aluminum chloride - $\text{AlCl}_3$ - (Acros Organic, extra pure anhydrous, 99.99%), ferric chloride - $\text{FeCl}_3$ - (Sigma–Aldrich, anhydrous powder, 99.99%), hydrogen peroxide - $\text{H}_2\text{O}_2$ - (3 wt% solution in water stabilized) and sulfuric acid - $\text{H}_2\text{SO}_4$ - (Sigma-Aldrich, ACS reagent, 95.0-98.0%). All of them were employed as received.

### **2.3.2. Sample preparation**

Nafion<sup>®</sup> membranes used in this study were first pre-treated to convert them into their acid form using the following procedure: the membrane was first treated with a hydrogen peroxide solution (3% wt) during one hour at 80°C, and then washed with deionized water also for one hour at 80°C. After the initial wash, the membrane was protonated with sulfuric acid (1 M), and finally washed with deionized water; both steps for one hour at 80°C each.

Nafion<sup>®</sup> membranes were processed with SCF  $\text{CO}_2$  at 40°C and 100 bar during one hour in a supercritical fluid extractor (Isco SFX 2-10). The SCF  $\text{CO}_2$  flowed parallel to the membrane during the experimentation. After the SCF processing, the membrane was submerged in a 1 M solution of KCl,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{AlCl}_3$  or  $\text{FeCl}_3$  (depending on the desired counter ion) for 48 hours. The resulting cation-exchanged Nafion<sup>®</sup> membranes were washed using deionized water and dried at 60°C during 24 hours.

### **2.3.3. Thermogravimetric analysis (TGA)**

The thermal degradation behavior and water loss for each membrane was determined using a Mettler Toledo 851e instrument. In each experiment, polymer samples weighing approximately 5-10 mg were used. Degradation temperatures were determined after heating the polymer samples to 800°C at 10°C/min under a nitrogen atmosphere.

### **2.3.4. Differential scanning calorimetry (DSC)**

The thermo physical properties were determined using differential scanning calorimetry (DSC). A Texas Instrument DSC Q2000 unit was used for this purpose. In each experiment, polymer samples weighing approximately 5-10 mg were used. The samples were pre-heated from 30°C to

110°C at 10°C/min and then cooled down from 110°C to -90°C at 5°C/min. Phase transitions ( $T_g$ ) and melting points for each membrane were determined after heating the polymer samples from -90°C to 350°C at 10°C/min under a nitrogen atmosphere.

### **2.3.5. Fourier transform infrared spectroscopy (FT-IR)**

Fourier-transform infrared (FT-IR) spectroscopy uses vibrational energy to characterize organic compounds. An attenuated total reflectance (ATR) cell was used with an FT-IR (Varian 800 FT-IR) to analyze the peak position and intensities of the perfluorocarbon backbone, the perfluoroether segment, and the sulfonic groups, before and after processing with SCF  $\text{CO}_2$  and cation substitution. Nafion® membranes were clamped on the ATR cell and all infrared spectra were collected using 64 scans, 4  $\text{cm}^{-1}$  resolution and a range of 600 – 4000  $\text{cm}^{-1}$ .

### **2.3.6. Small angle X-ray scattering (SAXS)**

The morphology of the membranes was studied using small angle X-ray scattering (SAXS). SAXS was performed on a beamline X27C. Two-dimensional scattering patterns were collected on a pinhole-collimated system using Fujitsu image plates and read by a Fujitsu BAS 200 image plate reader. The SAXSQuant software® was used to reduce two dimensional data to one-dimensional intensity versus scattering vector ( $q$ ) plots after background subtraction by circular averaging. The X-ray wavelength employed was 1.6 Å. The calibration standard was silver behenate and the sample distance to the detector was 210 cm.

### **2.3.7. Methanol liquid-phase permeability**

The methanol liquid-phase permeability was measured using a side-by-side glass diffusion cell discussed in detail elsewhere.<sup>13</sup> One side contained the permeant (*e.g.*, methanol) in a 2 M methanol-water solution, while the other side only contained deionized water. The concentration of the compound that permeated through the membrane was determined using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (Shimadzu GC-8). First a calibration curve was created, then measurements were determined after different times.

The liquid permeability was obtained from the continuity equation for diffusion in plane geometry<sup>15</sup> (Equation 2.1):

$$C_B(t) = \frac{PC_AA}{V_bL} \left( t - \frac{L^2}{6D} \right) \quad (2.1)$$

where,  $C_A$  {mol/cm<sup>3</sup>} is the methanol concentration (permeant),  $C_B$  {mol/cm<sup>3</sup>} is the concentration of the compound that permeated through the membrane after different times,  $L$  is the membrane thickness {cm},  $V_b$  the volume of the receptor compartment {0.39 cm<sup>3</sup>},  $A$  the diffusional cross-sectional area of the membrane {0.64 cm<sup>2</sup>} and  $P$  the permeability {cm<sup>2</sup>/s}. The permeability ( $P$ ) was determined from the slope of the concentration  $C_B(t)$  versus time.<sup>16</sup>

#### 2.3.8. Proton conductivity

The proton conductivity ( $\sigma$ ) of each membrane was measured normal to the plane using AC electrochemical impedance spectroscopy (EIS). The measurements were carried out on an AC Solartron impedance system: 1260 impedance analyzer, 1287 electrochemical interface, Zplot software. The range of frequency and voltage used were from 0.1 Hz to 1.0 MHz and 10-15 mV respectively at room temperature and 100% relative humidity. The membranes were first immersed in an excess of deionized water at 25 °C before the experimentation during 24 hours. The proton conductivity was calculated from the impedance data, using the following relation (equation 2.2):<sup>17</sup>

$$\sigma = \frac{L}{R_{\Omega} A} \quad (2.2)$$

where  $L$  is the distance between electrodes {0.3 cm},  $A$  {cm<sup>2</sup>} is the area obtained from the product of the thickness and the width of the membrane.  $R_{\Omega}$  was obtained from the low

intersect of the high frequency semicircle (Nyquist plot) on the complex impedance plane with the real component of the impedance axis ( $Re(z)$ ).

#### **2.3.9. X-Ray Diffraction (XRD)**

The crystallinity of the membranes was obtained using an X-ray diffraction (XRD) instrument (Bruker D8 Discover with GADDS). The X-ray wavelength employed was 1.54 Å and the 2-theta range was from 20 to 90 degrees. No previous sample preparation was performed before the measurements, including humidity pretreatment.

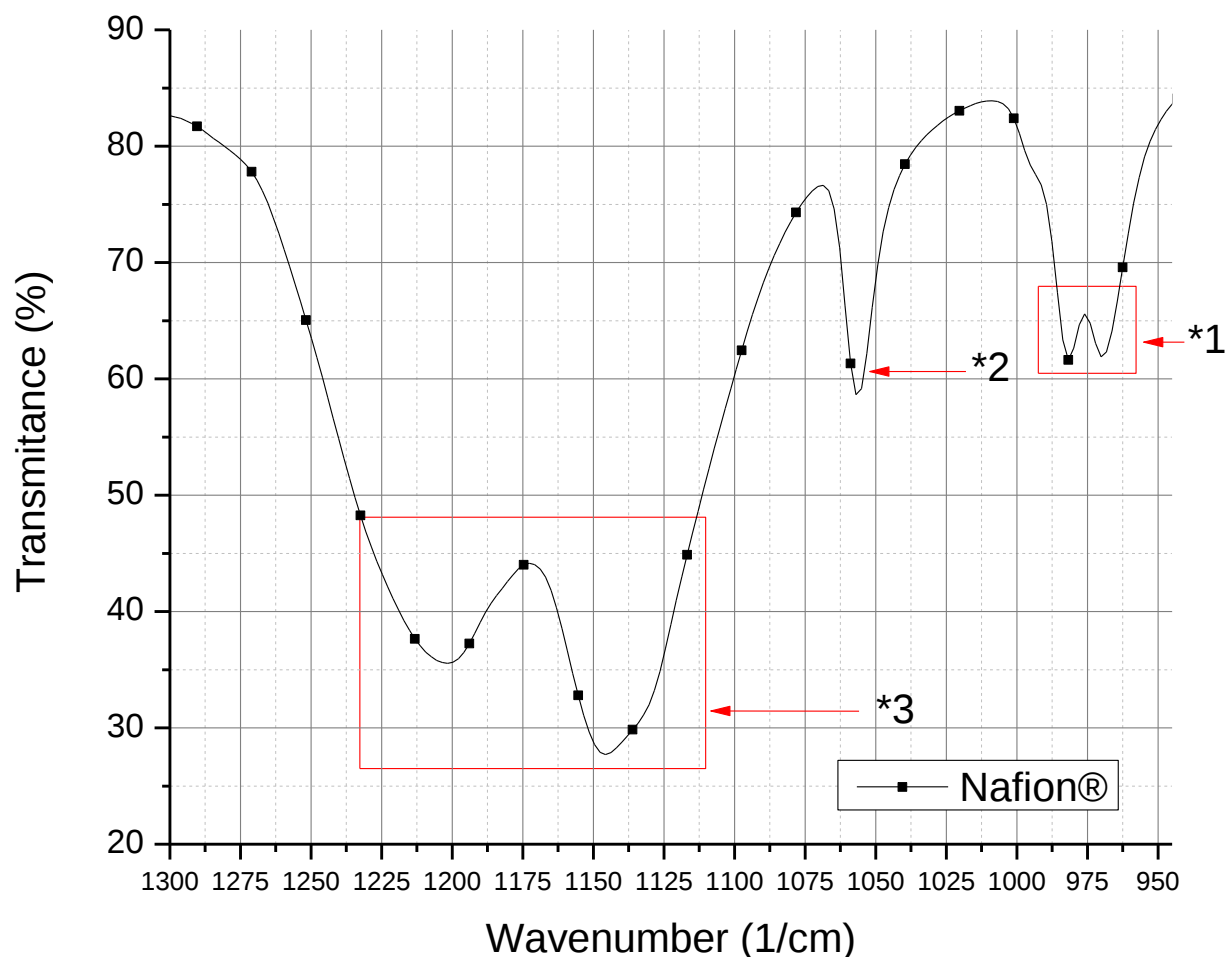
#### **2.3.10. Water swelling**

Water absorption or water swelling in the membranes was measured immersing each membrane in an excess of deionized water at 25°C. The sample was initially dried at 75°C for 24 hours in an oven. The weight of the membrane was recorded before immersion in water. Then weights were measured at different time intervals until swelling equilibrium was reached. Each reported result represents the average of at least three measurements.

### **2.4. RESULTS AND DISCUSSIONS**

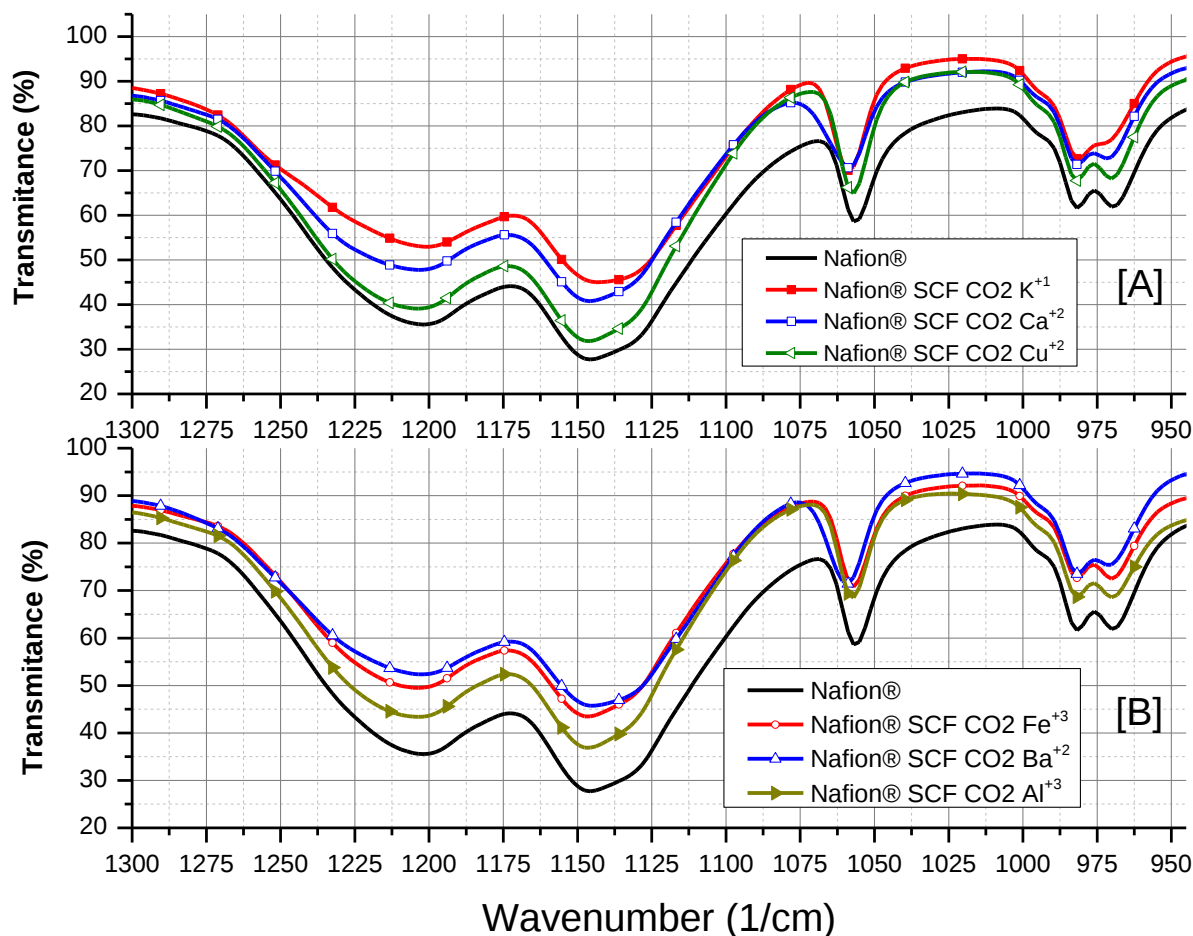
#### **2.4.1. FT-IR spectroscopy**

Figure 2.1 presents the FT-IR spectrum of Nafion®, where three distinctive regions can be observed. The sulfonic group appears as a medium band around 1055 cm<sup>-1</sup> (\*2). This band was caused by an asymmetric stretching vibration of the sulfonated functional group attributed to the S=O bond. The polymer backbone (-CF<sub>2</sub>-) has a strong band from 1100 to 1300 cm<sup>-1</sup> (\*3) and the ether linkage (-O-) from the perfluorovinyl ether appears around 980 cm<sup>-1</sup> (\*1).



**Figure 2.1.** FTIR spectra for Nafion® (—■—).

Figure 2.2 shows the FT-IR spectra for Nafion® and Nafion® processed with SCF CO<sub>2</sub> cation-exchanged with K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup> [A] and Fe<sup>3+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup> [B]. Nafion® processed with SCF CO<sub>2</sub> and cation-exchanged presented significant reductions in their intensities in all regions (\*1, \*2 and \*3). These results can represent the interaction of the cation-exchanged and the SCF processing with all the groups mentioned (not with a specific group). FT-IR results for counter-ion substituted sulfonated poly(styrene-isobutylene-styrene) show that the cations interact with the sulfonic group only shifting the asymmetric S=O band \*2,<sup>18</sup> this is not the case for Nafion®.



**Figure 2.2.** FTIR for Nafion® and Nafion® processed with SCF CO<sub>2</sub> and cation-exchanged: K<sup>+1</sup> (—■—), Ca<sup>+2</sup> (—□—), Cu<sup>+2</sup> (—△—) [A] and Fe<sup>+3</sup> (—○—), Ba<sup>+2</sup> (—△—), Al<sup>+3</sup> (—▶—) [B].

Table 2.1 shows the reduction or increase on the transmittance for each peak in the FTIR spectra. The intensity increased when Nafion® is processed first with SCF CO<sub>2</sub>, but decreased when exchanged with all the counter ions. This behavior is the same for Nafion® exchanged with the counter ion first and then processed with SCF CO<sub>2</sub>. Other experiments are presented ahead to understand the impact of the counter ion substitution in the membranes.

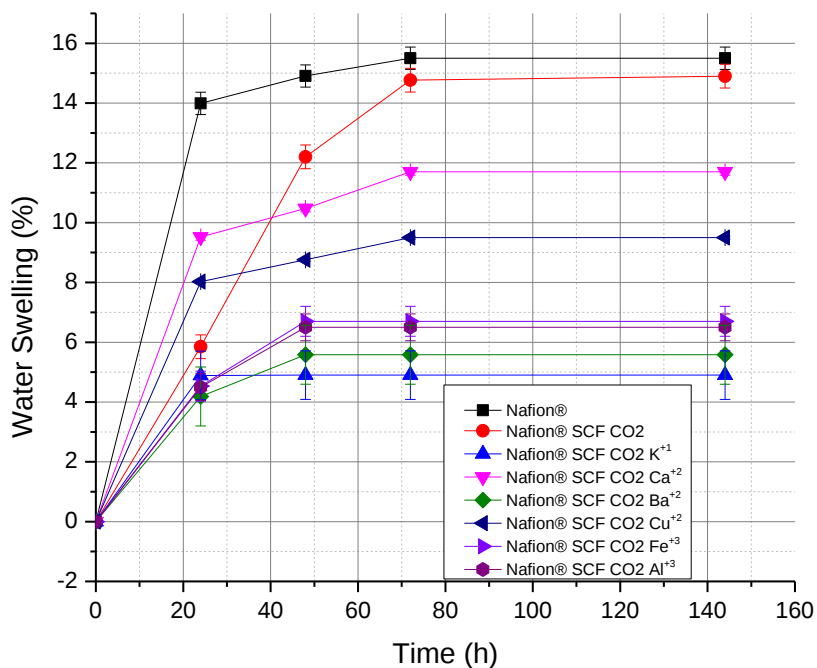
**Table 2.1. Reduction or increase on transmittance cation-exchanged Nafion® processed with SCF CO<sub>2</sub>.**

| Sample                                       | Polymer Backbone (CF <sub>2</sub> ) |            | Ether Linkage (-O-) (%) | Sulfonic Group (%) | Effect on the intensity |
|----------------------------------------------|-------------------------------------|------------|-------------------------|--------------------|-------------------------|
|                                              | Peak 1 (%)                          | Peak 2 (%) |                         |                    |                         |
| Nafion® SCF CO <sub>2</sub>                  | 14                                  | 10         | 4                       | 6                  | Higher                  |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 60                                  | 46         | 17                      | 18                 | Lower                   |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 46                                  | 35         | 15                      | 19                 | Lower                   |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 64                                  | 46         | 18                      | 20                 | Lower                   |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 14                                  | 10         | 10                      | 10                 | Lower                   |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 32                                  | 21         | 11                      | 15                 | Lower                   |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 55                                  | 39         | 18                      | 20                 | Lower                   |

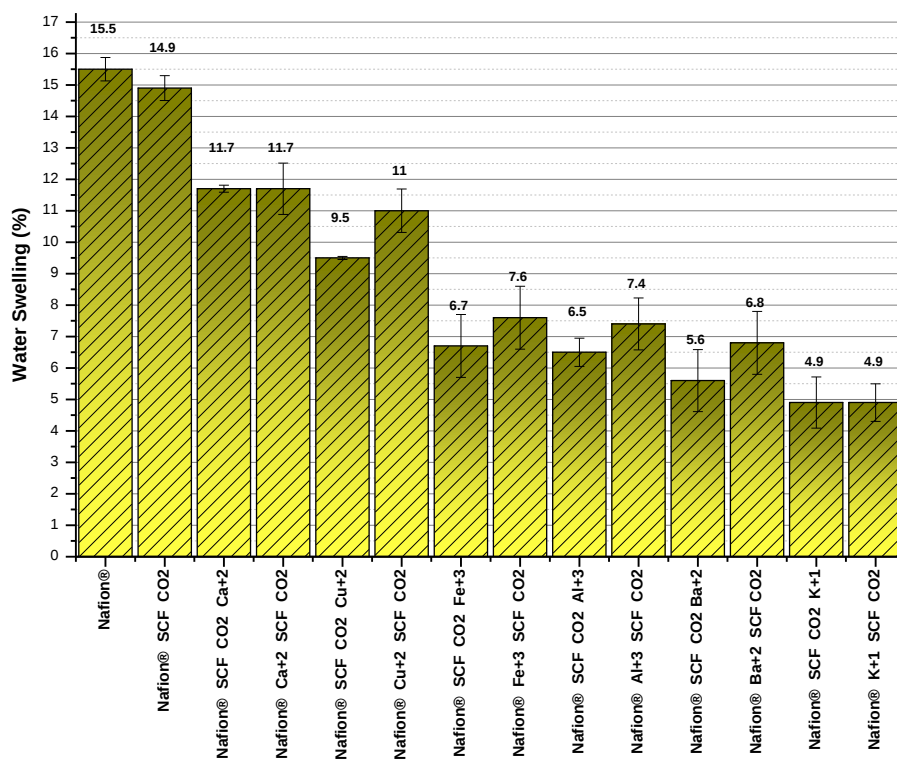
#### 2.4.2. Water swelling

The water absorbed by Nafion® is related to the molecular structure of the ionomer domains, and the morphology of the membrane.<sup>19</sup> Figure 2.3 presents the percent of water swelling vs. time for each of the membranes studied. Equilibrium for all Nafion® membranes was obtained after 70 hours of the membranes submerged in water.

Figure 2.4 shows the water swelling comparison between Nafion® processed with SCF CO<sub>2</sub> first and then cation-exchanged and Nafion® cation-exchanged first and then processed with SCF CO<sub>2</sub>. Unprocessed Nafion® showed the highest water swelling and this was slightly reduced when the membrane was processed with SCF CO<sub>2</sub>. This can be attributed to the rearrangement of the sulfonic groups, the polymer backbone and the perfluorovinyl ether after exposure to the SCF CO<sub>2</sub>.



**Figure 2.3.** Water swelling for Nafion® (■) processed with SCF CO<sub>2</sub> (●) and then cation-exchanged. K<sup>+</sup> (▲), Ca<sup>2+</sup> (▼), Ba<sup>2+</sup> (◆), Cu<sup>2+</sup> (◀), Fe<sup>3+</sup> (▶), Al<sup>3+</sup> (●).



**Figure 2.4.** Comparison between water swelling for Nafion® processed with SCF CO<sub>2</sub> and then cation-exchanged and Nafion® cation-exchanged and then processed with SCF CO<sub>2</sub>.

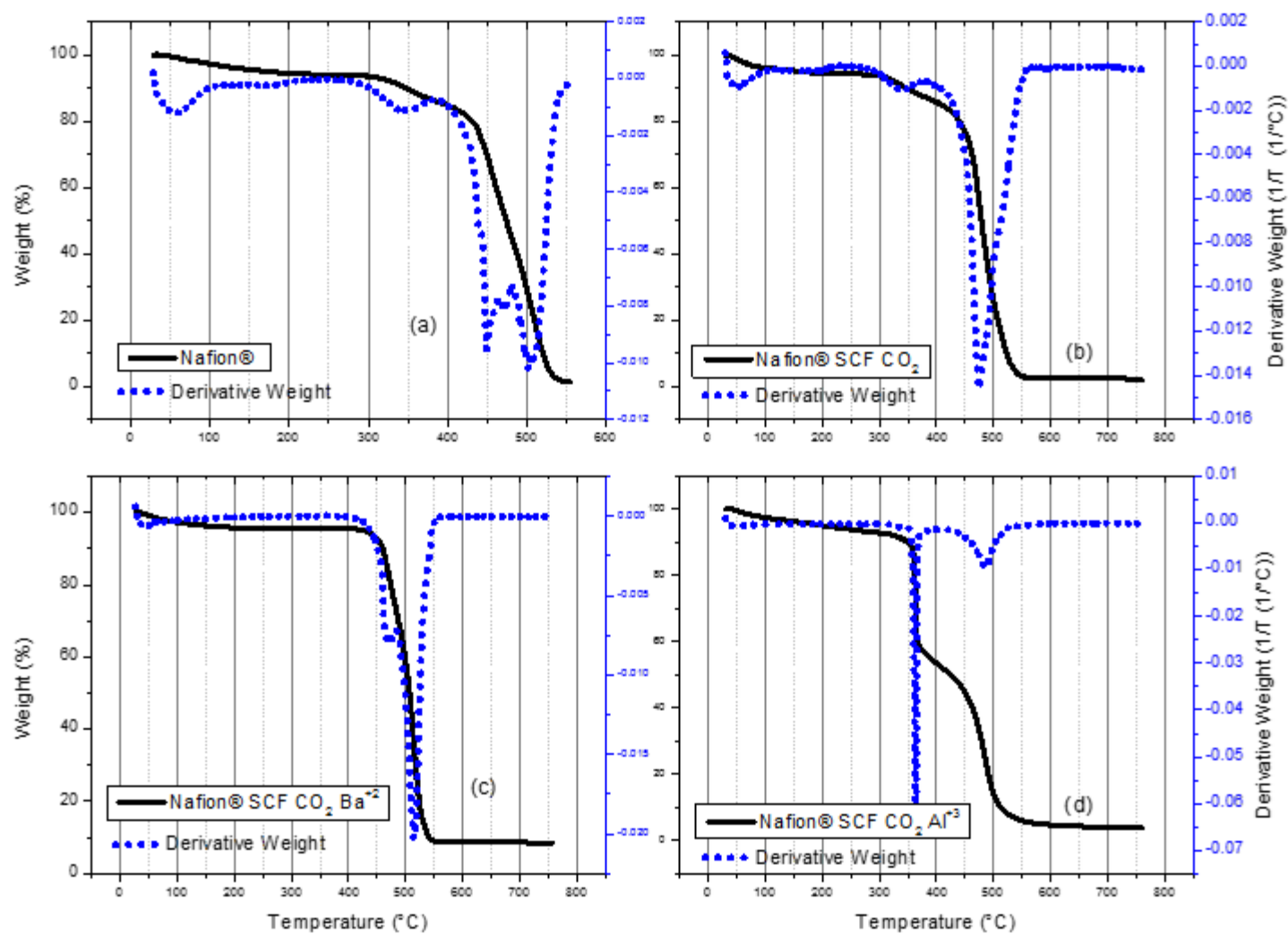
The incorporation of the counter ion into the membrane produced even lower but unique water swelling for each of the counter ion studied. The incorporation of the counter ion inverted all ionic domains towards a more hydrophobic environment.<sup>20</sup> Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with K<sup>+1</sup> obtained the lowest percent of water swelling and Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with Ca<sup>+2</sup> produced the highest amount of water swelling for all the cations studied. This behavior could be attributed to a complex arrangement in their morphologies due to the counter ion substitution and SCF CO<sub>2</sub> processing. This will be further evaluated with the additional materials characterization studies. Table 2 summarizes the water swelling results for these experiments.

**Table 2.2. Water Swelling for Nafion<sup>®</sup> membranes**

| <b>Membrane</b>                                          | <b>Water Swelling<br/>%</b> |   |      |
|----------------------------------------------------------|-----------------------------|---|------|
| Nafion <sup>®</sup>                                      | 15.5                        | ± | 0.4  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub>                  | 14.9                        | ± | 0.4  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ca <sup>+2</sup> | 11.7                        | ± | 0.1  |
| Nafion <sup>®</sup> Ca <sup>+2</sup> SCF CO <sub>2</sub> | 11.7                        | ± | 0.8  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Cu <sup>+2</sup> | 9.5                         | ± | 0.04 |
| Nafion <sup>®</sup> Cu <sup>+2</sup> SCF CO <sub>2</sub> | 11.1                        | ± | 0.7  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Fe <sup>+3</sup> | 6.7                         | ± | 1.2  |
| Nafion <sup>®</sup> Fe <sup>+3</sup> SCF CO <sub>2</sub> | 7.6                         | ± | 1.0  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Al <sup>+3</sup> | 6.5                         | ± | 0.4  |
| Nafion <sup>®</sup> Al <sup>+3</sup> SCF CO <sub>2</sub> | 7.4                         | ± | 0.8  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ba <sup>+2</sup> | 5.6                         | ± | 1.0  |
| Nafion <sup>®</sup> Ba <sup>+2</sup> SCF CO <sub>2</sub> | 6.8                         | ± | 1.6  |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup>  | 4.9                         | ± | 0.8  |
| Nafion <sup>®</sup> K <sup>+1</sup> SCF CO <sub>2</sub>  | 4.9                         | ± | 0.6  |

#### **2.4.3. Thermogravimetric analysis (TGA)**

Figure 2.5 (a) shows the TGA curve for unprocessed Nafion<sup>®</sup> observing five degradation temperatures, the first one corresponds to water absorbed inside the membrane, the second degradation region represents the sulfonic group, and all the other degradations represent different fluorocarbon backbones.<sup>21</sup>



**Figure 2.5.** Thermogravimetric analysis (TGA) for Nafion® (a) processed with SCF CO<sub>2</sub> (b) and processed with SCF CO<sub>2</sub> first and then the cation exchanged [Ba<sup>+2</sup> (c) and Al<sup>+3</sup> (d)]. Derivatives shown as dotted lines.

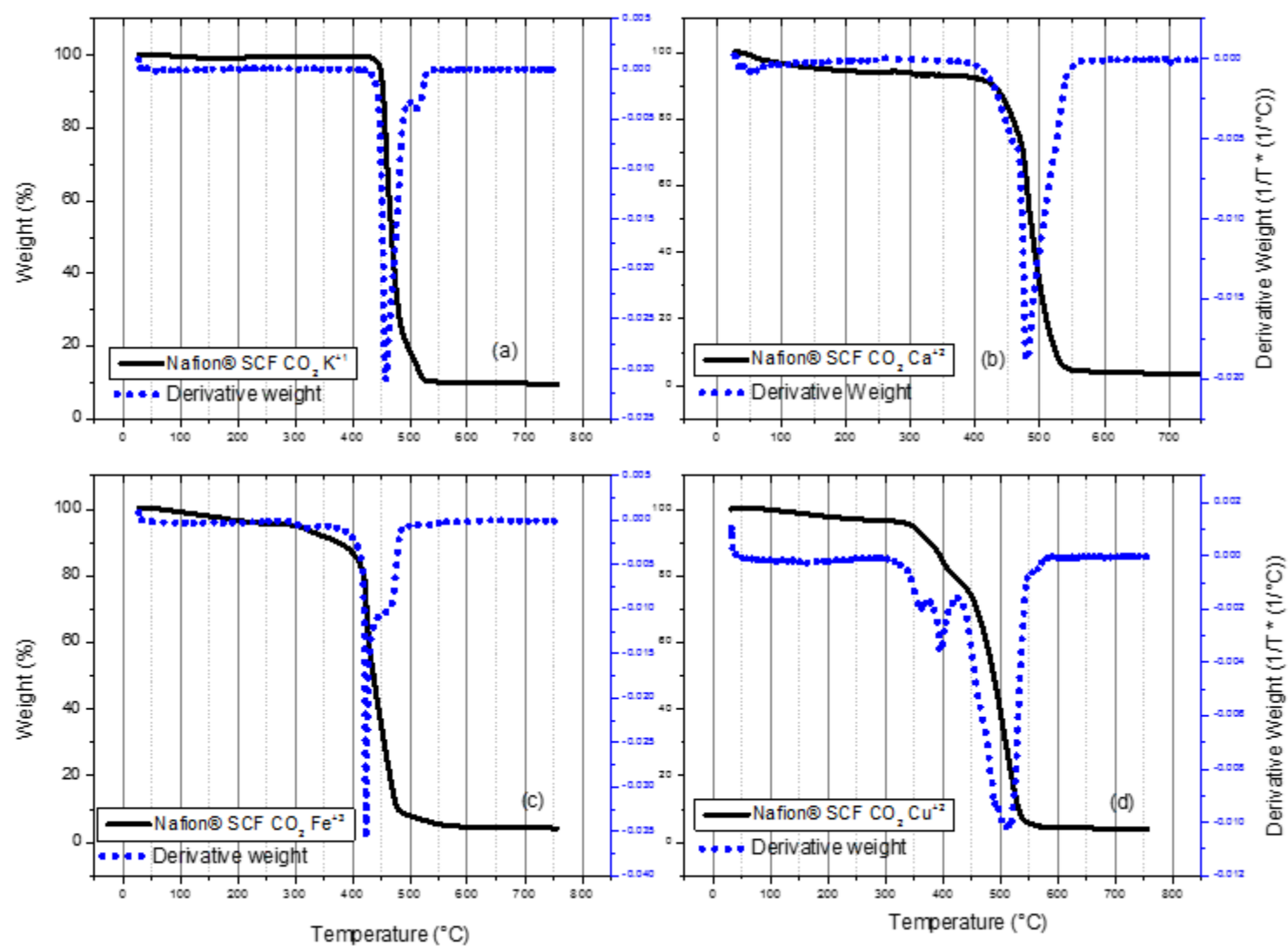
Nafion<sup>®</sup> processed with SCF CO<sub>2</sub>, panel (b) in Fig. 2.5, presented two regions in the TGA that remained unchanged, but the fluorocarbon backbone only showed one degradation temperature at 465°C. This behavior confirmed the interaction between the fluorocarbon backbone and the perfluorovinyl ether of Nafion<sup>®</sup> with SCF CO<sub>2</sub>.

When Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> was exposed to different counter ions; different degradation temperatures were obtained depending on the counter ion exchanged. Table 2.3 shows the exact degradation temperatures for each of the counter ion studied. A unique feature was observed for potassium-substituted Nafion<sup>®</sup>; although its structure degraded at 459.10°C, its second degradation region, (corresponding to the sulfonic group), is absent. This suggests that potassium interacts directly with the sulfonic groups. In addition, the fluorocarbon backbone and the ether linkage from the perfluorovinyl ether changed their thermal degradation (Fig. 2.6 (a)). The thermal stability of Nafion<sup>®</sup> significantly improved after the cation-substitution of the membrane using potassium, calcium and barium. For these counter ions, the second degradation (sulfonic group) was absent; suggesting that the counter ion interacted with the sulfonic group, but each counter ion presented a different and unique behavior in the other degradation regions. Calcium increased the thermal stability of Nafion<sup>®</sup> even further than potassium and barium.

**Table 2.3. Degradation temperatures for Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> first and then cation-exchanged.**

| <b>Membrane</b>                                          | <b>1<sup>st</sup><br/>degradation<br/>(°C)</b> | <b>2<sup>nd</sup><br/>degradation<br/>(°C)</b> | <b>3<sup>rd</sup><br/>degradation<br/>(°C)</b> | <b>4<sup>th</sup><br/>degradation<br/>(°C)</b> | <b>5<sup>th</sup><br/>degradation<br/>(°C)</b> |
|----------------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| Nafion <sup>®</sup>                                      | 65                                             | 330                                            | 450                                            | 470                                            | 500                                            |
| Nafion <sup>®</sup> SCF CO <sub>2</sub>                  | 55                                             | 340                                            | *                                              | 465                                            | *                                              |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup>  | *                                              | *                                              | 459.10                                         | *                                              | 533.02                                         |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ca <sup>+2</sup> | 55                                             | *                                              | *                                              | 479.44                                         | *                                              |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ba <sup>+2</sup> | *                                              | *                                              | *                                              | 469.54                                         | 514.78                                         |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Cu <sup>+2</sup> | *                                              | 360.38                                         | 395.85                                         | *                                              | 511.64                                         |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Al <sup>+3</sup> | *                                              | 350                                            | *                                              | 475                                            | *                                              |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Fe <sup>+3</sup> | *                                              | 335.54                                         | 423.22                                         | *                                              | *                                              |

\* Absent



**Figure 2.6.** Thermogravimetric analysis (TGA) for Nafion® processed with SCF CO<sub>2</sub> first and then the cation exchanged [K<sup>+</sup> (a), Ca<sup>2+</sup> (b), Fe<sup>3+</sup> (c) and Cu<sup>2+</sup> (d)]. Derivatives shown as dotted lines.

The thermal stability of Nafion<sup>®</sup> was adversely affected when exchanged with aluminum, iron, and copper. The aluminum cations gave rise to a catalytic decomposition of the perfluorovinyl ether side chains of Nafion<sup>®</sup>.<sup>14</sup> During this step of the decomposition, one or both of the two ether bonds are broken and a series of small fluorocarbon molecules are formed, which leave primarily the fluorocarbon backbone main chains.<sup>14</sup> Part of the fluorocarbon backbone and sulfonic group suffered thermal degradation below 350°C and the remaining polymer chain degraded at up to 475°C (Fig.2.5 (d)).

Figure 2.6 (c and d) shows the TGA curve for Nafion<sup>®</sup> SCF CO<sub>2</sub> exchanged with iron and copper. In the case of copper, the sulfonic group degraded at 360.38°C and the fluorocarbon backbone was thermally unstable and began the thermal degradation at 395.85°C. Nafion<sup>®</sup> SCF CO<sub>2</sub> exchanged with Fe<sup>+3</sup> had a loss weight small at 335.54°C (sulfonic group region), but the fluorocarbon backbone was also thermally unstable. Major weight loss for this cation occurred at 423.22°C. Nafion<sup>®</sup> membranes exchanged first with the cations and then processed with SCF CO<sub>2</sub> showed the same behavior than Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and then cation-exchanged, but had a small difference in the degradation temperatures (Table 2.4).

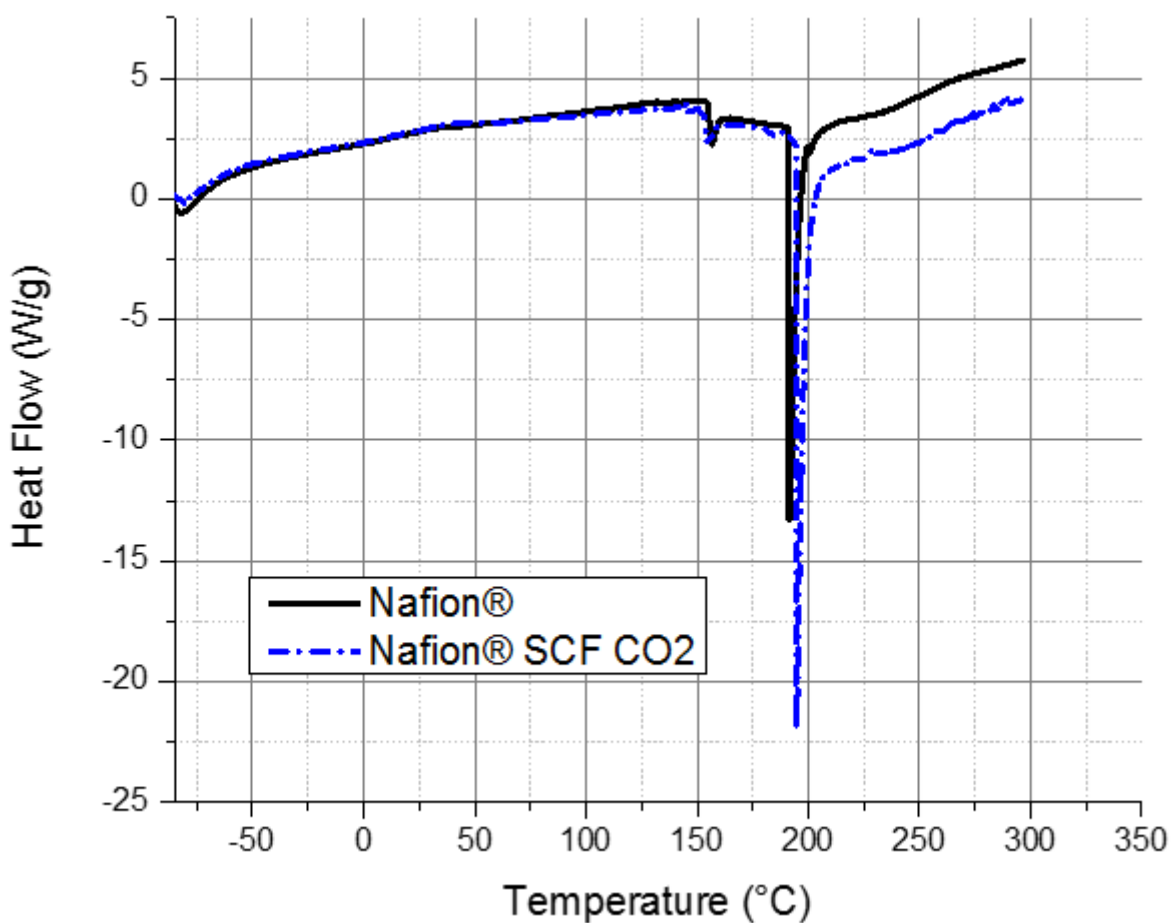
**Table 2.4. Degradation temperatures for Nafion<sup>®</sup> exchanged with cation first and then processed with SCF CO<sub>2</sub>**

| <b>Membrane</b>                                          | <b>1<sup>st</sup><br/>degradation<br/>(°C)</b> | <b>2<sup>nd</sup><br/>degradation<br/>(°C)</b> | <b>3<sup>rd</sup><br/>degradation<br/>(°C)</b> | <b>4<sup>th</sup><br/>degradation<br/>(°C)</b> | <b>5<sup>th</sup><br/>degradation<br/>(°C)</b> |
|----------------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| Nafion <sup>®</sup>                                      | 65                                             | 330                                            | 450                                            | 470                                            | 500                                            |
| Nafion <sup>®</sup> SCF CO <sub>2</sub>                  | 55                                             | 340                                            | *                                              | 465                                            | *                                              |
| Nafion <sup>®</sup> K <sup>+1</sup> SCF CO <sub>2</sub>  | *                                              | *                                              | 459.92                                         | *                                              | 527.13                                         |
| Nafion <sup>®</sup> Ca <sup>+2</sup> SCF CO <sub>2</sub> | *                                              | *                                              | *                                              | 489.19                                         | *                                              |
| Nafion <sup>®</sup> Ba <sup>+2</sup> SCF CO <sub>2</sub> | *                                              | *                                              | *                                              | 468.55                                         | 512.40                                         |
| Nafion <sup>®</sup> Cu <sup>+2</sup> SCF CO <sub>2</sub> | *                                              | 360.52                                         | 397.97                                         | *                                              | 513.76                                         |
| Nafion <sup>®</sup> Al <sup>+3</sup> SCF CO <sub>2</sub> | *                                              | 354.51                                         | *                                              | 492.35                                         | *                                              |
| Nafion <sup>®</sup> Fe <sup>+3</sup> SCF CO <sub>2</sub> | *                                              | 340.39                                         | 421.72                                         | *                                              | *                                              |

\* Absent

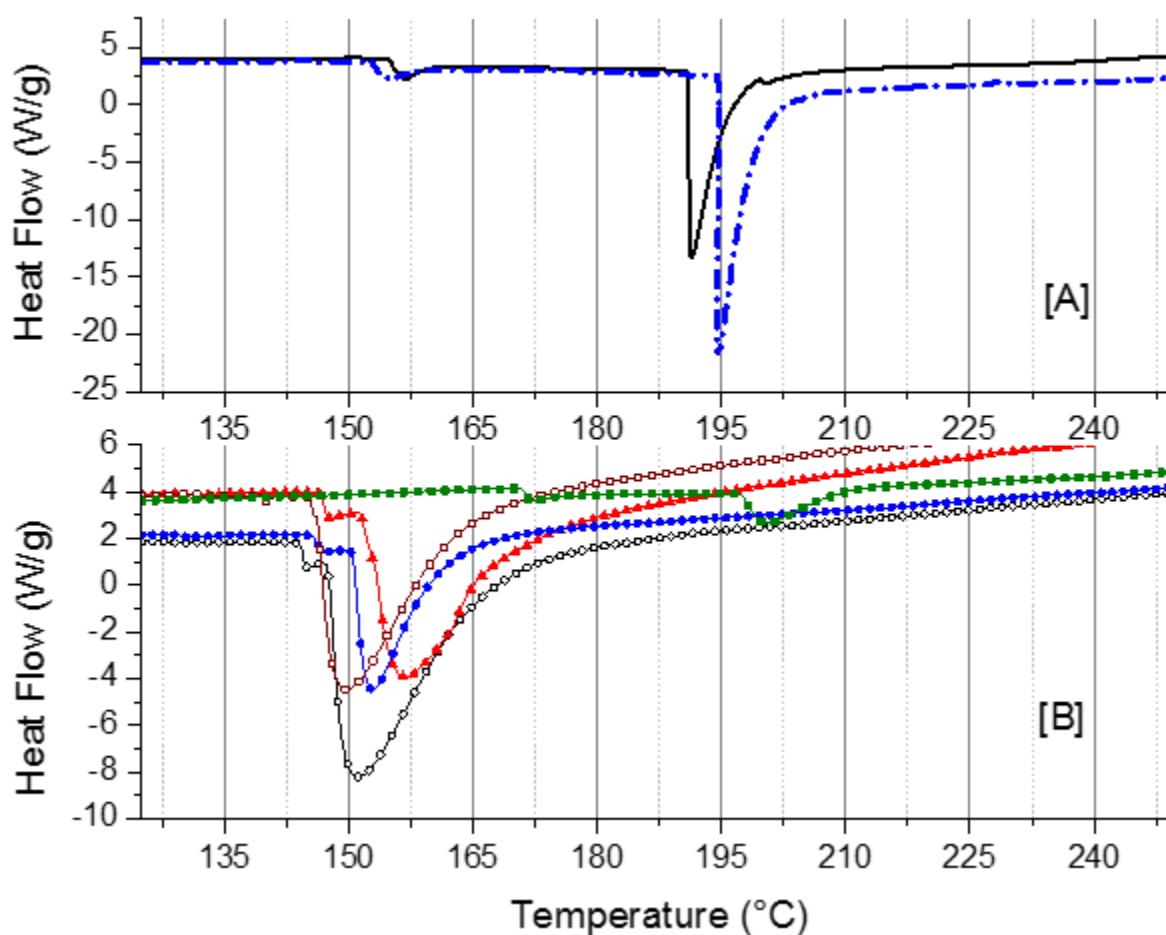
#### 2.4.4. Differential scanning calorimetry (DSC)

Figure 2.7 presents DSC curves for unprocessed Nafion® and Nafion® processed with SCF CO<sub>2</sub>. Unprocessed Nafion® presents two endothermic peaks; the first thermal transition at 156.8°C corresponds to the transition of the ionic domains, while the peak at higher temperature (191.7°C) is attributed to the crystalline regions.<sup>22</sup> Nafion® processed with SCF CO<sub>2</sub> also presents the two endothermic peaks, the first at 154.82°C and the second peak at 194.58°C. The changes in temperature, with respect to unprocessed Nafion®, are related to the energy needed to overcome the crystalline bonding forces and changes in the molecular conformation of the chains in the polymer.<sup>23</sup>



**Figure 2.7.** DSC for Nafion® (Straight line) and Nafion® processed with SCF CO<sub>2</sub> (Short dash dot line).

Figure 2.8 presents the comparison between DSC for unprocessed Nafion<sup>®</sup>, Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> [A] and Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and then cation-exchanged [B]. The incorporation of the counter ion to the membrane produced unique DSC curves for each of the counter ions studied. Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with potassium presented a difference in both the energy and temperature required to produce the endothermic transitions. The endothermic transitions for the ionic cluster and crystalline regions shifted towards higher temperature and the energy required for the endothermic transition of the crystalline region presented the highest reduction for all the cations in comparison with unprocessed Nafion<sup>®</sup>.



**Figure 2.8.** Comparison between DSC for Nafion<sup>®</sup> (Straight line), Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> (Short dash dot line) [A] and Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and then cation-exchanged [B]. K<sup>+</sup> (—■—), Ca<sup>2+</sup> (—□—), Ba<sup>2+</sup> (—●—), Fe<sup>3+</sup> (—○—), Al<sup>3+</sup> (—▲—).

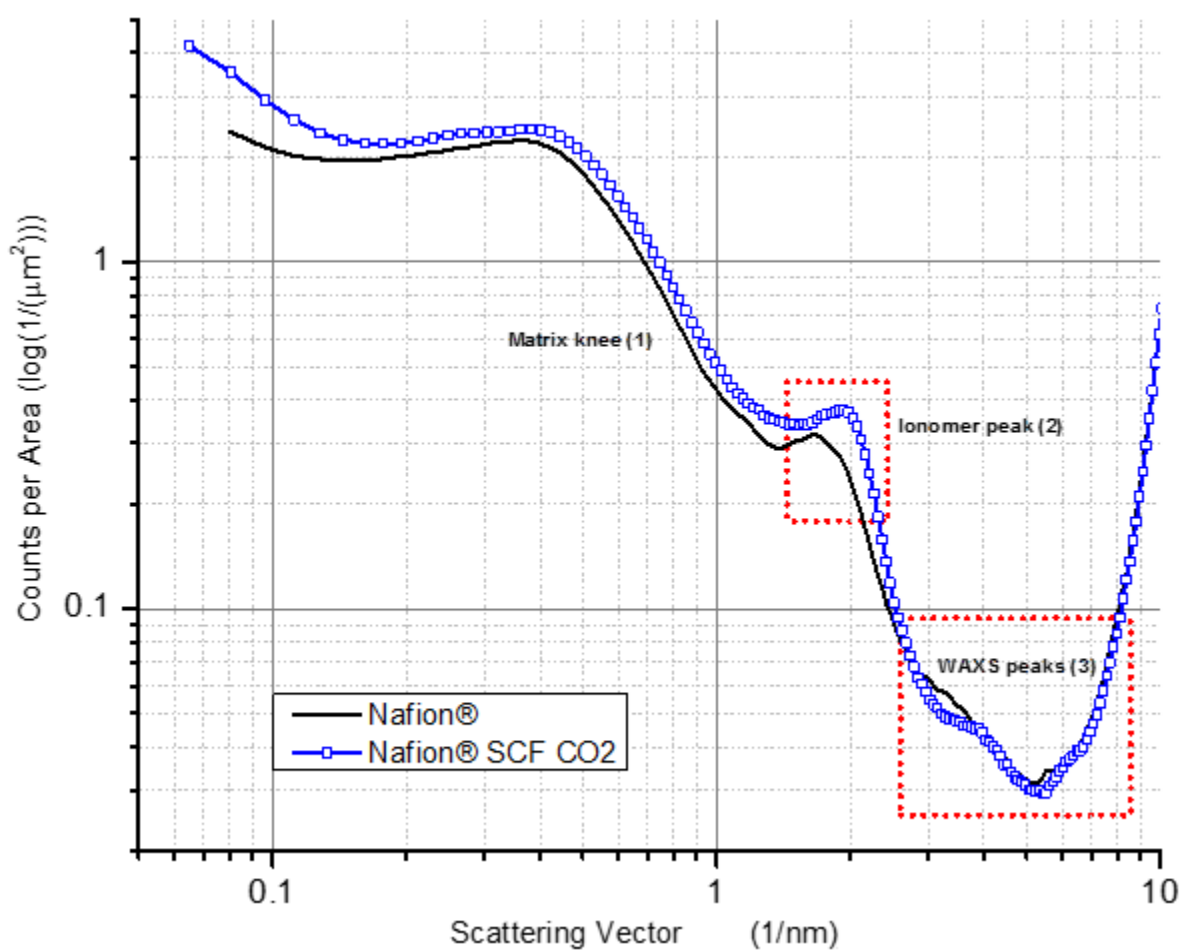
The other counter ions also presented changes in the energy required to produce the endothermic transitions but showed a reduction in temperature. Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> presented only one endothermic peak; in this case the incorporation of this counter ion reduced the temperature of the crystalline region and the ionic cluster to a single temperature. The other counter ions presented two endothermic peaks. Table 2.5 summarizes the endothermic transition temperatures and their corresponding energies for the Nafion® membranes studied.

**Table 2.5. Endothermic transition temperatures and corresponding energies for Nafion® membranes.**

| Membrane                                     | First Transition |                                    | Second Transition |                                    |
|----------------------------------------------|------------------|------------------------------------|-------------------|------------------------------------|
|                                              | T (°C)           | $\Delta H$<br>(J g <sup>-1</sup> ) | T (°C)            | $\Delta H$<br>(J g <sup>-1</sup> ) |
| Nafion®                                      | 156.8            | 4.7                                | 191.7             | 60.7                               |
| Nafion® SCF CO <sub>2</sub>                  | 154.8            | 2.8                                | 194.5             | 70.7                               |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 154.4            | 43.9                               | Absent            | Absent                             |
| Nafion® Cu <sup>+2</sup> SCF CO <sub>2</sub> | 152.3            | 2.6                                | 198.2             | 83.7                               |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 149.9            | 64.6                               | Absent            | Absent                             |
| Nafion® Ca <sup>+2</sup> SCF CO <sub>2</sub> | 149.3            | 51.3                               | Absent            | Absent                             |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 146.7            | 0.75                               | 152.8             | 34.8                               |
| Nafion® Ba <sup>+2</sup> SCF CO <sub>2</sub> | 149.7            | 1.9                                | 156.2             | 35.99                              |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 171.9            | 1.01                               | 200.8             | 9.96                               |
| Nafion® K <sup>+1</sup> SCF CO <sub>2</sub>  | 163.8            | 0.43                               | 178.9             | 7.4                                |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 147.5            | 1.15                               | 156.5             | 54.1                               |
| Nafion® Al <sup>+3</sup> SCF CO <sub>2</sub> | 151.5            | 3.2                                | 194.9             | 89.6                               |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 144.8            | 0.61                               | 151.0             | 94                                 |
| Nafion® Fe <sup>+3</sup> SCF CO <sub>2</sub> | 149.2            | 2.76                               | 183.1             | 93.8                               |

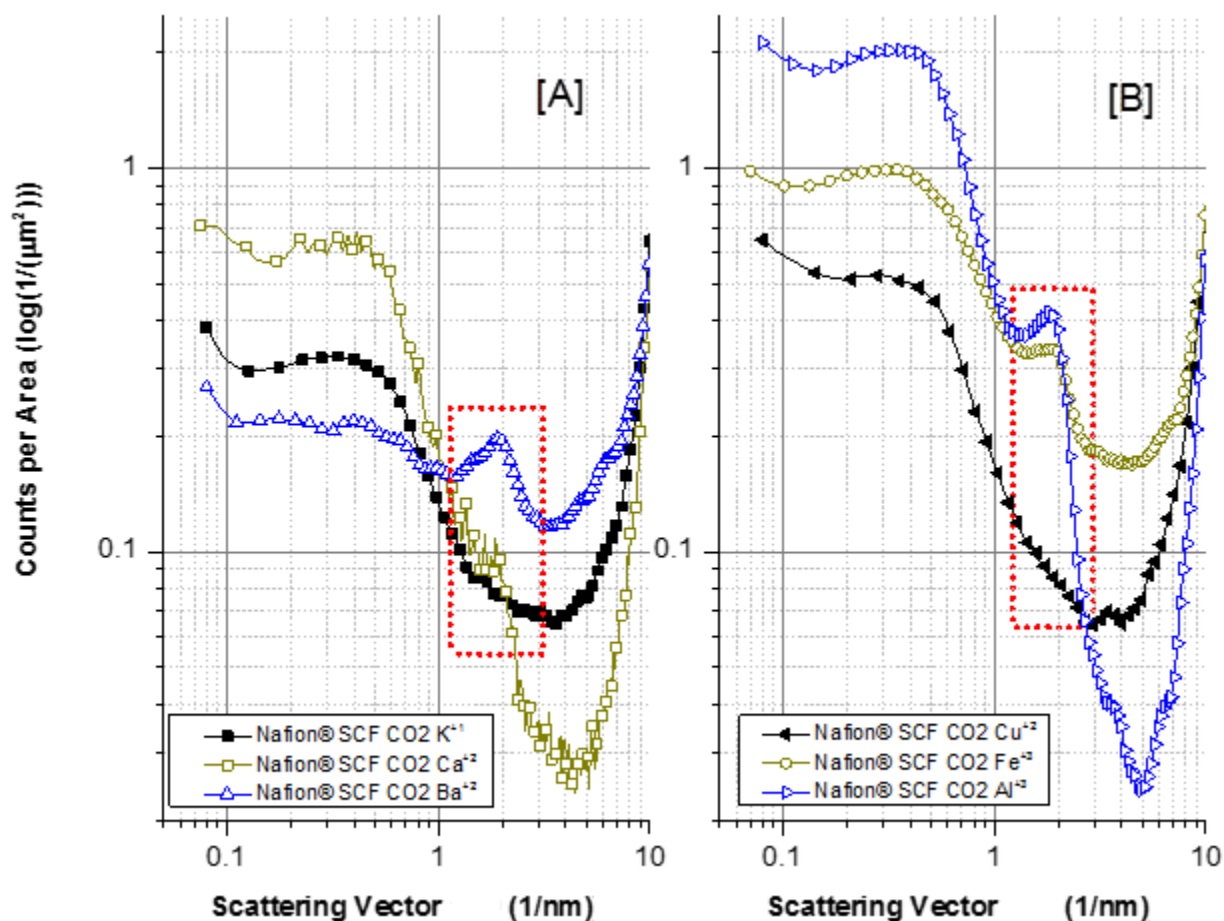
#### 2.4.5. Small angle X-ray scattering (SAXS)

SAXS profiles for Nafion® membranes are shown in Figures 2.9 and 2.10. Unprocessed Nafion® shows three characteristic regions in the SAXS profile: (1) corresponds to the matrix knee. The intensity of this region depends on the crystallinity of the membrane<sup>24</sup>; (2) the ionomer peak (this region plays an important role in the transport of certain compounds, like methanol or protons, through the membrane) and (3), correspond to large q-vectors, the ultra low angle area.<sup>5</sup>



**Figure 2.9.** SAXS profile for Nafion® (Solid line) and Nafion® processed with SCF CO<sub>2</sub> (—□—).

Nafion® processed with SCF CO<sub>2</sub> presented changes in regions 1, 2 and 3 in the SAXS profile with respect to unprocessed Nafion® (Figure 2.9). This behavior agrees with the results obtained with FTIR, where the different intensities from FTIR spectra were related with the interaction between the perfluorocarbon backbone and the ionomer group with the SCF CO<sub>2</sub>. The SAXS results also agree with the DSC experiments where a different ionic configuration and crystallinity were obtained upon SCF CO<sub>2</sub> processing.



**Figure 2.10.** SAXS profile Nafion® processed with SCF CO<sub>2</sub> and cation-exchanged: K<sup>+</sup> (■), Ca<sup>2+</sup> (□), Ba<sup>2+</sup> (△) [A] and Cu<sup>2+</sup> (▲), Fe<sup>3+</sup> (○), Al<sup>3+</sup> (▴) [B].

Nafion® membranes processed with SCF CO<sub>2</sub> and cross-linked with counter ions showed different positions for the ionomer peak with respect to unprocessed Nafion® (Figure 2.10). The positions of these peaks for some counter ions obtained by the scattering vector appear from 1.58 to 2.04 nm<sup>-1</sup>. In other cases this peak disappears due to the interaction between the counter ion and the ionomer group (Figure 2.10). Combining Bragg's law with the scattering vector (Q) obtained from the SAXS plot, the interstitial distance for the ionic domains was obtained. Table 2.6 shows the Bragg's distance for the ionomer peak for Nafion® and Nafion® processed with SCF CO<sub>2</sub> and then exchanged with counter ions. The variations in the ionomer peak agree with the previously presented DSC results, where a new and unique ionic configuration was obtained depending on the SCF CO<sub>2</sub> processing and the cation selected.

**Table 2.6. Bragg distance for ionomer peak for Nafion® membranes.**

| <b>Sample</b>                                | <b>d<sub>bragg</sub> (nm)</b> | <b>Atomic radius of the cation (nm)</b> |
|----------------------------------------------|-------------------------------|-----------------------------------------|
| Nafion®                                      | 3.97                          | ---                                     |
| Nafion® SCF CO <sub>2</sub>                  | 3.47                          | ---                                     |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 3.53                          | 0.180                                   |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | Absent                        | 0.135                                   |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 3.53                          | 0.215                                   |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 3.08                          | 0.14                                    |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 3.69                          | 0.125                                   |
| Nafion® SCF CO <sub>2</sub> K <sup>+</sup>   | Absent                        | 0.22                                    |
| Nafion® Ca <sup>+2</sup> SCF CO <sub>2</sub> | 3.29                          | 0.18                                    |
| Nafion® Ba <sup>+2</sup> SCF CO <sub>2</sub> | 3.81                          | 0.215                                   |
| Nafion® Cu <sup>+2</sup> SCF CO <sub>2</sub> | 3.98                          | 0.135                                   |
| Nafion® Al <sup>+3</sup> SCF CO <sub>2</sub> | 3.90                          | 0.125                                   |
| Nafion® Fe <sup>+3</sup> SCF CO <sub>2</sub> | 4.39                          | 0.14                                    |
| Nafion® K <sup>+</sup> SCF CO <sub>2</sub>   | Absent                        | 0.22                                    |

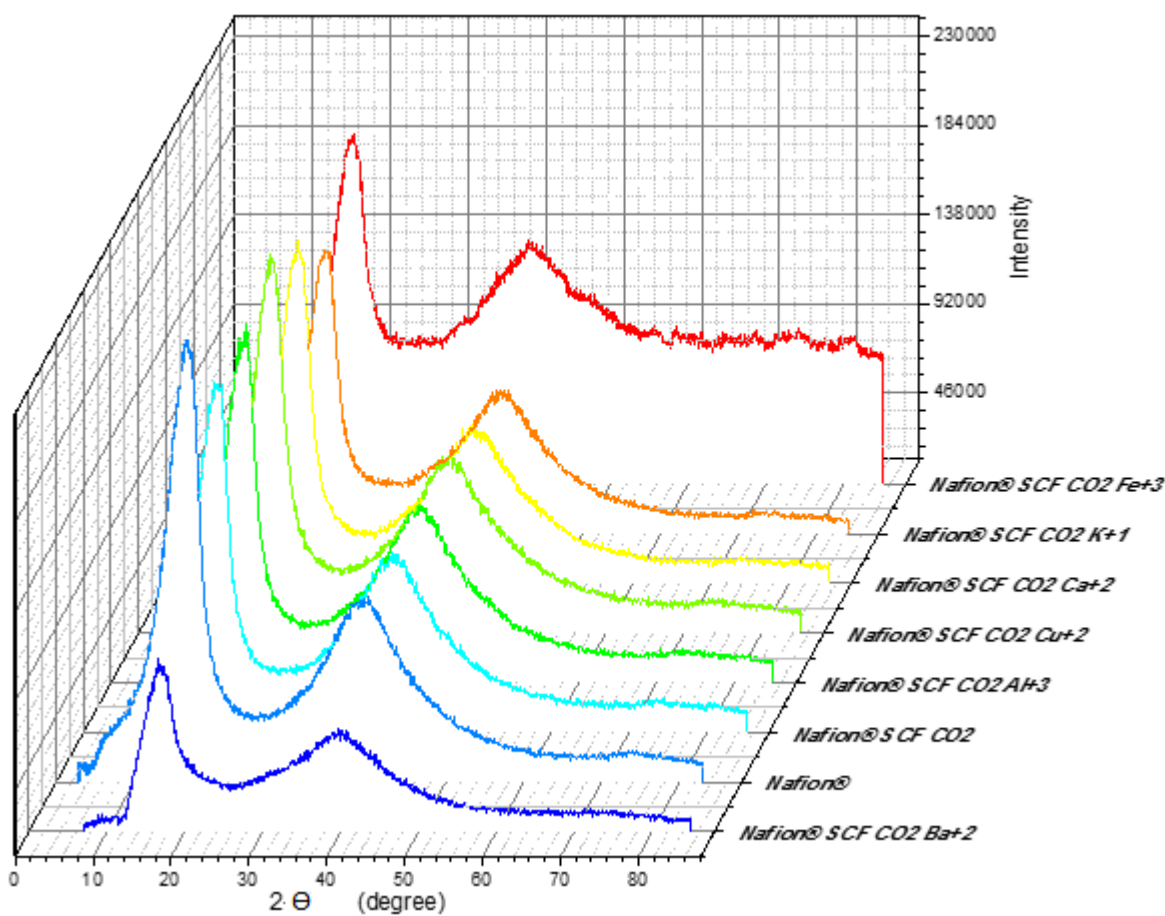
Another important parameter that was obtained from the SAXS data is the radius of gyration ( $R_g$ ). For polymers, this parameter represents the dimension of a polymer chain and can be used to evaluate changes with the variables studied. This parameter was obtained using the Guinier equation, which provides the relation between  $R_g$ , the intensity in a SAXS profile and the scattering vector ( $Q$ ).  $R_g$  was estimated using the slope of the linear relationship between  $\ln(I(Q))$  and  $Q^2$ .<sup>25</sup> Nafion® processed with SCF CO<sub>2</sub> presented a reduction in the radius of gyration of 2.29% with respect to unprocessed Nafion®. The incorporation of the counter ion into the Nafion® membrane produced unique  $R_g$ 's. Nafion® processed with SCF CO<sub>2</sub> and exchanged with counter ions had an even greater reduction in the radius of gyration. Nafion® SCF CO<sub>2</sub> with Al<sup>+3</sup> reduced  $R_g$  by 5% with respect to unprocessed Nafion®. The incorporation of barium reduced this parameter the most (54%) and was the lowest  $R_g$  for all the membranes studied. The  $R_g$  results for Nafion® processed with SCF CO<sub>2</sub> and cation-exchanged are summarized in Table 2.7. SCF CO<sub>2</sub> processing and the incorporation of counter ion substitution compacted all the polymeric chains, creating a new molecular configuration. These results agree with the water swelling, DSC and TGA experiments, where a new configuration for the ionic domain and the perfluorocarbon backbone was obtained depending on the processing and the counter ion selected.

**Table 2.7. Radius of gyration for Nafion® membranes.**

| <b>Membrane</b>                              | <b>Radius of gyration (nm)</b> |
|----------------------------------------------|--------------------------------|
| Nafion®                                      | 2.66                           |
| Nafion® SCF CO <sub>2</sub>                  | 2.59                           |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 1.89                           |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 2.36                           |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 1.22                           |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 2.20                           |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 1.83                           |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 2.51                           |

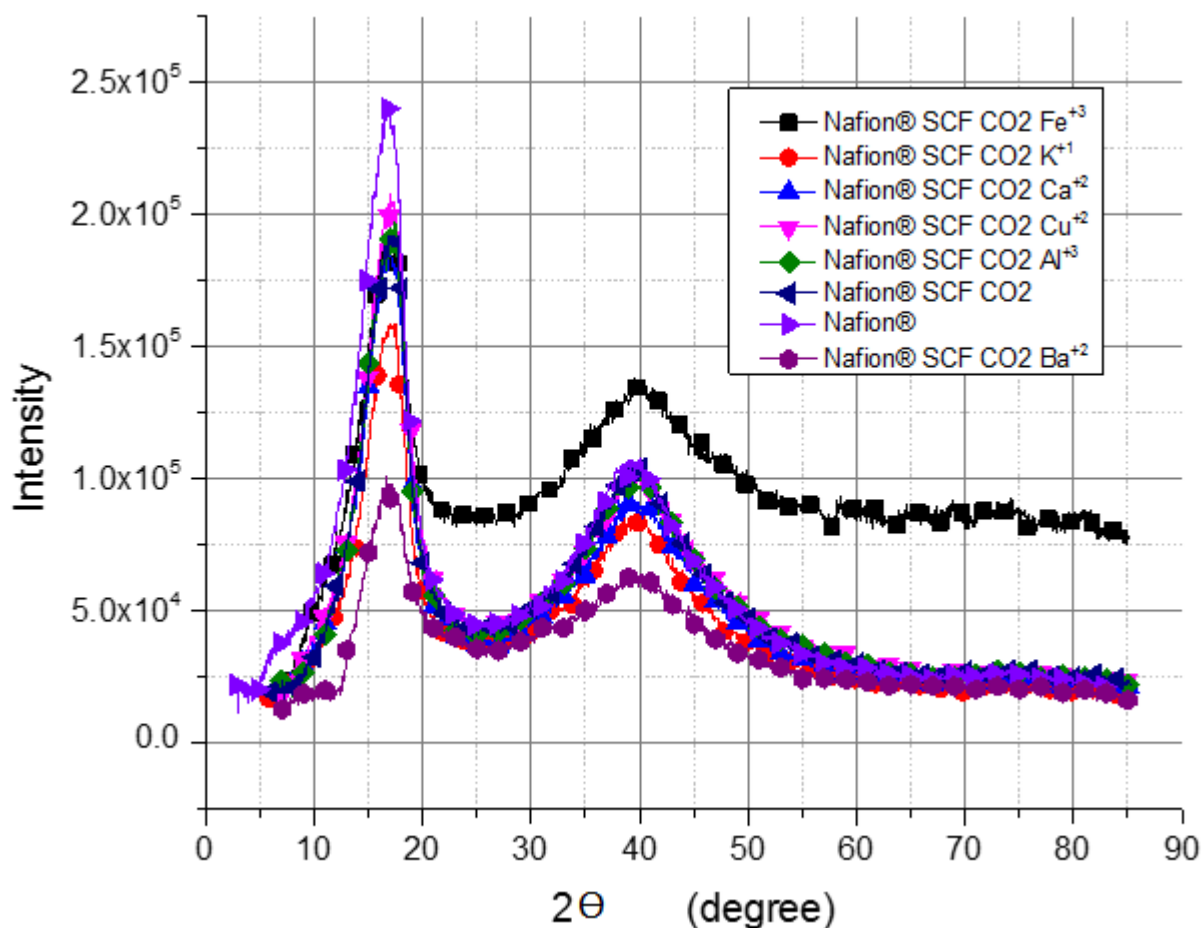
#### 2.4.6. X-Ray diffraction (XRD)

X-ray diffraction measurements were performed to evaluate changes in the crystallinity of the Nafion® membranes. Figure 2.11 shows the XRD patterns of Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with different counter ions. Nafion® presents a large peak at the 2 $\theta$  angle of 17°, which is formed by the superposition of amorphous scattering at 16° in the polymeric chain and the crystalline scattering at 17.5°<sup>26</sup>. A wide peak appears at the 2 $\theta$  angle of 38°–39° (amorphous region)<sup>26</sup>. Crystallinity values were obtained using the area of the deconvoluted crystalline peak divided by the total area (crystalline plus amorphous peaks).



**Figure 2.11.** XRD patterns for Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with cation.

The crystallinity of Nafion® processed with SCF CO<sub>2</sub> increased 11% compared with unprocessed Nafion®. This behavior agrees with the results in the literature, where perfluorosulfonic membranes increased their crystallinity after processing with SCF CO<sub>2</sub>.<sup>11,12,27</sup> The incorporation of the counter ion into the membrane produced changes in the intensity of both peaks in the XRD pattern. The crystallinity of Nafion® membrane increased or decreased depending on the cation-exchanged. Figure 2.12 presents a frontal view of the XRD patterns for Nafion® membranes. The incorporation of potassium reduced the crystallinity of Nafion® by 12% and was the lowest value for all the membranes studied.



**Figure 2.12.** XRD patterns for Nafion® ( —▶ ) membranes processed with SCF CO<sub>2</sub> ( —◄ ) and exchanged with cation. (Frontal view): Fe<sup>+3</sup> ( —■— ), K<sup>+1</sup> ( —●— ), Ca<sup>+2</sup> ( —▲— ), Cu<sup>+2</sup> ( —▼— ), Al<sup>+3</sup> ( —◆— ), Ba<sup>+2</sup> ( —●— ).

Nafion® processed with SCF CO<sub>2</sub> and then exchanged with calcium presented the largest value for the crystallinity of all the counter ions studied. These results agree with the DSC, TGA and SAXS results presented in the previous sections, where the reordering induced by the SCF CO<sub>2</sub> processing and the counter ion exchanged on the polymeric matrix changed the ionic cluster and matrix knee configuration (related to R<sub>g</sub>). Table 2.8 summarizes the changes in crystallinity for all the Nafion® membranes studied.

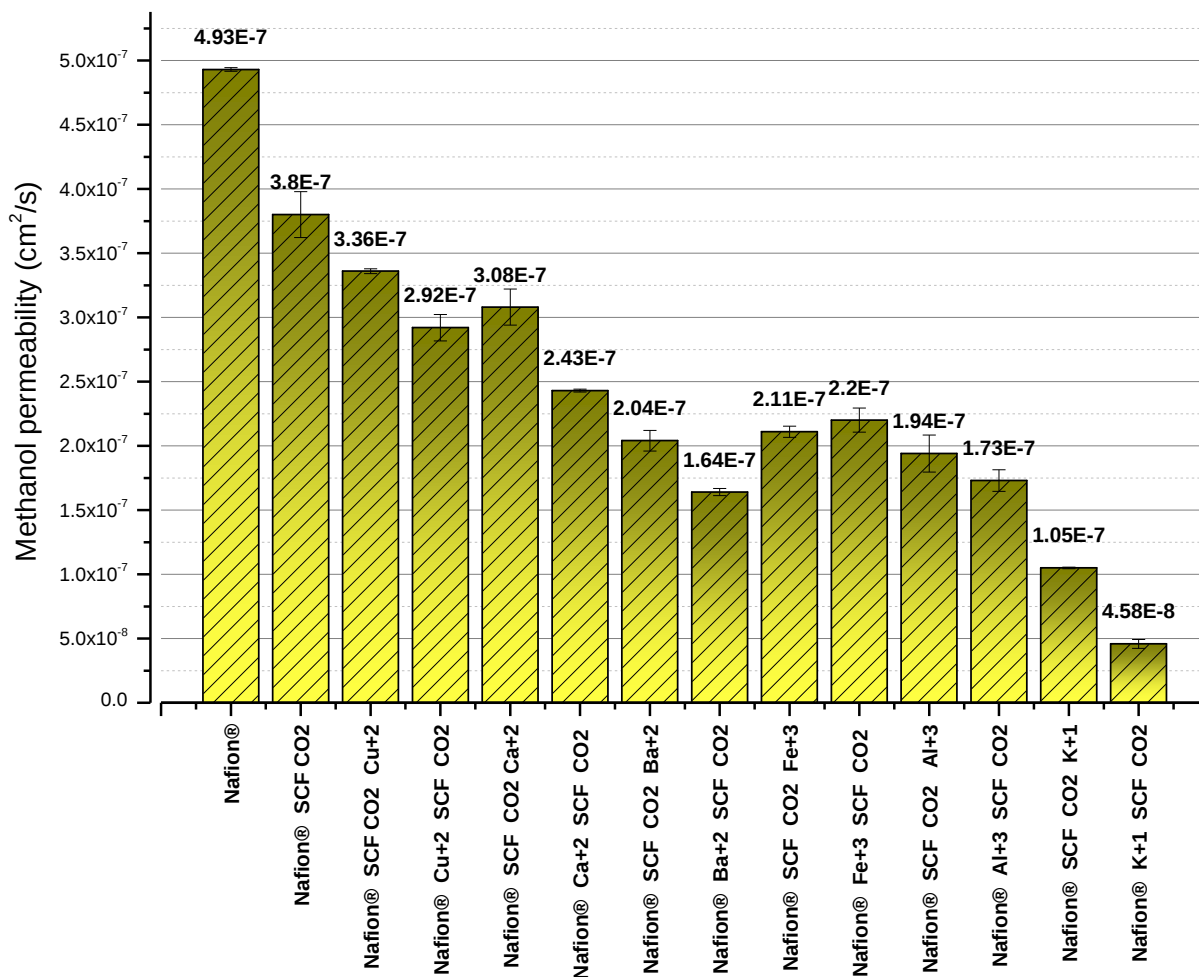
**Table 2.8. Percent of crystallinity of Nafion® membranes.**

| <b>Membrane</b>                              | <b>Crystallinity (%)</b> |
|----------------------------------------------|--------------------------|
| Nafion®                                      | 26.9                     |
| Nafion® SCF CO <sub>2</sub>                  | 29.8                     |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 29.0                     |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 32.0                     |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 28.0                     |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 30.3                     |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 25.1                     |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 23.6                     |

#### **2.4.7. Methanol permeability**

Methanol permeability for Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with counter ions are presented in Figure 2.13. The methanol permeability of Nafion® was reduced by  $15 \pm 2\%$  compared with unprocessed Nafion® after processing with SCF CO<sub>2</sub>. The permeability of small molecules through a membrane is defined as the product of a solubility coefficient and a diffusion coefficient. The limiting step of the diffusion process in a polymeric membrane is determined by the capacity of the compound to move through the free volume available in the system, which is related to morphology and crystallinity.<sup>28</sup> Nafion® processed with SCF CO<sub>2</sub> presents a reduction of the methanol permeability. One explanation for this is related to the results presented in the previous sections (*e.g.* TGA, DSC, SAXS), where the reordering induced by the SCF CO<sub>2</sub> processing on the polymeric matrix changed the morphology and crystallinity and

produced a unique molecular configuration. This new molecular configuration inhibited the diffusion process reducing the methanol permeability.



**Figure 2.13.** Comparison between methanol permeability for Nafion® processed with SCF CO<sub>2</sub> and then cation-exchanged.

The incorporation of counter ions significantly reduced the methanol permeability of the Nafion® membranes even further. Nafion® SCF CO<sub>2</sub> with Cu<sup>+2</sup> reduced by 32 ± 2% the methanol permeability with respect to unprocessed Nafion®. The incorporation of potassium reduced the permeability of methanol by 79 ± 2% and was the lowest methanol permeability for all the membranes studied.

These results agree with the previously presented DSC, SAXS and XRD results, where the variation of the methanol permeability for each counter ion is linked to the new sulfonic group conformation and the change in the crystallinity; each counter ion produced a unique morphology (related to its free volume) inhibiting the methanol permeability. Table 2.9 presents the methanol permeability corresponding to each Nafion® membrane studied. Nafion® membranes exchanged first with the counter ion and then processed with SCF CO<sub>2</sub> obtained the same tendency that Nafion® SCF CO<sub>2</sub> and then cation-exchanged but had a different methanol permeability value.

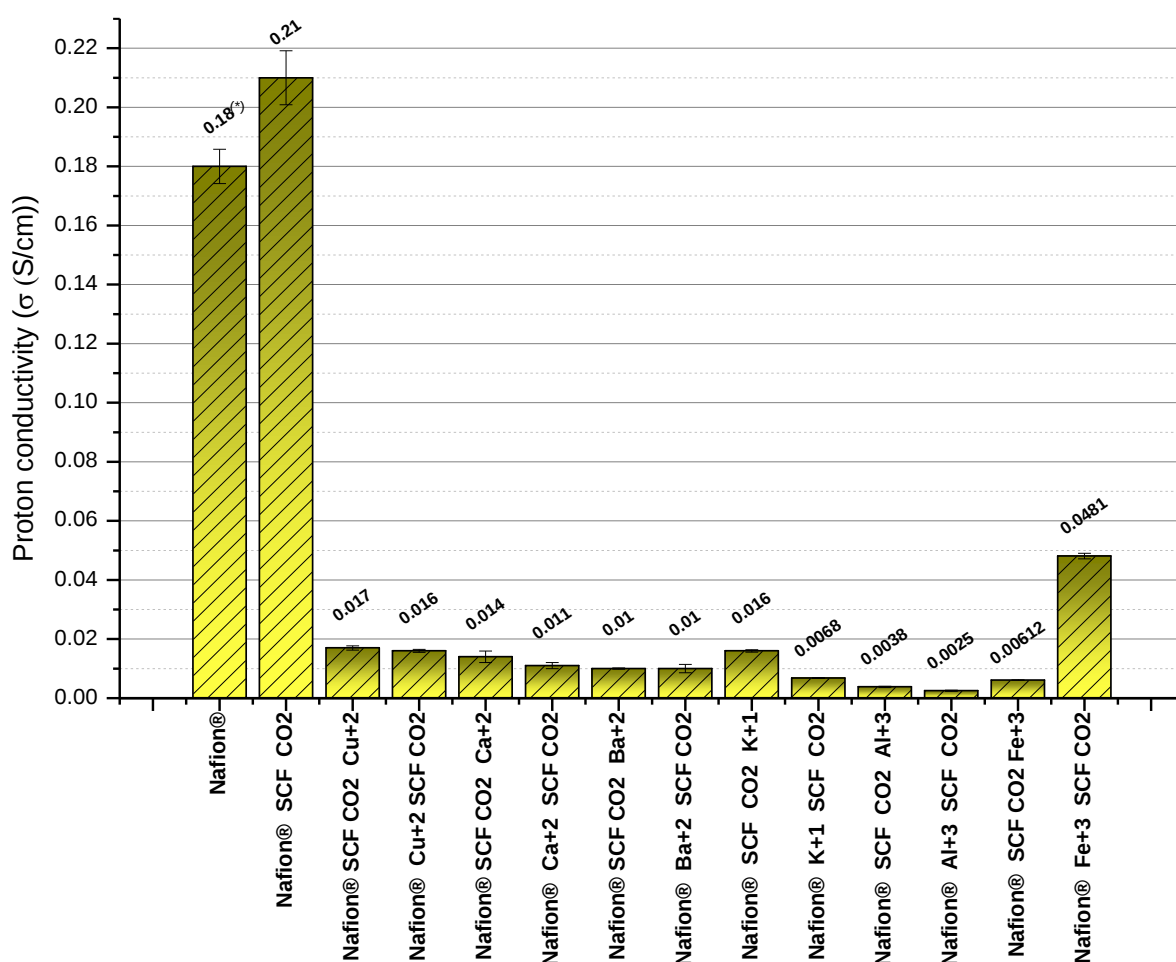
**Table 2.9. Methanol permeability for Nafion® membranes.**

| <b>Membrane</b>                              | <b>Methanol<br/>Permeability * 10<sup>7</sup><br/>(cm<sup>2</sup>/s)</b> |
|----------------------------------------------|--------------------------------------------------------------------------|
| Nafion®                                      | 4.93                                                                     |
| Nafion® SCF CO <sub>2</sub>                  | 3.80                                                                     |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 3.36                                                                     |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 3.08                                                                     |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 2.04                                                                     |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 2.11                                                                     |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 1.94                                                                     |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 1.05                                                                     |
| Nafion® Cu <sup>+2</sup> SCF CO <sub>2</sub> | 2.92                                                                     |
| Nafion® Ca <sup>+2</sup> SCF CO <sub>2</sub> | 2.43                                                                     |
| Nafion® Ba <sup>+2</sup> SCF CO <sub>2</sub> | 1.64                                                                     |
| Nafion® Fe <sup>+3</sup> SCF CO <sub>2</sub> | 2.20                                                                     |
| Nafion® Al <sup>+3</sup> SCF CO <sub>2</sub> | 1.73                                                                     |
| Nafion® K <sup>+1</sup> SCF CO <sub>2</sub>  | 0.4                                                                      |

#### **2.4.8. Proton conductivity**

Proton conductivity of Nafion® membranes processed with SCF CO<sub>2</sub> and the counter ion exchanged are presented in Figure 2.14. The proton conductivity of Nafion® processed with SCF CO<sub>2</sub> compared with unprocessed Nafion® improved  $14 \pm 1\%$ . When the Nafion® membranes were exchanged with the counter ions, the proton conductivity of these membranes was significantly

reduced over one order of magnitude for all of them. Kim et al<sup>29</sup> used molecular dynamics to study the transport mechanism of protons through the membrane. They proposed a transport of protons using hydrated sulfonic groups and suggested that the predominant mechanism consists in a series of Eigen-Zundel-Eigen or Zundel-Zundel transformations depending on: the sulfonic group, the water contained inside the membrane, and the polymeric structure<sup>29</sup>. The transport of certain compounds was also associated with their free volume available in the system<sup>28</sup>.



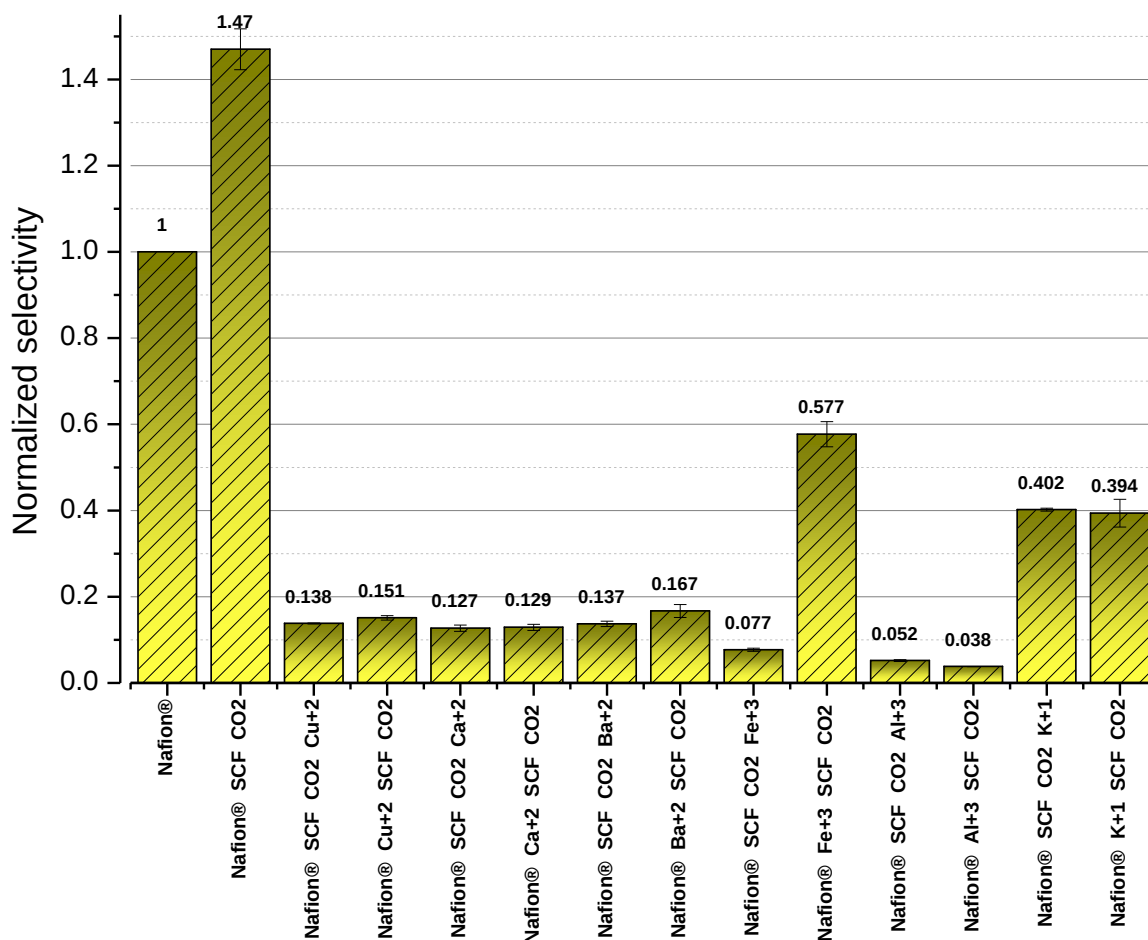
**Figure 2.14.** Comparison between proton conductivity for Nafion® processed with SCF CO<sub>2</sub> and then cation-exchanged and Nafion® cation-exchanged and then processed with SCF CO<sub>2</sub>.

The processing with SCF CO<sub>2</sub> produced a reordering of the perfluorinated and perfluorovinylether chains in Nafion®. This is due to the affinity of perfluorinated and perfluorovinyl ether chains with CO<sub>2</sub>, described by their polarizability per volume<sup>30</sup>. The counter ion interact with the ionic domains that inhibit the complex formation between the proton, water and the sulfonic group described above. Also the transport was inhibited since each counter ion created new morphologies and changed the mobility of the proton through the membrane. These results are related to the changes induced by the SCF CO<sub>2</sub> and the counter ion on the molecular conformation of the polymeric chains in the membrane shown in the DSC, SAXS and XRD experiments. Table 2.10 shows the results for all the membranes studied.

**Table 2.10. Proton conductivity for Nafion® membranes.**

| Membrane                                     | Proton conductivity<br>(S/cm) |   |          |
|----------------------------------------------|-------------------------------|---|----------|
| Nafion®                                      | 0.18                          | ± | 0.006    |
| Nafion® SCF CO <sub>2</sub>                  | 0.21                          | ± | 0.009    |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup> | 0.017                         | ± | 0.0007   |
| Nafion® Cu <sup>+2</sup> SCF CO <sub>2</sub> | 0.016                         | ± | 0.0005   |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> | 0.014                         | ± | 0.002    |
| Nafion® Ca <sup>+2</sup> SCF CO <sub>2</sub> | 0.011                         | ± | 0.001    |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup> | 0.010                         | ± | 0.0002   |
| Nafion® Ba <sup>+2</sup> SCF CO <sub>2</sub> | 0.010                         | ± | 0.001    |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>  | 0.016                         | ± | 0.0004   |
| Nafion® K <sup>+1</sup> SCF CO <sub>2</sub>  | 0.0068                        | ± | 0.0001   |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup> | 0.0038                        | ± | 0.0002   |
| Nafion® Al <sup>+3</sup> SCF CO <sub>2</sub> | 0.0025                        | ± | 0.0002   |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup> | 0.0061                        | ± | 2.06E-05 |
| Nafion® Fe <sup>+3</sup> SCF CO <sub>2</sub> | 0.0481                        | ± | 0.001    |

Figure 2.15 presents the normalized selectivities (proton conductivity / methanol permeability) for Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with counter ions (normalized with the selectivity of unprocessed Nafion®). SCF CO<sub>2</sub> processing alone presents the largest effect on selectivity. The incorporation of counter ions significantly reduced the normalized selectivity of Nafion®, primarily due to the reduction in proton conductivity.



**Figure 2.15.** Normalized Selectivities (Proton Conductivity / Methanol Permeability) for Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with cation. (Normalized with selectivity of unprocessed Nafion®).

## 2.5. CONCLUSIONS

Nafion® membranes were processed with SCF CO<sub>2</sub> and exchanged with different types of +1, +2 and +3 counter ions. The SCF processing with CO<sub>2</sub> promotes the transport of protons through the membrane and inhibits the methanol permeability. The molecular interaction between CO<sub>2</sub> and the fluorocarbon backbone makes a unique rearrangement in the polymer changing its water swelling, thermal degradation, crystallinity and morphology.

Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and counter ion exchanged inhibited both the transport of protons and methanol through the membrane. The incorporation of the counter ion into Nafion<sup>®</sup> influences the ionic domains uniquely for each counter ion studied, but also influences the crystallinity, the morphology, and the water swelling, which are very important in the transport of protons through the membrane. Although the transport properties of both protons and methanol were reduced upon the incorporation of counter ions, suggesting some similarities in their transport mechanism, the magnitude of the changes were significantly different, suggesting that there are fundamental differences in their transport mechanism that can be further explored to create more selective membranes.

The best normalized selectivity (proton conductivity/methanol permeability, normalized with unprocessed Nafion<sup>®</sup>) was obtained using only SCF CO<sub>2</sub> (higher than unprocessed Nafion<sup>®</sup>). The use of cations significantly reduced the normalized selectivity of Nafion<sup>®</sup>, primarily due to the reduction in proton conductivity.

The processing order (SCF processing vs. counter ion substitution) shows that although the magnitude of the methanol permeability and proton conductivity are affected, the trends are primarily depends on by the nature of the counter ion and not the order, suggesting that the physically-induced-changes by the supercritical fluid although important, do not limit the chemically-induced-changes.

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## CHAPTER 3

### Supercritical Fluid CO<sub>2</sub> Processing and Counter Ion Substitution of Nafion® Membranes.

#### Part II: Vapor Methanol Permeability and Double Counter-Ion Substitution.

##### 3.1. ABSTRACT

Nafion® membranes were processed with SCF CO<sub>2</sub> and then exchanged using a combination of three different counter ions: Fe<sup>+3</sup>, Ca<sup>+2</sup> and K<sup>+1</sup>. The resulting inorganic composite membranes were characterized using several techniques: thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and small angle X-Ray scattering (SAXS). These techniques were used to identify the changes in the chemical and thermal properties of the membranes, as well as to evaluate changes in the resulting morphology. Proton conductivity and methanol permeability were obtained to understand how the different combination of counter ions promote or inhibit the transport of certain substances through the membrane, specifically for direct methanol fuel cell (DMFC) applications. Vapor-methanol permeability were measured for Nafion® processed with SCF CO<sub>2</sub>, and then exchanged using six different counter ions: Al<sup>+3</sup>, Fe<sup>+3</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup> K<sup>+1</sup> and for the double counter ion substitution membranes. Significant differences in their thermal, physical and transport properties were observed when the membrane was processed with SCF CO<sub>2</sub> and exchanged with the counter ions.

### 3.2. INTRODUCTION

Fuel cells are a promising power source for portable applications. A principal component for this technology is the proton exchange membrane (PEM); its function is to allow the transport of protons from anode to cathode while blocking the passage of fuel.<sup>1</sup> Non-fluorinated polymers, like sulfonated poly(styrene-isobutylene-styrene)<sup>2</sup>, sulfonated aromatic poly(etheretherketone) with (1,4-butanediol divinyl ether (BDVE)/triallyl isocyanurate (TAIC)<sup>3</sup>, sulfonated poly(arylene thioether sulfone)<sup>4</sup> and fluorinated polymers like polytetrafluoroethylene–poly(ethersulphone)–poly(vinylpyrrolidone) composite membranes with phosphoric acid, have been studied as proton exchange membranes (PEMs) for fuel cells applications<sup>5</sup>. Fluoropolymers have been used because they exhibited a range of outstanding properties such as chemical resistance and high-temperature stability.<sup>6</sup>

The most commonly used PEM today remains a sulfonated fluoropolymer called Nafion®. This membrane consists of a polytetrafluoroethylene backbone and regular spaced long perfluorovinyl ether pendant side chains terminated by a sulfonate ionic group.<sup>7</sup> Nafion® membranes are commonly used in direct methanol fuel cells, because they have very high proton conductivity ( $\sigma$ ) but also even Nafion® has higher than desired methanol permeability leading to the well-known methanol cross-over limitation.

Different researches have investigated the incorporation of acidic inorganic-organic fillers to Nafion® with the objective of obtaining Nafion® membranes with lower methanol permeability<sup>8,9</sup>, but some of these composite Nafion® membranes decreased the proton conductivity similar to the reduction in methanol permeability.

Supercritical fluid (SCF) processing with CO<sub>2</sub> has been another alternative used to modify the morphology of fluoroelastomers. SCF CO<sub>2</sub> possesses gas-like mass transport properties (*e.g.* high diffusivity and low viscosity) and liquid-like densities to easily penetrate the membrane, while aligning functional groups according to physico-chemical affinities. NMR studies suggest specific

interactions between  $^{19}\text{F}$  isotope and supercritical  $\text{CO}_2$  which may support the high solubility of many fluorocarbon polymers in  $\text{CO}_2$ .<sup>10</sup>

Studies suggested that SCF  $\text{CO}_2$  promotes the transport of protons through Nafion<sup>®</sup> membranes and inhibits the methanol permeability. The molecular interaction between  $\text{CO}_2$  and the fluorocarbon backbone of Nafion<sup>®</sup> makes a unique rearrangement in the polymer chain. Additionally, the incorporation of counter ions into Nafion<sup>®</sup> influences the ionic domains uniquely for each counter ion studied, but also influences the crystallinity, the morphology, and the water swelling, which are very important in the transport of protons through the membrane.<sup>11</sup> Therefore, the goal of this investigation is to understand how the changes in the morphology of Nafion<sup>®</sup> exposed to SCF  $\text{CO}_2$  and different combination of counter ions affects their transport, thermal and physical properties. Additionally, the membranes were characterized for vapor and liquid methanol permeability, proton conductivity and water swelling; the results were explained with some additional materials characterization techniques (*e.g.*, TGA and SAXS).

### **3.3. EXPERIMENTAL**

#### **3.3.1. Materials**

Ultra high purity  $\text{CO}_2$  (99.998% purity) was acquired from Linde Gas Puerto Rico, Inc. Nafion<sup>®</sup> 117 was obtained from Ion Power, Inc. Other chemicals used include: Potassium chloride –KCl-, (Sigma-Aldrich, anhydrous powder, 99.99%), calcium chloride anhydrous – $\text{CaCl}_2$ -, (Acros Organic, anhydrous powder, 96%), barium chloride – $\text{BaCl}_2$ -, (Fisher Scientific, anhydrous powder, 99.99%), copper chloride – $\text{CuCl}_2$ -, (Sigma-Aldrich, anhydrous powder, 99.99%), aluminum chloride – $\text{AlCl}_3$ -, (Acros Organic, extra pure anhydrous, 99.99%), ferric chloride – $\text{FeCl}_3$ -, (Sigma-Aldrich, anhydrous powder, 99.99%), Hydrogen peroxide – $\text{H}_2\text{O}_2$ - (3 wt% solution in water stabilized), Sulfuric acid – $\text{H}_2\text{SO}_4$ - (Sigma-Aldrich, ACS reagent, 95.0-98.0%) and Methanol – $\text{CH}_3\text{OH}$ - (Fisher Scientific, ACS reagent) were employed as received.

### **3.3.2. Sample preparation**

Nafion® membranes used were pre-treated using a procedure as follows: the membrane was first treated with a hydrogen peroxide solution (3% wt) during 1 h at 80°C, and then washed with deionized water for 1 h at 80°C. After the initial wash, the membrane was protonated with sulfuric acid (1 M), and finally washed with deionized water; both steps for 1 h at 80°C each.

#### **3.3.2.1. Double cation-substitution**

Nafion® membranes were processed with SCF CO<sub>2</sub> at 40°C and 100 bar during one hour in a supercritical fluid extractor (Isco SFX 2-10). The SCF CO<sub>2</sub> flowed parallel to the membrane during the experimentation. The double counter ion solution was obtained mixing equal volumes of a 1M solution of KCl and 1M solution of CaCl<sub>2</sub>, for example. After the SCF processing, the membrane was submerged in a double-cation solution for 48 hours. The resulting cation-exchanged Nafion® membranes were washed using deionized water and dried at 60°C during 24 h.

### **3.3.3. Thermogravimetric analysis (TGA)**

The thermal degradation behavior and water loss for each membrane was determined using a Mettler Toledo 851e instrument. In each experiment, polymer samples weighting approximately 5-10 mg were used. Degradation temperatures were determined after heating the polymer samples to 800°C at 10°C/min under a nitrogen atmosphere.

### **3.3.4. Differential scanning calorimetry (DSC)**

The thermo physical properties were determined using differential scanning calorimetry (DSC). A Texas Instrument DSC Q2000 unit was used for this purpose. In each experiment, polymer samples weighting approximately 5-10 mg were used. The samples were pre-heated from 30°C to 110°C at 10°C/min and then cooled down 110°C to -90°C at 5°C/min. Phase transitions (T<sub>g</sub>) and melting points for each membranes were determined after heating the polymer samples from -80°C to 350°C at 10°C/min under nitrogen atmosphere.

### 3.3.5. Small angle X-Ray scattering (SAXS)

The structure and morphology of the membranes were obtained using a small angle X-ray scattering (SAXS) instrument, to evaluate morphological differences between Nafion® and Nafion® processed with SCF CO<sub>2</sub> and cation exchanged. The data were analyzed using a one dimension SASXess mc<sup>2</sup> and a SAXSquan™ Software.

### 3.3.6. Methanol Liquid-Phase Permeability

The liquid-phase permeability was measured using a side-by-side glass diffusion cell. One side contained the permeant (*e.g.*, methanol) in a 2 M methanol-water solution, while the other side only contained deionized water. The concentration of the compound that permeated through the membrane was determined using a gas chromatography (GC) equipped with a thermal conductivity (TC) detector (Shimadzu, GL-8). First a calibration curve was created, then measurements were determined after different times. Permeability was determined by using equation (2.1)

$$C_B(t) = \frac{PC_A A}{V_b L} \left( t - \frac{L^2}{6D} \right) \quad (2.1)$$

where,  $C_A$  {mol/cm<sup>3</sup>} is the methanol concentration (permeant),  $C_B$  {mol/cm<sup>3</sup>} is the concentration of the compound that permeated through the membrane after different times,  $L$  is the membrane thickness {cm},  $V_b$  the volume of the receptor compartment {0.39 cm<sup>3</sup>},  $A$  the diffusional cross-sectional area of the membrane {0.64 cm<sup>2</sup>} and  $P$  the permeability {cm<sup>2</sup>/s}. The permeability ( $P$ ) was determined from the slope of the concentration  $C_B(t)$  versus time.

### 3.3.7. Methanol Vapor-Phase permeability

Vapor permeability for each membrane was measured using an oven at 35°C with inert atmosphere of nitrogen. The experiment consisted in obtaining the weight loss of methanol,

during a period of time. An equation obtained by Aviles-Barreto and Suleiman<sup>12</sup> was used to determine effective permeability ( $P_{eff}$ ).

$$P_{eff} \left[ \frac{cm^2}{s} \right] = \frac{L * VTR}{(P_{I_1} - P_{I_2}) \left( \frac{MW_i}{RT} \right)} \quad (3.1)$$

VTR is the vapor transfer rate.  $VTR$  calculates the permeant rate through the membrane in the vapor phase during a period of time.

$$VTR \left[ \frac{g}{cm^2 s} \right] = \frac{G}{tA} \quad (3.2)$$

$G$  is the permeant weight [g],  $t$  is the time [s] and  $A$  is the diffusion cross-sectional area [ $cm^2$ ],  $L$  is the thickness of the membrane [cm],  $P_{I_1}$  is the partial pressure of the permeant inside the vial and  $P_{I_2}$  is the partial pressure of the permeant outside the vial approximated to zero.  $R$  is the universal gas constant [62400  $cm^3$  mmHg / mol K],  $MW_i$  is the permeant molecular weight [g/mol] and  $T$  is the experimental temperature. For the experimentation, because exists 100% of permeant saturation  $P_{I_1} = P_i^{vap}$  of the compound and  $P_{I_2} = 0$  because,  $P_{N_2} \gg P_{I_2}$ , simplifying equation 3.2 to:

$$P_{eff} \left[ \frac{cm^2}{s} \right] = \frac{L * VTR}{P_i^{vap} \left( \frac{MW_i}{RT} \right)} \quad (3.3)$$

### 3.3.8. Proton conductivity

The proton conductivity ( $\sigma$ ) [S / cm] of each membrane was measured normal to the plane using AC electrochemical impedance spectroscopy (EIS). The measurements were carried out on an AC Solartron impedance system: 1260 impedance analyzer, 1287 electrochemical interface, Zplot software. The range of frequency and voltage used were from 0.1 Hz to 1 MHz and 10-15 mV respectively at room temperature and 100% relative humidity. The membranes were first immersed in an excess of deionized water at 25°C before the experimentation during 24 h. The proton conductivity was calculated from the impedance data, using the equation 2.2:

$$\sigma = \frac{L}{R_{\Omega} A} \quad (2.2)$$

where  $L$  is the distance between electrodes {0.3 cm},  $A$  {cm<sup>2</sup>} is the area obtained from the product of the thickness and the width of the membrane.  $R_{\Omega}$  {1/S} was obtained from the low intersect of the high frequency semicircle (Nyquist plot) on the complex impedance plane with the real component of the impedance axis ( $Re(z)$ ).

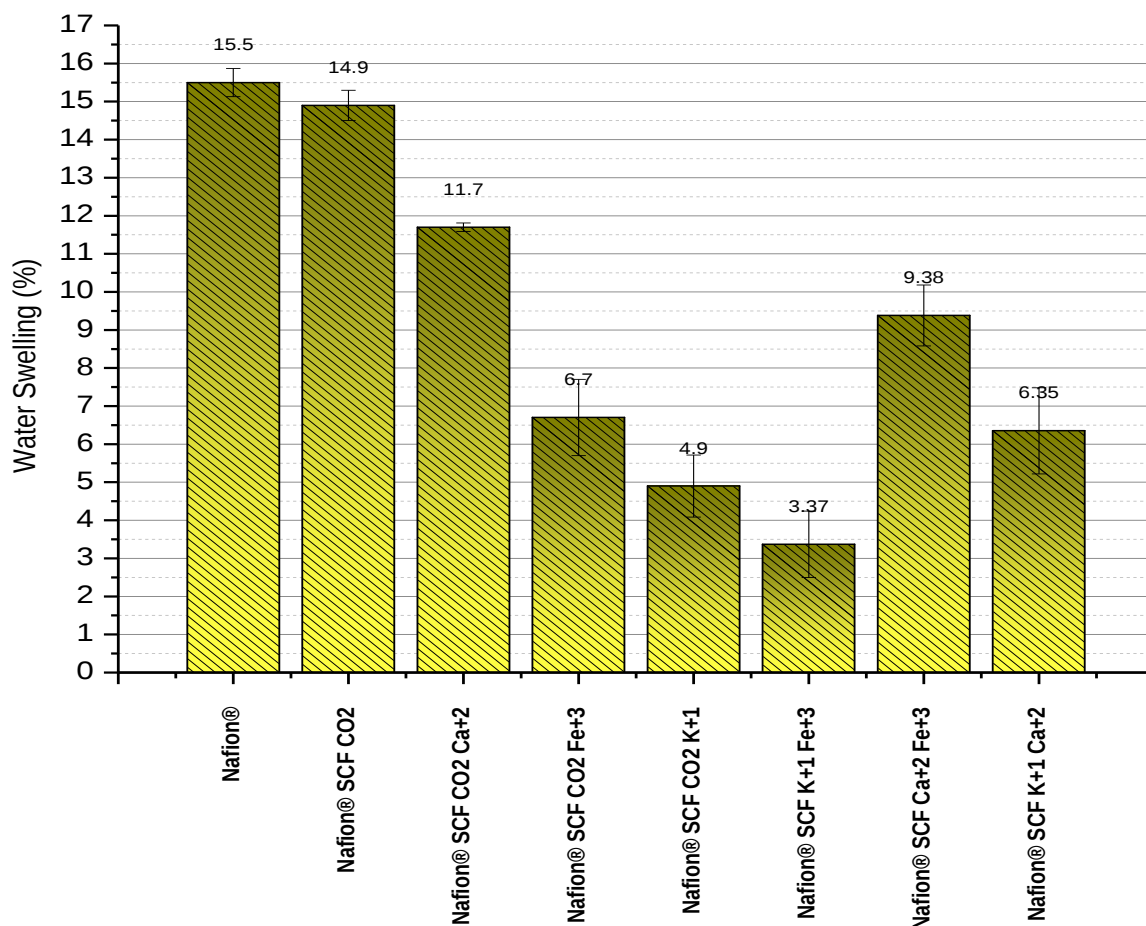
### 3.3.9. Water Swelling

Water absorption in the membranes was measured immersing each membrane in an excess of deionized water at 25°C. The weight of the sample initially dried at 60°C for 24 h in an oven was originally recorded, as well as the weight of the membrane after immersion in water. The weights of the wet membranes were measured after different time interval until swelling equilibrium was reached. Each reported result represents the average of at least three repetitions.

### 3.4. RESULTS AND DISCUSSIONS

#### 3.4.1. Water Swelling

Figure 3.1 shows the comparison between water swelling for Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and double counter ion exchanged. Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with K<sup>+</sup> and Fe<sup>3+</sup> reached the lowest percent of water swelling; however, Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with Ca<sup>2+</sup> and Fe<sup>3+</sup> obtained the highest water swelling for the double counter ion combination. Complex arrangement in their morphologies due to the substitution of both counter ion and SCF CO<sub>2</sub> processing can be attributed to this behavior. Studies with Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with counter ions demonstrated that the capacity of Nafion<sup>®</sup> to absorb water decreased; therefore, this behavior correspond to a complex arrangement in the structure of the ionomer domains and the morphology of the membrane.<sup>11</sup>



**Figure 3.1.** Comparison between the water swelling for Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and then the double counter ion exchanged.

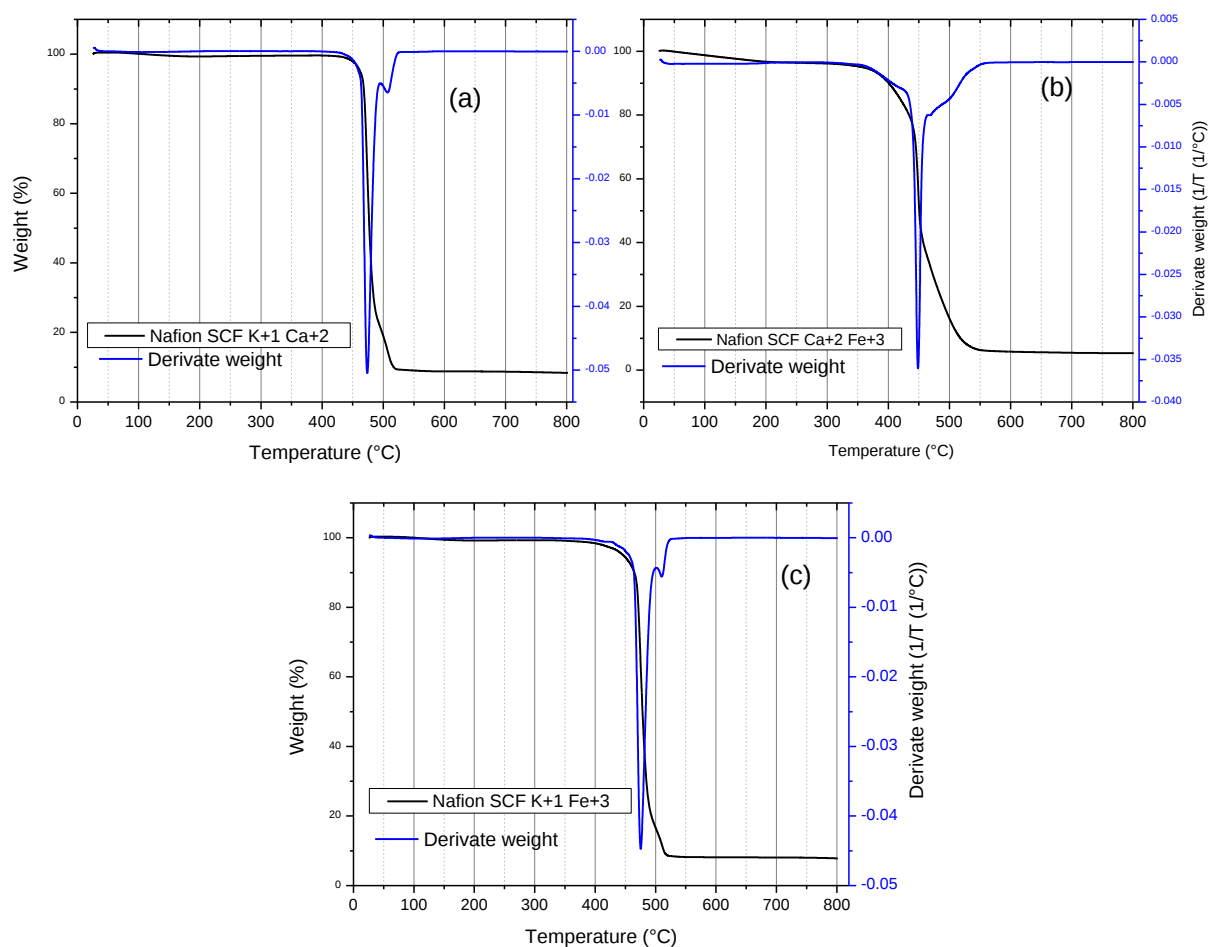
The incorporation of two counter ions into the membrane produced unique water swelling for each of the combination studied. The interaction between the water and the sulfonic group is lower, because this chemical group was exchanged by counter ions and the water absorbed depends on the chemical nature of the ionic group. Table 3.1 summarizes the water swelling results for these experiments.

**Table 3.1** Water Swelling for Nafion® membranes

| Membrane                                                      | Water Swelling<br>% |   |      |
|---------------------------------------------------------------|---------------------|---|------|
| Nafion®                                                       | 15.5                | ± | 0.4  |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | 6.35                | ± | 1.13 |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | 3.37                | ± | 0.87 |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 9.38                | ± | 0.8  |

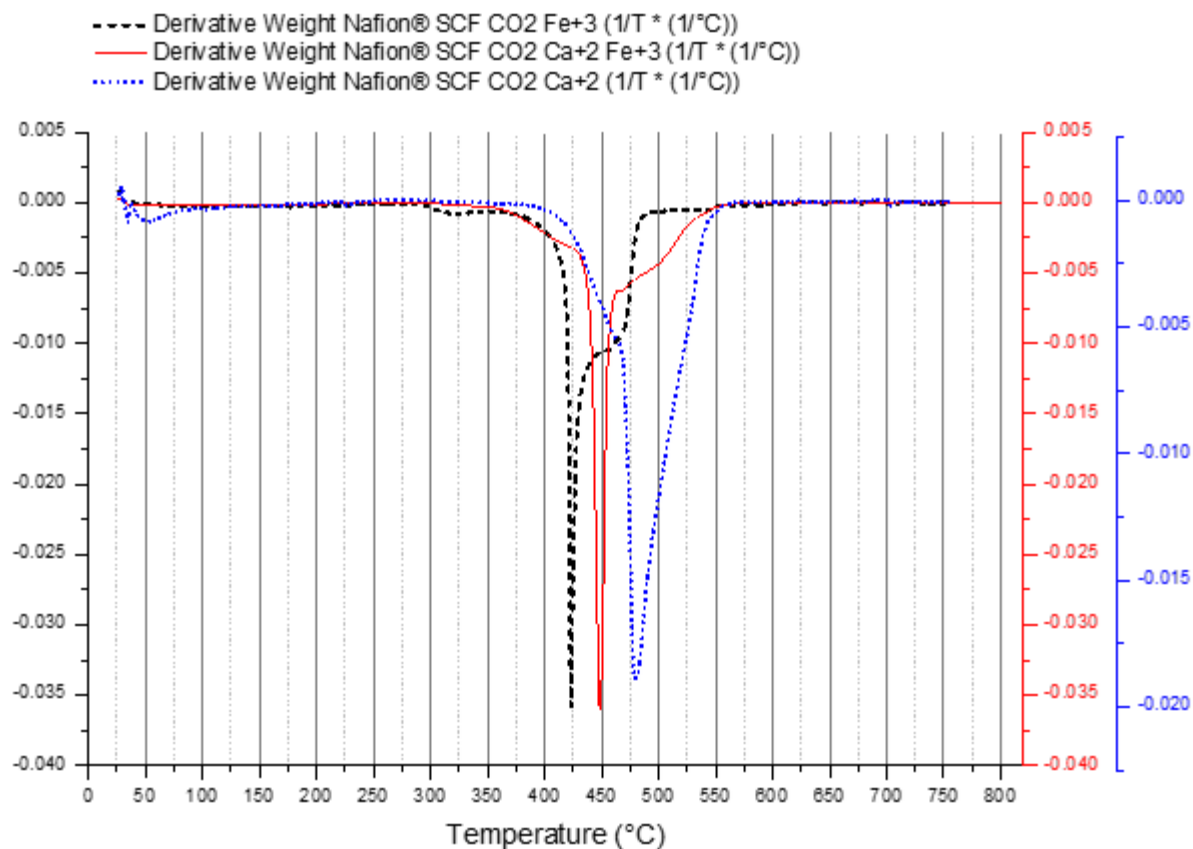
### 3.4.2. Thermogravimetric Analysis (TGA)

Figure 3.2 presents the TGA curves for Nafion®, processed with SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup>, SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup>, SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup>. A unique feature was observed for Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup>; this combination of counter ions improved the thermal stability of the Nafion® membrane significantly after the double counter ion substitution. Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> increased the thermal stability of Nafion® even further than Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> even though the degradation temperature of Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> was not reached. Figure 3.3 shows the comparison between the derivative weight of the TGA curve of Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup>, Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> and Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup>. Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> obtained a small weight loss at 335.54 °C and other major weight loss at 423.22°C; instead Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> present only one weight loss at 479.44°C. The combination of both counter ions stabilized the sulfonic group, fluorocarbon backbone, perfluorovinyl ether improved their degradation temperature until 449°C.

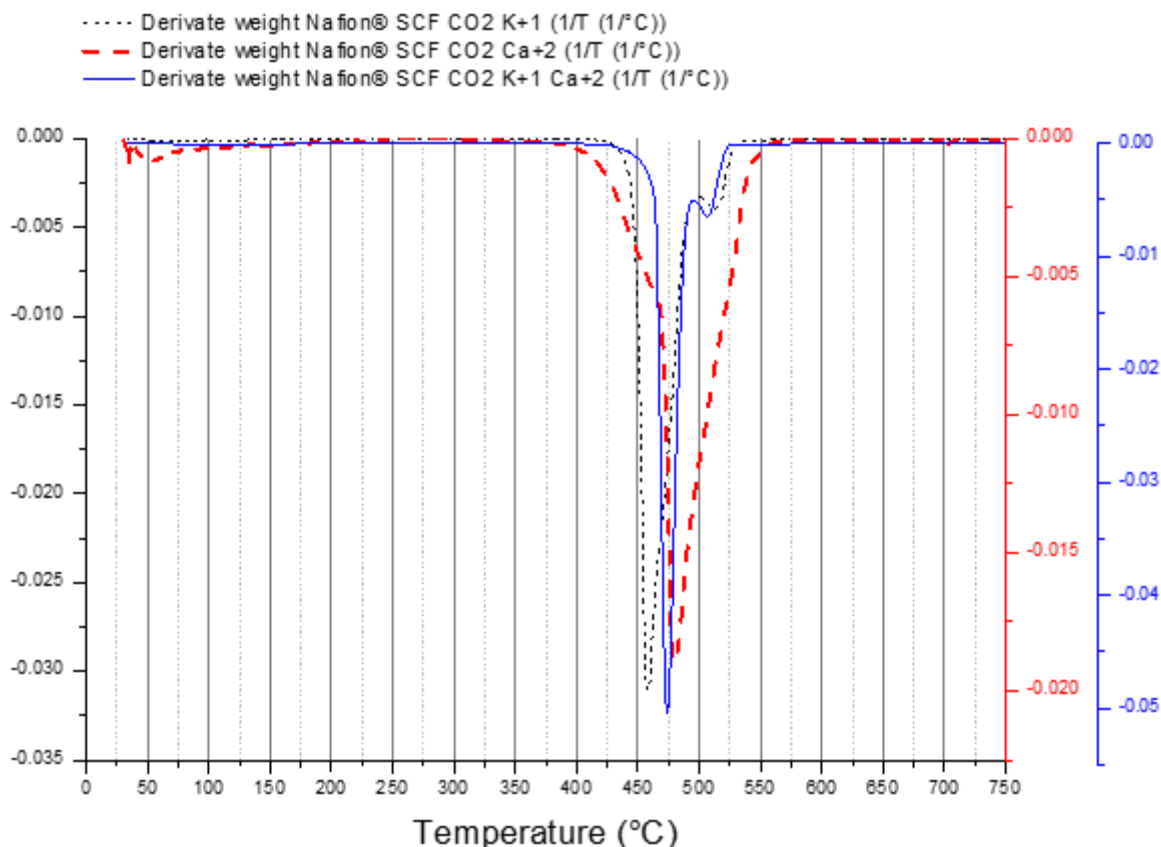


**Figure 3.2.** Thermogravimetric analysis (TGA) for Nafion® (a), processed with SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup> (b) SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> (c) SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup>.

Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup> increased the thermal stability of Nafion® even further than Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> but the degradation temperature of Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> was not reached. Figure 3.4 presents the comparison between the derivative weight curves of TGA for these combinations of cations. Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> present two peaks at 459°C and 533°C. Nafion® SCF CO<sub>2</sub> exchanged with the double-combination of counter ions improved the temperature for the first peak at 474°C, even though decreased the second one from 523 to 507°C. Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> present only one peak at 479°C.

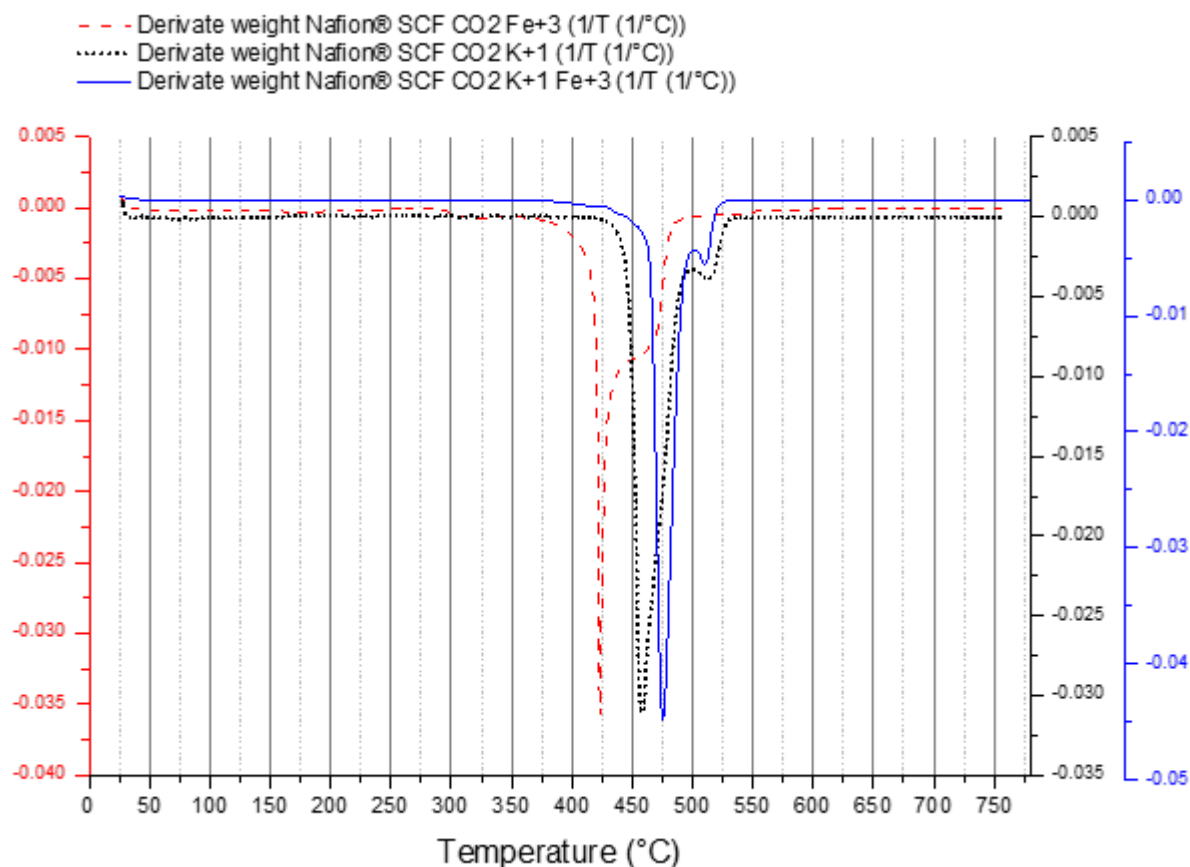


**Figure 3.3.** Comparison between the derivative weight of TGA for Nafion®, processed with SCF CO<sub>2</sub> Ca<sup>2+</sup>, SCF CO<sub>2</sub> Fe<sup>3+</sup>, SCF CO<sub>2</sub> Ca<sup>2+</sup> Fe<sup>3+</sup>.



**Figure 3.4.** Comparison between the derivate weight of TGA for Nafion®, processed with SCF CO<sub>2</sub> K<sup>+</sup>, SCF CO<sub>2</sub> Ca<sup>2+</sup>, SCF CO<sub>2</sub> K<sup>+</sup> Ca<sup>2+</sup>.

Nafion® SCF CO<sub>2</sub> K<sup>+</sup> Fe<sup>3+</sup> obtained the same behavior than Nafion® SCF CO<sub>2</sub> K<sup>+</sup> Ca<sup>2+</sup>. Figure 3.5 shows the comparison between the derivate weight curves of TGA for the combination of potassium and iron. The degradation behavior for the combination of counter ions was limited by the chemical nature of the potassium; however the degradation behavior of Nafion® SCF CO<sub>2</sub> Ca<sup>2+</sup> Fe<sup>3+</sup> was limited by the nature of both counter ions.



**Figure 3.5.** Comparison between the derivative weight of TGA for Nafion®, processed with SCF CO<sub>2</sub> K<sup>+</sup>, SCF CO<sub>2</sub> Fe<sup>3+</sup>, SCF CO<sub>2</sub> K<sup>+</sup> Fe<sup>3+</sup>.

Studies of Nafion® processed with SCF CO<sub>2</sub> demonstrated that the supercritical fluid changed the degradation temperature of the fluorocarbon backbone and the perfluorovinyl ether of Nafion® but the corresponding degradation of the sulfonic group remained unchanged. Nafion® processed with SCF CO<sub>2</sub> exposed to different counter ions, presented changes in the degradation temperatures of both fluorocarbon backbone, perfluorovinyl ether and the sulfonic group. Table 3.2 summarized the degradation temperatures for each combination of the counter ions studied.

**Table 3.2.** Degradation temperatures for Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and double cation-exchanged.

| <b>Membrane</b>                                                           | <b>1<sup>st</sup><br/>degradation<br/>(°C)</b> | <b>2<sup>nd</sup><br/>degradation<br/>(°C)</b> | <b>3<sup>rd</sup><br/>degradation<br/>(°C)</b> | <b>4<sup>th</sup><br/>degradation<br/>(°C)</b> | <b>5<sup>th</sup><br/>degradation<br/>(°C)</b> |
|---------------------------------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| Nafion <sup>®</sup>                                                       | 65                                             | 330                                            | 450                                            | 470                                            | 500                                            |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | *                                              | *                                              | *                                              | 474                                            | 507                                            |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | *                                              | *                                              | *                                              | 475                                            | 510                                            |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | *                                              | *                                              | 449                                            | *                                              | *                                              |

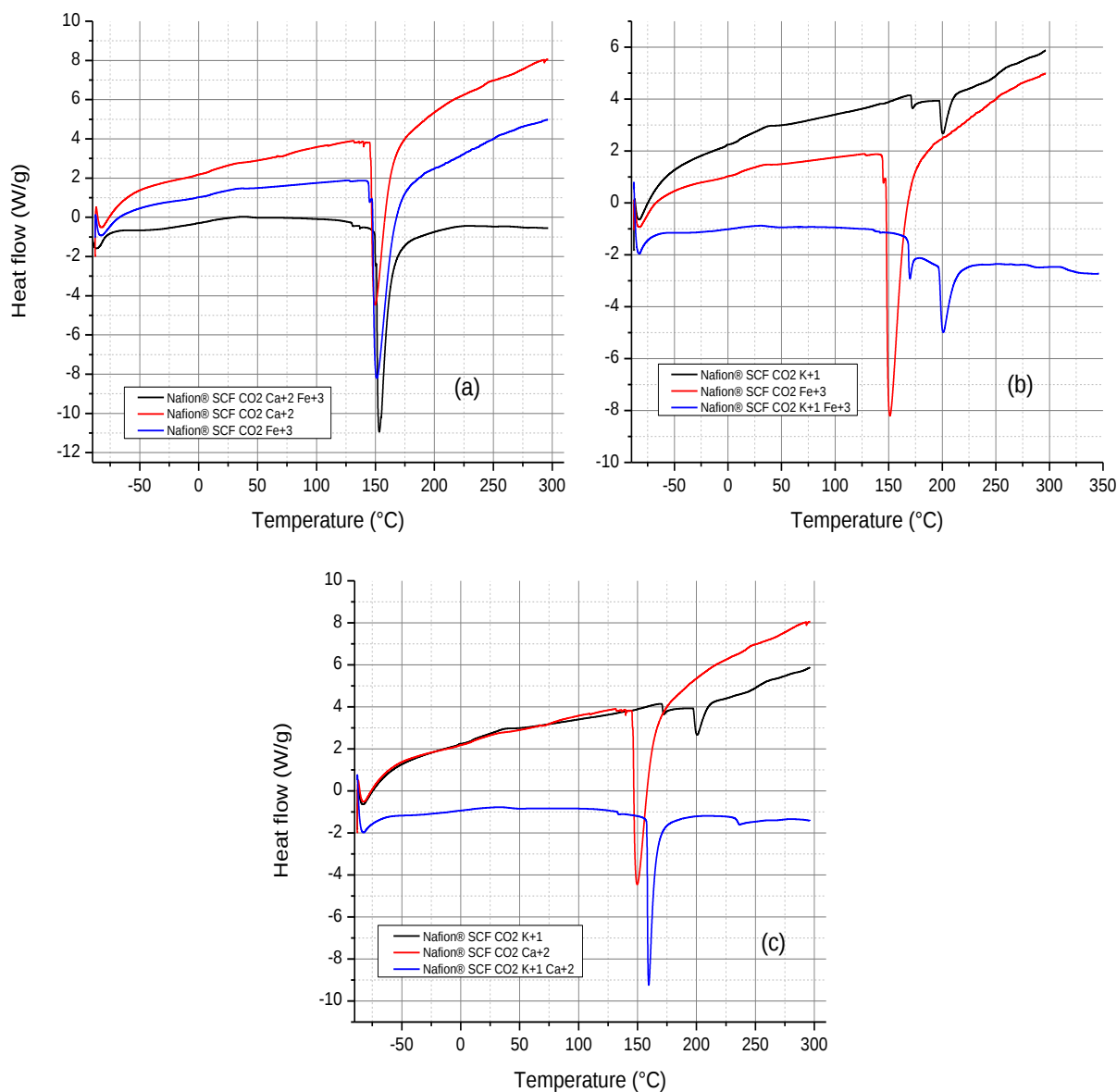
\* Absent

### 3.4.3. Differential Scanning Calorimetry (DSC)

Figure 3.6 presents the comparison between DSC for Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup>, SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> and SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup>. The combination of counter ions produced a unique modification on the molecular conformation of the ionic domain and the crystalline region of Nafion<sup>®</sup> SCF CO<sub>2</sub>. Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> present shifts in the energy and melting temperature the respect to Nafion<sup>®</sup> SCF CO<sub>2</sub> Ca<sup>+2</sup> and Nafion<sup>®</sup> SCF CO<sub>2</sub> Fe<sup>+3</sup>. Nafion SCF CO<sub>2</sub> Ca<sup>+2</sup> present only one endothermic peak; in this case the counter ion reduced the temperature of the crystalline region and ionic cluster to a single temperature for the membrane; instead Nafion<sup>®</sup> SCF CO<sub>2</sub> Fe<sup>+3</sup> obtained changes related to the melting temperature although presented two endothermic peaks. The combination of both counter ions produced a shift in the ionic and the crystalline peak; a new molecular conformation of the polymeric chain was created. The double cation-exchanged reduced the temperature of the crystalline region and ionic cluster to a single temperature for this membrane to 153.2°C.

The processing of Nafion<sup>®</sup> with SCF CO<sub>2</sub> and exchanged with K<sup>+1</sup> and Ca<sup>+2</sup> produced shifts in the energy and melting temperature respect to Nafion<sup>®</sup> SCF CO<sub>2</sub> K<sup>+1</sup> and Nafion<sup>®</sup> SCF CO<sub>2</sub> Ca<sup>+2</sup>. Nafion SCF CO<sub>2</sub> Ca<sup>+2</sup> present only one endothermic peak at lower temperatures than Nafion<sup>®</sup>; the processing of Nafion<sup>®</sup> SCF CO<sub>2</sub> with K<sup>+1</sup> presented changes related to the melting temperature, obtained two endothermic peaks at higher temperatures than Nafion<sup>®</sup>. The combination of both

counter ions produced a shift in the ionic and the crystalline peak. The new peak position of the crystalline region is located at higher temperature (236.3°C) respect to a both single counter ion; instead a reduction in the melting energy was obtained.



**Figure 3.6.** Comparison between DSC for Nafion® processed with (a) SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup>(b) SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> and (c) SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup>.

DSC curves for Nafion® processed with SCF CO<sub>2</sub> presented shifts in two endothermic peaks, the first at 154.82 correlated to the transition of the ionic domains, and the second peak at 194.58 °C was attributed to the crystalline regions.<sup>11</sup> The changes in temperature with respect to unprocessed Nafion®, were related to the energy needed to overcome the crystalline bonding forces and changes in the molecular conformation of the chains in the polymer. Nafion® SCF CO<sub>2</sub> exchanged with cations produced shifts in the energy and melting temperature with respect to unprocessed Nafion® and Nafion® SCF CO<sub>2</sub>. These changes in the membrane were associated with new arrangements in the polymeric structure, specifically in the ionic cluster and the crystalline region, related to changes in free volume and attractive forces induced by the SCF CO<sub>2</sub> and the cation on the sulfonic groups, the polymer backbone and perfluorovinyl ether.<sup>11</sup>

Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> increased the energy required to produce the melting peak for the ionic domain and the crystalline region. The temperatures for both peak, remained almost equal to Nafion® SCF CO<sub>2</sub> K<sup>+1</sup>. In this case the DSC trend was limited by the chemical nature of potassium, although exists a new molecular configuration of the polymeric chain induced by both counter ions. Table 3.3 summarized the melting enthalpies and temperatures for Nafion® membranes.

**Table 3.3.** Melting enthalpies and temperatures for Nafion® membranes.

| Membrane                                                      | First Transition       |                                         | Second Transition      |                                         |
|---------------------------------------------------------------|------------------------|-----------------------------------------|------------------------|-----------------------------------------|
|                                                               | T <sub>m</sub><br>(°C) | ΔH <sub>m</sub><br>(J g <sup>-1</sup> ) | T <sub>m</sub><br>(°C) | ΔH <sub>m</sub><br>(J g <sup>-1</sup> ) |
| Nafion®                                                       | 156.8                  | 4.7                                     | 191.7                  | 60.7                                    |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | 159.5                  | 34.6                                    | 236.3                  | 0.54                                    |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | 169.6                  | 3.65                                    | 200.9                  | 24.75                                   |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 153.2                  | 60.4                                    | Absent                 | Absent                                  |

#### 3.4.4. Small angle X-Ray scattering (SAXS)

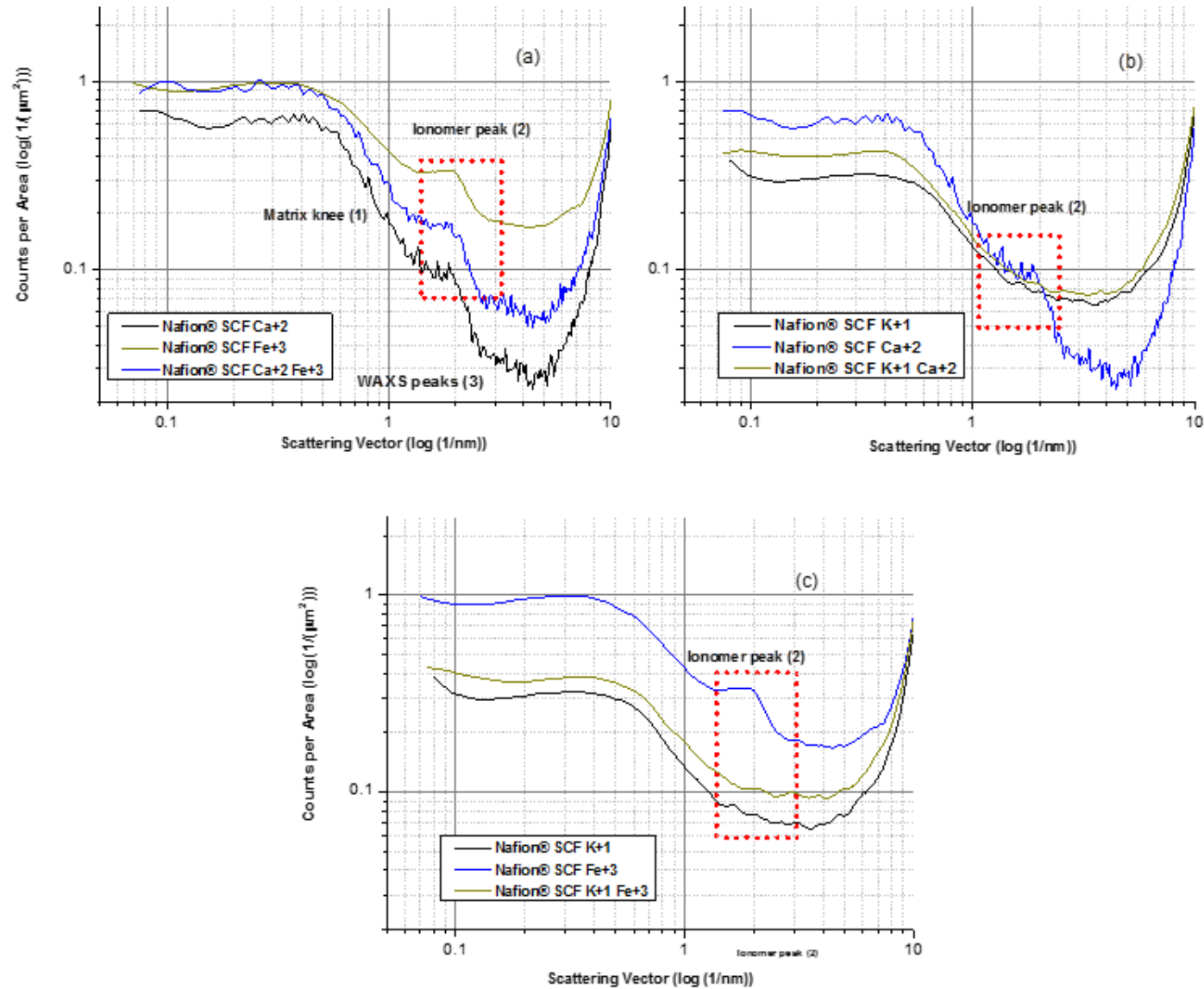
SAXS profiles for Nafion® membranes are shown in Figures 3.7. Nafion® processed with SCF CO<sub>2</sub> and exchanged with Ca<sup>+2</sup> and Fe<sup>+3</sup> presented changes in the SAXS profile with respect to Nafion®

exchanged with a single counter ion, specialty in ionomer peak (2) and the WAXS area (3). (Figure 3.7(a)). The variation in the ionomer peak and the crystallinity for the Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> agrees with the previously presented DSC results. The Bragg distance suffered a decreased with respect to Nafion®; even though the Bragg distance for Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> (3.52 nm) and Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> (3.08 nm) was not reached.

The ionomer peak of Nafion® processed with SCF CO<sub>2</sub> and exchanged with K<sup>+1</sup> and Ca<sup>+2</sup> presented changes in the SAXS profile with respect to Nafion® exchanged with a single counter ion. (Figure 3.7(b)). In this case the SAXS profile was limited by the chemical nature of potassium, although a new molecular configuration of the polymeric chain was induced by both counter ion. Nafion SCF CO<sub>2</sub> and exchanged with K<sup>+1</sup> and Fe<sup>+3</sup> presented almost the same trend than SCF CO<sub>2</sub> and exchanged with K<sup>+1</sup> and Ca<sup>+2</sup>: in both SAXS profile the intensity of the ionomer peak disappeared due the interaction with the cations. These results seem to indicate that the double cation-exchanged produced a new molecular conformation of the polymer different that Nafion® exchanged with a single counter ion. The proton conductivity and methanol permeability (liquid and vapor) will be linked with these results, which seem to indicate the effect of the double counter ion over the interconnection of sulfonic groups and the crystallinity (associated with the free volume) of Nafion®. Table 3.4 shows Bragg distance for ionomer peak for Nafion® and Nafion® processing with SCF CO<sub>2</sub> and exchanged with the cation combination.

**Table 3.4.** Bragg distance for ionomer peak for Nafion® and Nafion® processing with SCF CO<sub>2</sub> and exchanged with cations.

| Sample                                                        | d <sub>bragg</sub> (nm) | Cation-atomic<br>radius (nm) |      |
|---------------------------------------------------------------|-------------------------|------------------------------|------|
| Nafion®                                                       | 3.97                    | -----                        |      |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | Absent                  | 0.22                         | 0.18 |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | Absent                  | 0.22                         | 0.14 |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 3.72                    | 0.18                         | 0.14 |



**Figure 3.7.** SAXS profile Nafion® processed with (a) SCF CO<sub>2</sub> Ca<sup>2+</sup> Fe<sup>3+</sup> (b) SCF CO<sub>2</sub> K<sup>+</sup> Ca<sup>2+</sup> and (c) SCF CO<sub>2</sub> K<sup>+</sup> Fe<sup>3+</sup>.

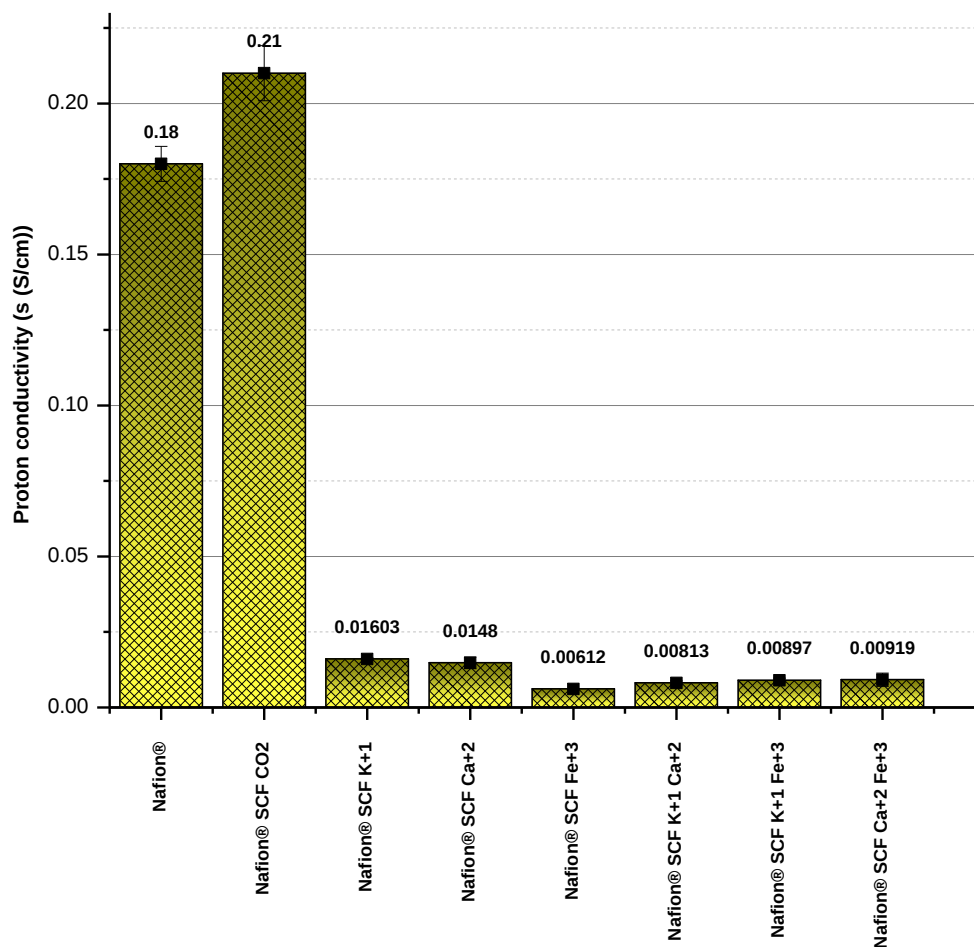
### 3.4.5. Proton conductivity

Figure 3.8 shows the comparison between proton conductivity for Nafion® processed with SCF CO<sub>2</sub> and exchanged with a single and double counter ion. Nafion® SCF CO<sub>2</sub> exchanged with K<sup>+1</sup> and Ca<sup>+2</sup> decreased the proton conductivity more than Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> and Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup>. Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> shows a further decrease in the proton conductivity as compared to Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> although the proton conductivity of Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> was not reached. Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> obtained the same behavior than Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup>: the proton conductivity of Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> decreased although the proton conductivity of Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> was not reached.

The processing with SCF CO<sub>2</sub> and exchanged with double counter ion produced a different reordering of the perfluorinated, perfluorovinylether chains and the ionic domain than Nafion® processing with SCF CO<sub>2</sub> exchanged with a single counter ion. The proton conductivity was inhibited since each combination of counter ions created new morphologies and changed the mobility of the proton through the membrane; also inhibited the complex formation between the proton and the sulfonic group. Table 3.5 shows the results for the membranes exchanged with the double counter ions.

**Table 3.5** Proton Conductivity for Nafion® membranes.

| Membrane                                                      | Proton conductivity<br>$\sigma$ (S/cm) |   |         |
|---------------------------------------------------------------|----------------------------------------|---|---------|
| Nafion®                                                       | 0.18                                   | ± | 0.006   |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | 0.00813                                | ± | 6.2E-4  |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | 0.00897                                | ± | 7.6E-4  |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 0.00919                                | ± | 0.00218 |



**Figure 3.8.** Comparison between proton conductivity for Nafion® processed with SCF CO<sub>2</sub> and exchanged with a single and double cation.

### 3.4.6. Methanol Liquid-Phase Permeability

Methanol permeability of Nafion® membranes processed with SCF CO<sub>2</sub> and double cation-exchanged are presented in Figure 3.9. The incorporation of two counter ions (using potassium like one of both) significantly reduced the methanol permeability of these membranes even further than Nafion® SCF CO<sub>2</sub> K<sup>+</sup>1 (this membrane possessed the lowest methanol permeability of the membranes exchanged with a single cation).

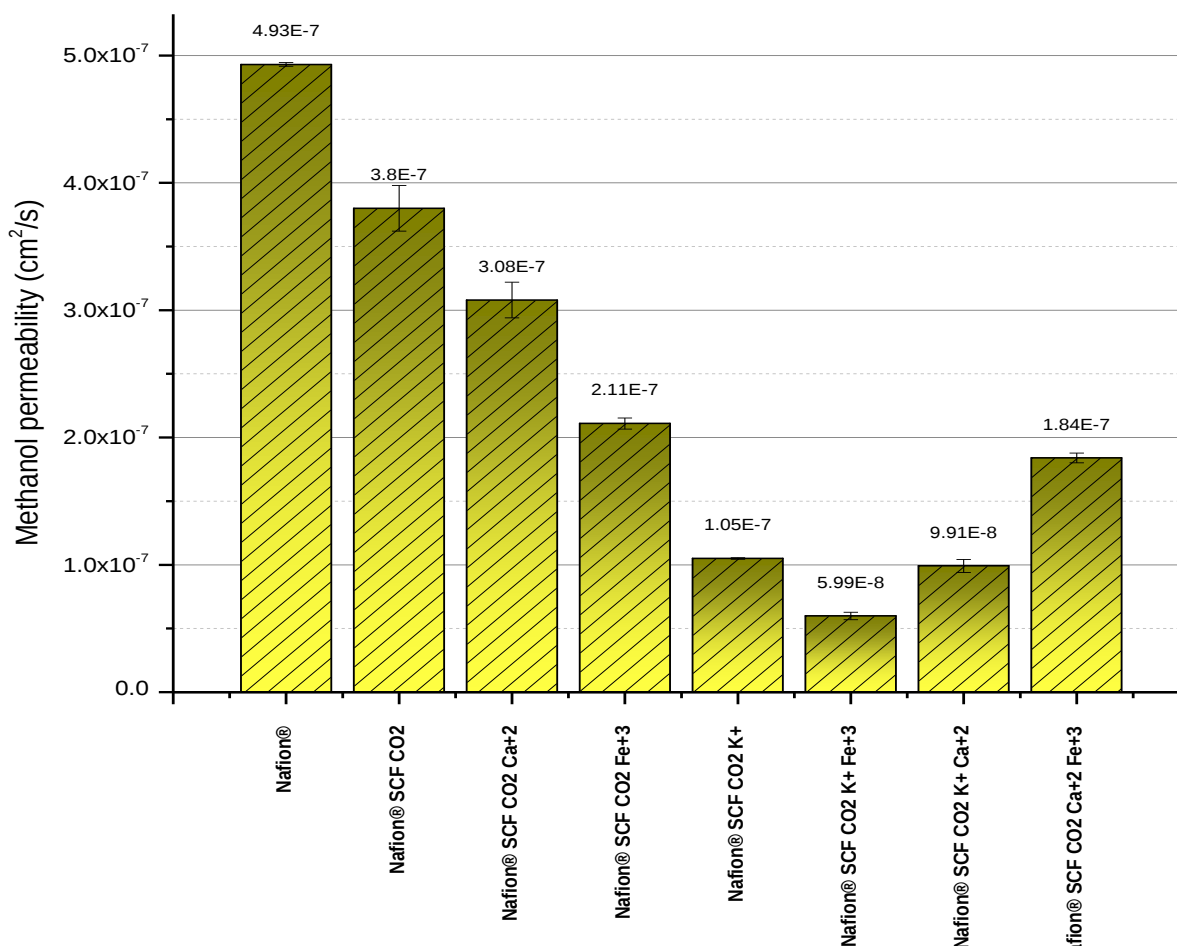
The methanol permeability of Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> decreased, and the incorporation of two counter ions significantly reduced the methanol permeability of these membranes even further. The molecular conformation induced by the SCF CO<sub>2</sub> and the cations exchanged inhibited the permeability of methanol through the membrane.

Nafion<sup>®</sup> SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> obtained the lowest methanol permeability of all the counter ion combination. This combination of counter ions reduced the methanol permeability of Nafion<sup>®</sup> a  $88 \pm 1 \%$  and  $43 \pm 1 \%$  with respect to Nafion<sup>®</sup> SCF CO<sub>2</sub> K<sup>+1</sup>. Nafion<sup>®</sup> SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup> decreased the methanol permeability of Nafion<sup>®</sup> an  $80 \pm 1 \%$  although only was obtained  $6 \pm 1 \%$  of reduction respect to Nafion<sup>®</sup> SCF CO<sub>2</sub> K<sup>+1</sup>.

Nafion<sup>®</sup> processed with SCF CO<sub>2</sub> and exchanged with calcium and iron obtained the highest methanol permeability for all the counter ion combination; instead decreased the methanol permeability of Nafion<sup>®</sup> more than Nafion<sup>®</sup> SCF CO<sub>2</sub> Ca<sup>+2</sup> and Nafion<sup>®</sup> SCF CO<sub>2</sub> Fe<sup>+3</sup>. The percent of reduction of methanol permeability were  $40 \pm 1\%$  and  $12 \pm 1\%$ , respectively. Table 3.6 presents the methanol permeability corresponding to each Nafion<sup>®</sup> membrane studied.

**Table 3.6** Methanol permeability for Nafion<sup>®</sup> membranes.

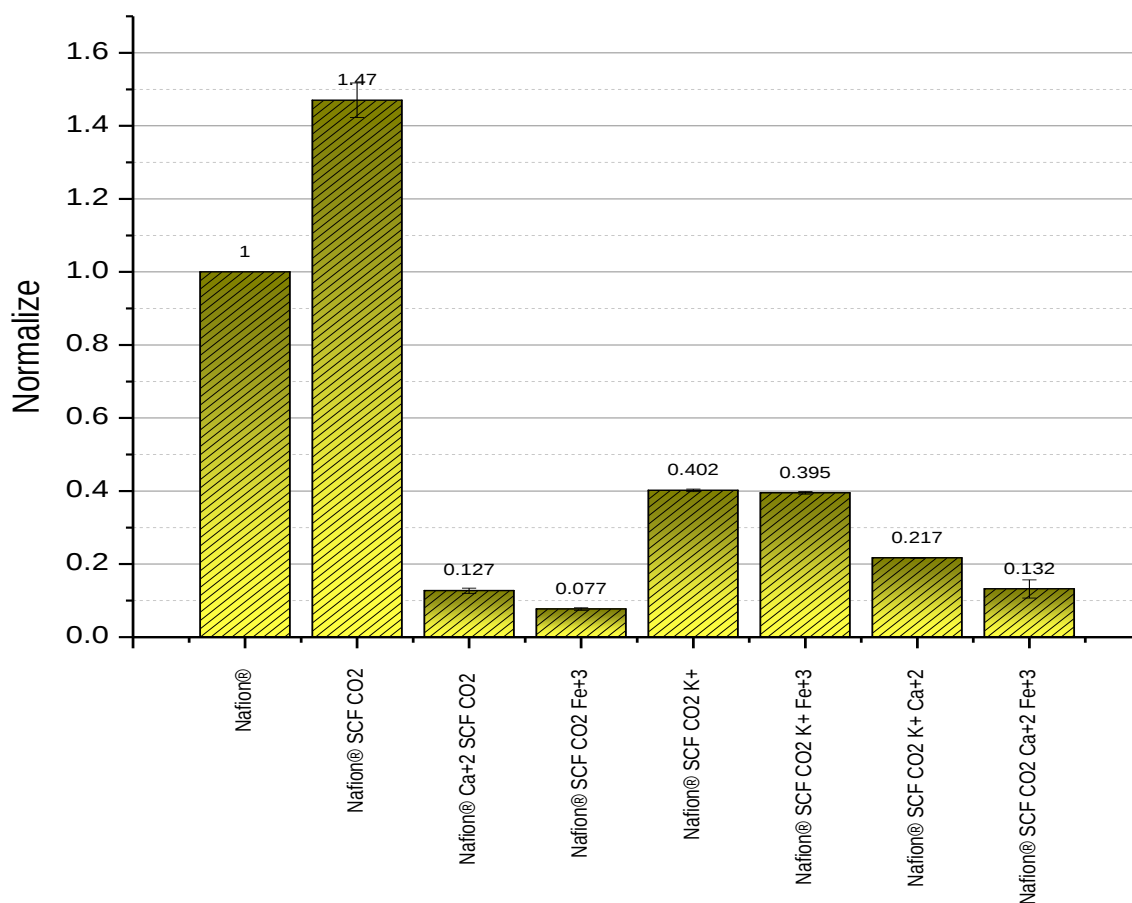
| Membrane                                                                  | Methanol<br>Permeability * 10 <sup>7</sup><br>(cm <sup>2</sup> /s) |
|---------------------------------------------------------------------------|--------------------------------------------------------------------|
| Nafion <sup>®</sup>                                                       | 4.93                                                               |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | 0.991                                                              |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | 0.599                                                              |
| Nafion <sup>®</sup> SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 1.84                                                               |



**Figure 3.9.** Comparison between methanol permeability for Nafion® processed with SCF CO<sub>2</sub> and then cation-exchanged.

This new molecular conformation induced by the double counter ion inhibited the diffusion of methanol through the membrane reducing its permeability. Each combination of cation produced a unique morphology (related to its free volume), changed the configuration of the ionic domain, inhibiting the chemical interaction of methanol with the sulfonic group.

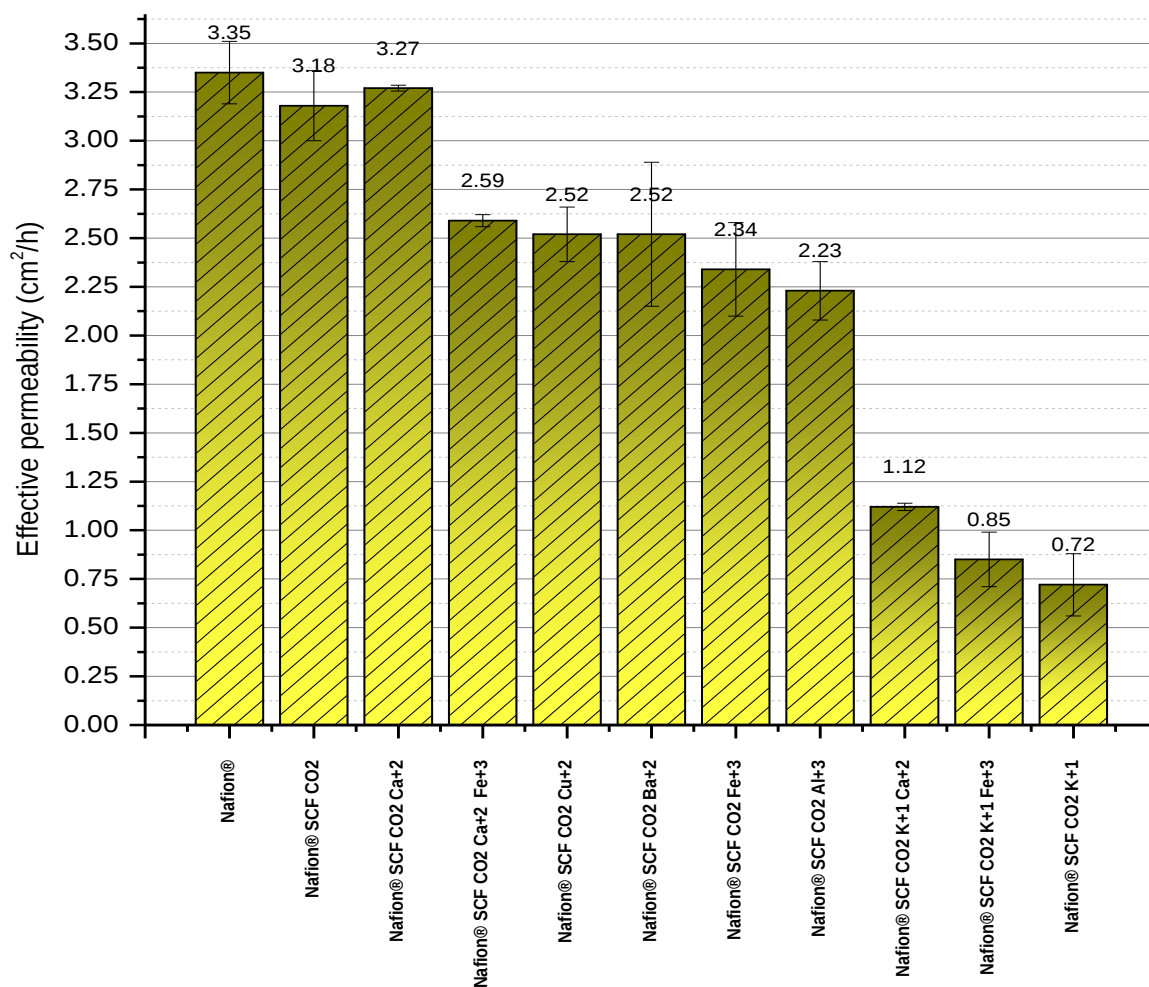
Figure 3.10 presents the normalized selectivities (Proton Conductivity / Methanol Permeability) for Nafion® Membranes processed with SCF CO<sub>2</sub> and exchanged with single and double counter ion (Normalized with selectivity of unprocessed Nafion®). Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> presented the largest effect in selectivity for the membranes exchanged with the combination of counter ions.



**Figure 3.10.** Normalized Selectivities (Proton Conductivity / Methanol Permeability) for Nafion® membranes processed with SCF CO<sub>2</sub> and exchanged with cations. (Normalized with selectivity of unprocessed Nafion®).

### 3.4.7. Methanol Vapor-Phase permeability

Nafion® was processed with supercritical fluid CO<sub>2</sub> and cation-exchanged using monovalent (e.g. potassium), divalent (e.g. calcium), trivalent (e.g. iron) and the combination of potassium, calcium and iron. Figure 3.10 shows the effective permeability of methanol of Nafion® processed with SCF CO<sub>2</sub> and exchanged with K<sup>+</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Cu<sup>+2</sup>, Al<sup>+3</sup> Fe<sup>+3</sup> or the double counter ion. Nafion® obtained the higher vapor-methanol permeability, decreasing 5% when processed with SCF CO<sub>2</sub>. Vapor-methanol effective permeability of Nafion® SCF CO<sub>2</sub> and exchanged with counter ions was reduced even further.



**Figure 3.11.** Comparison between vapor-methanol effective permeability for Nafion® processed with SCF CO<sub>2</sub> and then cation-exchanged.

Table 3.7 presents the vapor-methanol permeability for each Nafion® membrane studied. Nafion® processed with SCF CO<sub>2</sub> exchanged with potassium possessed the highest percent of reduction ( $78.5 \pm 5\%$ ) and Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> possessed the lowest percent of reduction ( $5.07 \pm 5\%$ ). The supercritical processing and the counter ions produced a unique combination of effects on the morphological configurations of the polymer membrane, inhibiting the transport mechanism for vapor-methanol.

**Table 3.7.** Vapor-methanol permeability for Nafion® membranes.

| Membrane                                                      | Vapor-methanol effective permeability (cm <sup>2</sup> h <sup>-1</sup> ) |   |       |
|---------------------------------------------------------------|--------------------------------------------------------------------------|---|-------|
| Nafion®                                                       | 3.35                                                                     | ± | 0.16  |
| Nafion® SCF CO <sub>2</sub>                                   | 3.18                                                                     | ± | 0.18  |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup>                  | 3.27                                                                     | ± | 0.015 |
| Nafion® SCF CO <sub>2</sub> Ca <sup>+2</sup> Fe <sup>+3</sup> | 2.59                                                                     | ± | 0.031 |
| Nafion® SCF CO <sub>2</sub> Cu <sup>+2</sup>                  | 2.52                                                                     | ± | 0.14  |
| Nafion® SCF CO <sub>2</sub> Ba <sup>+2</sup>                  | 2.52                                                                     | ± | 0.37  |
| Nafion® SCF CO <sub>2</sub> Fe <sup>+3</sup>                  | 2.34                                                                     | ± | 0.24  |
| Nafion® SCF CO <sub>2</sub> Al <sup>+3</sup>                  | 2.23                                                                     | ± | 0.15  |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Ca <sup>+2</sup>  | 1.12                                                                     | ± | 0.019 |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup> Fe <sup>+3</sup>  | 0.85                                                                     | ± | 0.14  |
| Nafion® SCF CO <sub>2</sub> K <sup>+1</sup>                   | 0.72                                                                     | ± | 0.16  |

Nafion® processed with SCF CO<sub>2</sub> and exchanged with double counter ions possessed different vapor-methanol effective permeability with respect to the single counter ions. Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> Fe<sup>+3</sup> presented the higher vapor-methanol permeability of all the combination of counter ions. This combination reduced the permeability of Nafion® 22.7 ± 5%. In this case the double-counter ions reduced the vapor-methanol permeability more than Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup> although the permeability of Nafion® SCF CO<sub>2</sub> Fe<sup>+3</sup> was not reached. Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Ca<sup>+2</sup> obtained a reduction the percent of effective permeability of 67% respect to Nafion®. In this case the double-cation reduced the vapor-methanol permeability more than Nafion® SCF CO<sub>2</sub> Ca<sup>+2</sup>. The permeability of Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> was not reached either. This behavior was the same for Nafion® SCF CO<sub>2</sub> K<sup>+1</sup> Fe<sup>+3</sup> although obtained the lowest vapor-methanol permeability for the combination of counter ions. Table 3.8 shows the percent of reduction of effective permeability.

Different morphological configurations induced by the combination of counter ions on the polymer membrane, inhibited the diffusion of vapor-methanol through the membrane. Changes on the crystallinity and ionic domain presented in the DSC and SAXS profile confirm these results.

**Table 3.8.** Percent of reduction of methanol effective permeability ( $P_{eff}$ ) for Nafion®.

| <b>Membrane</b>                                         | <b>% reduction of <math>P_{eff}</math><br/>(<math>\text{cm}^2 \text{h}^{-1}</math>)</b> |
|---------------------------------------------------------|-----------------------------------------------------------------------------------------|
| Nafion® SCF $\text{CO}_2$                               | 5.07                                                                                    |
| Nafion® SCF $\text{CO}_2 \text{Ca}^{+2}$                | 2.4                                                                                     |
| Nafion® SCF $\text{CO}_2 \text{Ca}^{+2} \text{Fe}^{+3}$ | 22.7                                                                                    |
| Nafion® SCF $\text{CO}_2 \text{Cu}^{+2}$                | 24.78                                                                                   |
| Nafion® SCF $\text{CO}_2 \text{Ba}^{+2}$                | 24.78                                                                                   |
| Nafion® SCF $\text{CO}_2 \text{Fe}^{+3}$                | 30.1                                                                                    |
| Nafion® SCF $\text{CO}_2 \text{Al}^{+3}$                | 33.43                                                                                   |
| Nafion® SCF $\text{CO}_2 \text{K}^{+1} \text{Ca}^{+2}$  | 66.57                                                                                   |
| Nafion® SCF $\text{CO}_2 \text{K}^{+1} \text{Fe}^{+3}$  | 74.6                                                                                    |
| Nafion® SCF $\text{CO}_2 \text{K}^{+1}$                 | 78.5                                                                                    |

### 3.5. CONCLUSIONS

Nafion® membranes were processed with SCF  $\text{CO}_2$  and exchanged with different combination of counter ions. These membranes presented a reduction in the proton conductivity, the liquid and vapor methanol permeability. The incorporation of two counter ions after the processing with SCF  $\text{CO}_2$  produced unique thermal degradations and morphologies for each combination. The degradation behavior for Nafion® exchanged with the mixture of potassium was limited by the chemical nature of the  $\text{K}^{+1}$ ; instead the mixture of calcium and iron present a combination of their properties on the degradation of Nafion® SCF  $\text{CO}_2$ . Major stability occurs when Nafion® is exchanged with potassium and iron.

Although the transport properties of both vapor and liquid permeability of methanol were reduced upon the incorporation of cations, suggesting some similarities in their transport mechanism, the magnitude of the changes were significantly different, suggesting that there are fundamental differences in their transport mechanism that can be further explored to create more selective membranes.

The best selectivity (proton conductivity over methanol permeability) normalized with unprocessed Nafion® was obtained using the combination of potassium and iron. A unique combination of effects on the morphological configurations produced by the combination of cations on the polymer membrane inhibited the transport mechanism for protons and methanol in both phases.

### 3.6. REFERENCES

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## CHAPTER 4

### **Synthesis and Characterization of Poly(4-fluorostyrene)-b-poly(styrene)-b-poly(isobutylene) using Atom transfer and Cationic Polymerization**

#### **4.1. ABSTRACT**

This investigation studied the synthesis and characterization of ionic membranes composed of sulfonated copolymers with a novel trifluoroblock copolymer. The trifluoroblock copolymer composed of Zonyl®-b- Zonyl®-b-poly(4-fluorostyrene)-b-poly(styrene)-b-poly(isobutylene) [P4FS-b-PS-b-PIB] was synthesized using Atom Transfer Radical Polymerization (ATRP) and cationic polymerization. The block copolymer properties were measured using different characterization techniques such as Gel Permeation Chromatography (GPC), and Thermogravimetric Analysis (TGA). The chemical composition was monitored with Fourier Transform Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The resulting block copolymer was incorporated into an elastomeric matrix; therefore, physical blends of sulfonated poly(styrene-isobutylene-styrene) and sulfonated P4FS-b-PS-b-PIB copolymer were cast and analyzed. The newly developed fluoro-membrane was characterized using several techniques including: Elemental Analysis (EA), TGA, and DSC.

## 4.2. INTRODUCTION

Morphology and chemical-physical interactions are very important parameters being investigated to obtain proton exchange membranes (PEM) with higher proton conductivity and low methanol permeability<sup>1</sup> or membranes for chemical and biological protecting clothes applications.<sup>2</sup> Polymer blends emerged like an alternative to obtain membranes with a controlled morphology in order to improve the proton conductivity. Blend membranes with partially sulfonated polystyrene and partially sulfonated poly(2,6-dimethyl-1,4-phenylene)<sup>3</sup> or sulfonated poly(styrene-block-methyl methacrylate) and polyvinylidene fluoride<sup>4</sup> were characterized and functionalized for fuel cells application.

The use of well-ordered fluoroblock copolymers in blended membranes is an additional approach that has been investigated to modify the membrane's final morphology. G.J.D Kalaw et al.<sup>5</sup> studied polymeric blends composed of hydrophilic and hydrophobic perfluorocyclobutyl (PFCB) polymers. Blending these polymers, the membrane obtained a proton conductivity of 0.015 S/cm induced by a nanophase-separated morphology. J. Hou et al.<sup>6</sup> enhanced the proton conductivity of polyelectrolyte-fluoropolymer blends membranes changing the phase homogeneity increasing the degree of tetrabutylammonium hydroxide. Controlled radical polymerization (CRP) allows the synthesis of advanced well-defined fluoropolymers with specific structures and lower polydispersity.<sup>7</sup> The polymer structure contributes to mechanical, physical, thermal and chemical properties in polymeric materials. CRP methods generally rely on a reversible activation-deactivation process between dormant and active polymer chains, and as the double bond of monomers containing fluorine is additionally activated by the electron withdrawing group, this sometimes leads to considerably higher rates of polymerization.<sup>8</sup> Atom transfer radical polymerization (ATRP) is a CRP technique that used an alkyl halide like initiator, a transition metal in the lower oxidation state and a ligand to synthesize different fluoropolymers like, perfluoroalkyl ethyl methacrylate and fluoropolymers with polyether blocks for examples. Initiators for ATRP must have a halogen (Br or Cl) and a functional group that can stabilize the formed radical.<sup>9</sup>

These active halogen end groups can be used to extend additional polymeric chains using cationic polymerization. L. Toman et al.<sup>10</sup> synthesized a pentablock copolymer of methyl methacrylate,

styrene, and isobutylene using a combination of both ATRP and cationic polymerization. Poly(isobutylene) was synthesized with cationic polymerization using diethylaluminum chloride and a macroinitiator ( $\alpha,\omega$ -dichloro-poly(styrene)-*b*-poly(methyl methacrylate)-*b*-poly(styrene) triblock copolymer)) synthesized by ATRP.<sup>10</sup> Therefore, the goal of this study was to synthesize an ionic membrane composed of sulfonated poly(styrene-isobutylene-styrene) with a sulfonated trifluoroblock copolymer composed of Zonyl<sup>®</sup>-*b*-poly(4-fluorostyrene)-*b*-poly(styrene)-*b*-poly(isobutylene) [P4FS-*b*-PS-*b*-PIB]. PIB was synthesized using cationic polymerization using a macroinitiator (P4FS-*b*-PS) obtained by ATRP; the resulting polymer blend membranes were characterized using FTIR, NMR, TGA and DSC.

### **4.3. EXPERIMENTAL**

#### **4.3.1. Materials**

Isobutylene (99.9% purity) was acquired from Linde Gas Puerto Rico, Inc. Diethylaluminum chloride, 1M solution in hexanes, AcroSeal<sup>®</sup> (Acros-Organics). The other materials used in this section correspond to the same in section 5.3. The macroinitiator used, was the polymer obtained in chapter 5: P4FS-*b*-PS.

#### **4.3.2. Cationic Polymerization**

The synthesis of P4FS-*b*-PS-*b*-PIB was carried out in dichloromethane at  $-41^{\circ}\text{C}$  for 6 h. The polymerization process is described in more detail elsewhere.<sup>10</sup> A Schlenk tube was charged with P4FS-*b*-PS and the monomer; then the polymerization reaction was initialized with diethyl aluminum chloride. Upon completion of the experiment, the solution was precipitated in methanol, where the polymer appeared as a fluffy white material that was recovered after vacuum drying.

#### **4.3.3. Characterization**

FTIR was employed to identify the chemical nature of the polymers and the membranes analyzing the vibrational band of the functional groups. FT-IR (Brucker Alpha Platinum-ATR) to characterize the homopolymer, block copolymers and the membranes. The sample was clamped on the ATR

cell and all infrared spectra were collected using 64 scans, 4 cm<sup>-1</sup> resolution and a range of 600 – 4000 cm<sup>-1</sup>.

The homopolymers and the block copolymers were characterized by <sup>1</sup>H NMR, using a NMR Bruker 500 MHz spectrometer with d-chloroform as a solvent.

GPC was performed on a Waters GPC system equipped with a mixed column (PLgel 5μm MIXED-C, Varian Inc.) and a differential refractometer (BI-DNDC, Brookhaven Instruments). THF HPLC solvent was used as the mobile phase with a flow rate of 0.5 ml/min. Molecular weight distributions were obtained with reference to polystyrene standards (Varian Inc.).

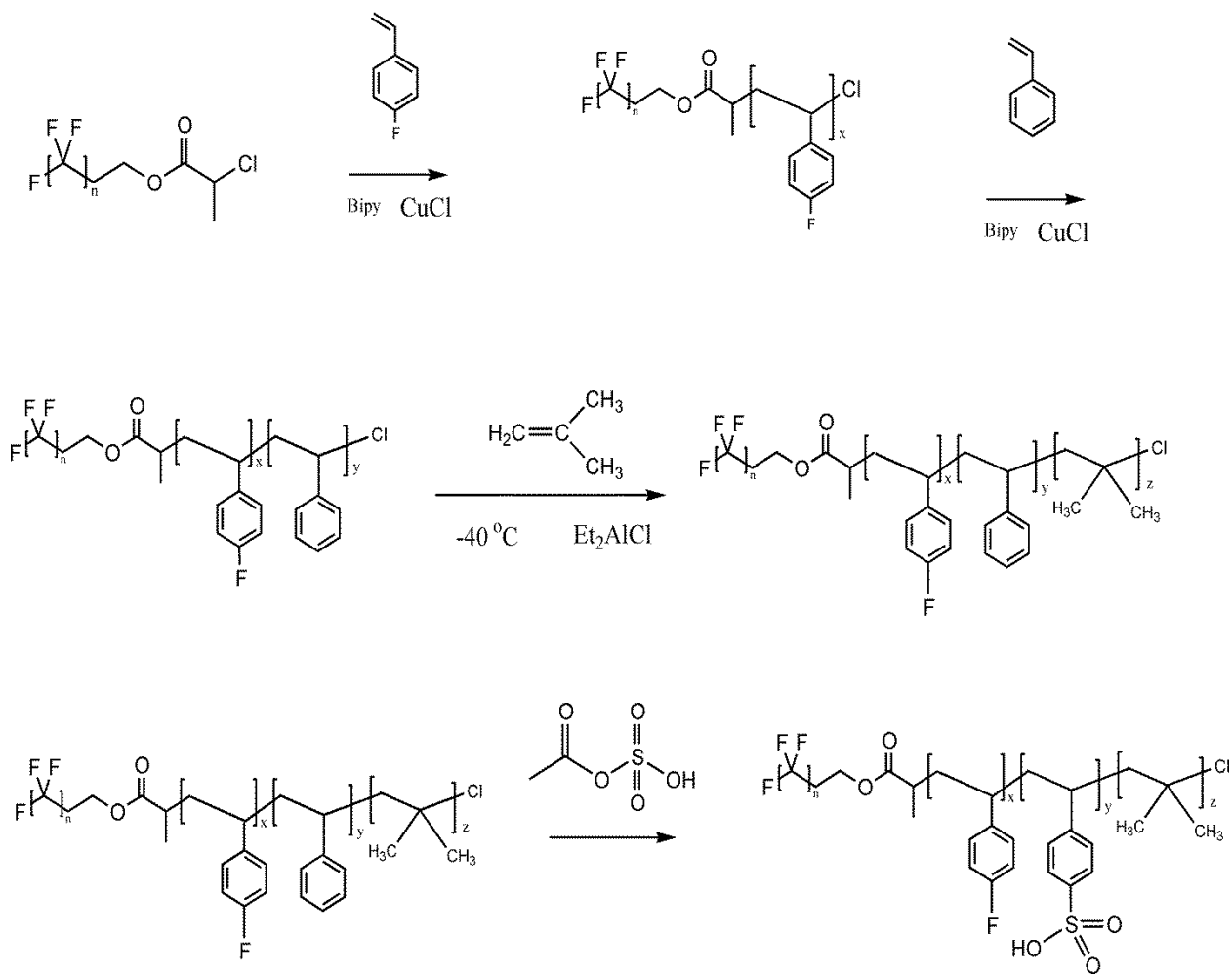
The thermal degradation behavior for each homopolymer, diblock copolymer and membranes was determined using TGA. A Mettler Toledo 851e instrument was used for this purpose. In each experiment, polymer samples weighting approximately 5-10 mg were used. Degradation temperatures were determined after heating the polymer samples to 800 °C at 10 °C/min under a nitrogen atmosphere.

Thermo physical properties were determined using DSC. A Texas Instrument DSC Q2000 unit was used for this purpose. In each experiment, polymer samples weighting approximately 5-10 mg were used. Phase transitions (T<sub>g</sub>) and melting temperatures for each polymer were determined after heating the polymer samples from -80°C to 350°C at 10°C/min under a nitrogen atmosphere.

#### **4.3.4. Blend Preparation**

Poly(styrene-isobutylene-styrene) (SIBS) and P4FS-b-PS-b-PIB was sulfonated using acetyl sulfate as the sulfonating agent. The sulfonation process is described in more detail elsewhere.<sup>1,2</sup> The preparation of physical blends consisted of mixing sulfonated SIBS and sulfonated P4FS-b-PS-b-PIB. Sulfonated SIBS and the sulfonated fluoroblock copolymer were dissolved in a solution (85/15) (v/v) of toluene and hexyl alcohol with a polymer concentration of 5 wt%. Sulfonated SIBS/fluoropolymer membranes were solvent casted in Teflon® Petri dishes for 72 h at room temperature as the solvent evaporated; then dried at 60°C for 24 h to remove the residual solvent. Elemental Analysis (EA) was used to determine the exact amount of the mole percent of sulfonated styrene in the membrane. EA was conducted by Atlantic Microlab, Norcross, Georgia.

Scheme 4.1 shows the polymerization path-way for the triblock copolymer and the sulfonation process.



**Scheme 4.1.** Polymerization reaction for P4FS-b-PS-b-PIB and P4FS-b-PS-b-PIB SO<sub>3</sub>H.

#### 4.3.5. Ion Exchange Capacity (IEC)

IEC was measured by immersing a specific amount of the membrane in a 1.0 M solution of NaCl for 24 h. After removing the membrane, the solution was titrated using a 0.1 M solution of NaOH

until the pH was neutral. The IEC was calculated from the moles of ion substituted divided by the initial dry mass of the membrane.

#### 4.3.6. Water Swelling

Water absorption or water swelling in the membranes was measured immersing each membrane in an excess of deionized water at 25°C. The weight of the sample initially dried at 60°C for 24 hours in an oven was originally recorded, as well as the weight of the membrane after immersion in water. The weight of the wet membranes was measured after different time intervals until swelling equilibrium was reached. Each reported result represents the average of at least three repetitions.

### 4.4. RESULTS

#### 4.4.1. Polymer Characterization

##### 4.4.1.1. GPC

The molecular weight of tri fluoroblock copolymers were determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene as the calibration standard. After the cationic polymerization, the molecular weight ( $M_n$ ) increased from 36.1 to 39.1 g/mol. The molecular weight, polydispersities ( $M_w/M_n$ ) and the polymer composition results and are shown in Table 4.1A and 4.1B.

**Table 4.1A.** Molecular weight characterization for homopolymer and block copolymers Prepared by ATRP (using polystyrene standards)

| Sample                         | Initiator            | $M_n \times E-3$ | $M_w \times E-3$ | $M_w/M_n$ |
|--------------------------------|----------------------|------------------|------------------|-----------|
| Poly(4FS)                      | esterified Zonyl®    | 9.11             | 13.5             | 1.48      |
| Poly(4FS)-b-Poly(ST)           | Poly(4FS)            | 36.1             | 69.4             | 1.92      |
| Poly(4FS)-b-Poly(S)-b-Poly(IB) | Poly(4FS)-b-Poly(ST) | 39.1             | 71.5             | 1.83      |

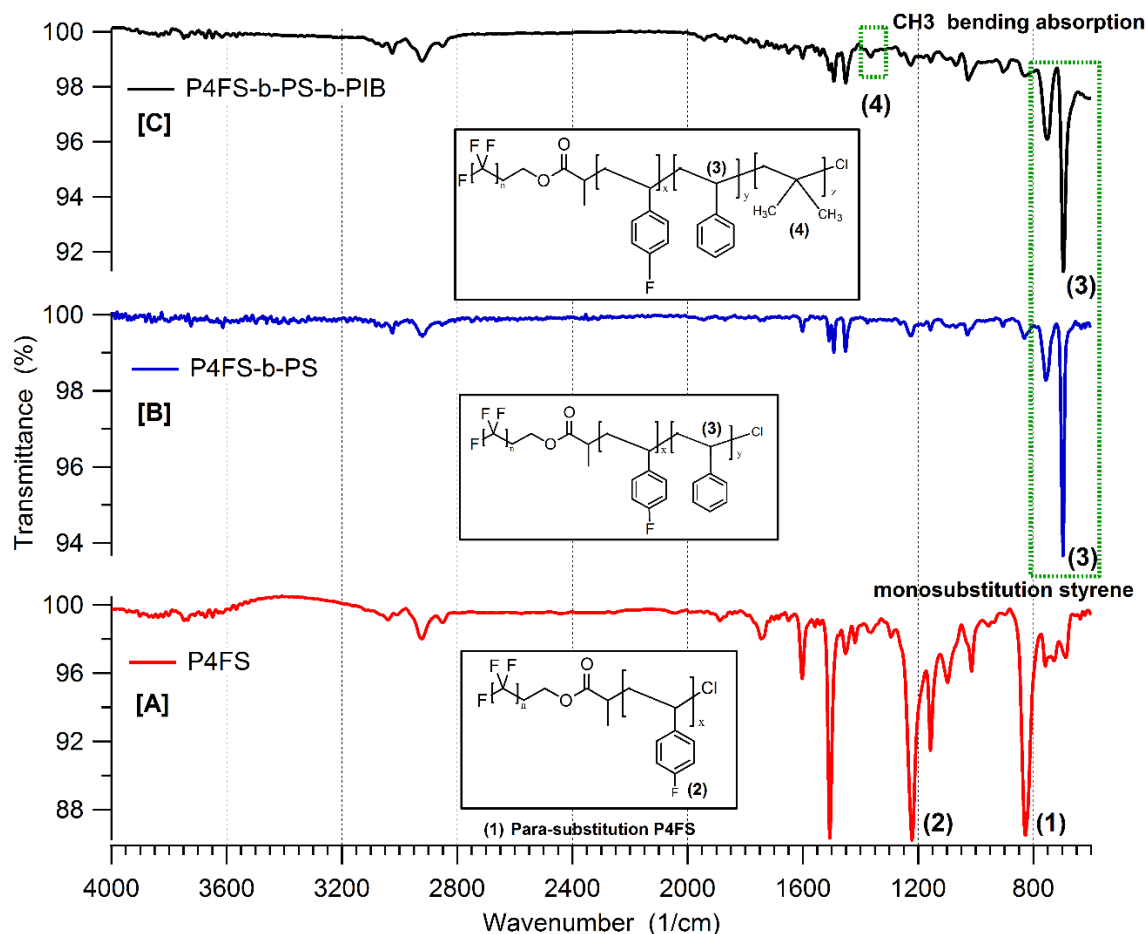
**Table 4.1B.** Polymer composition (wt%).

| Sample            | (wt)% |
|-------------------|-------|
| Esterified Zonyl® | 1.6   |
| P4FS              | 6.3   |
| PS                | 72.1  |
| PIB               | 19.9  |

#### 4.4.1.2. FTIR

Figure 4.1 [A] exhibits the FT-IR spectra of P4FS. Three distinctive regions are observed in this figure: A para-substitution band correspond to 4-fluorostyrene group was presented at  $820\text{ cm}^{-1}$  (1). The second bands corresponds to overtone absorptions induced by the aromatic ring; these bands appear between  $2000$  and  $1667\text{ cm}^{-1}$ . An additional band appears between  $1300$  and  $1000\text{ cm}^{-1}$ ; this band corresponds to the C – F group attached to 4FST (2). Figure 4.1 [B] shows the FT-IR spectra of P4FS-b-PS; two distinctive regions were observed in this figure. A mono-substitution band corresponding to the styrene group was present at  $700\text{ cm}^{-1}$  (3).

Figure 4.1 [C] shows the FT-IR spectra of P4FS-b-PS-b-PIB. This polymer shows a characteristic peak around  $1375\text{ cm}^{-1}$  (4) that correlates to the bending absorption of the  $\text{CH}_3$  group attached to PIB.

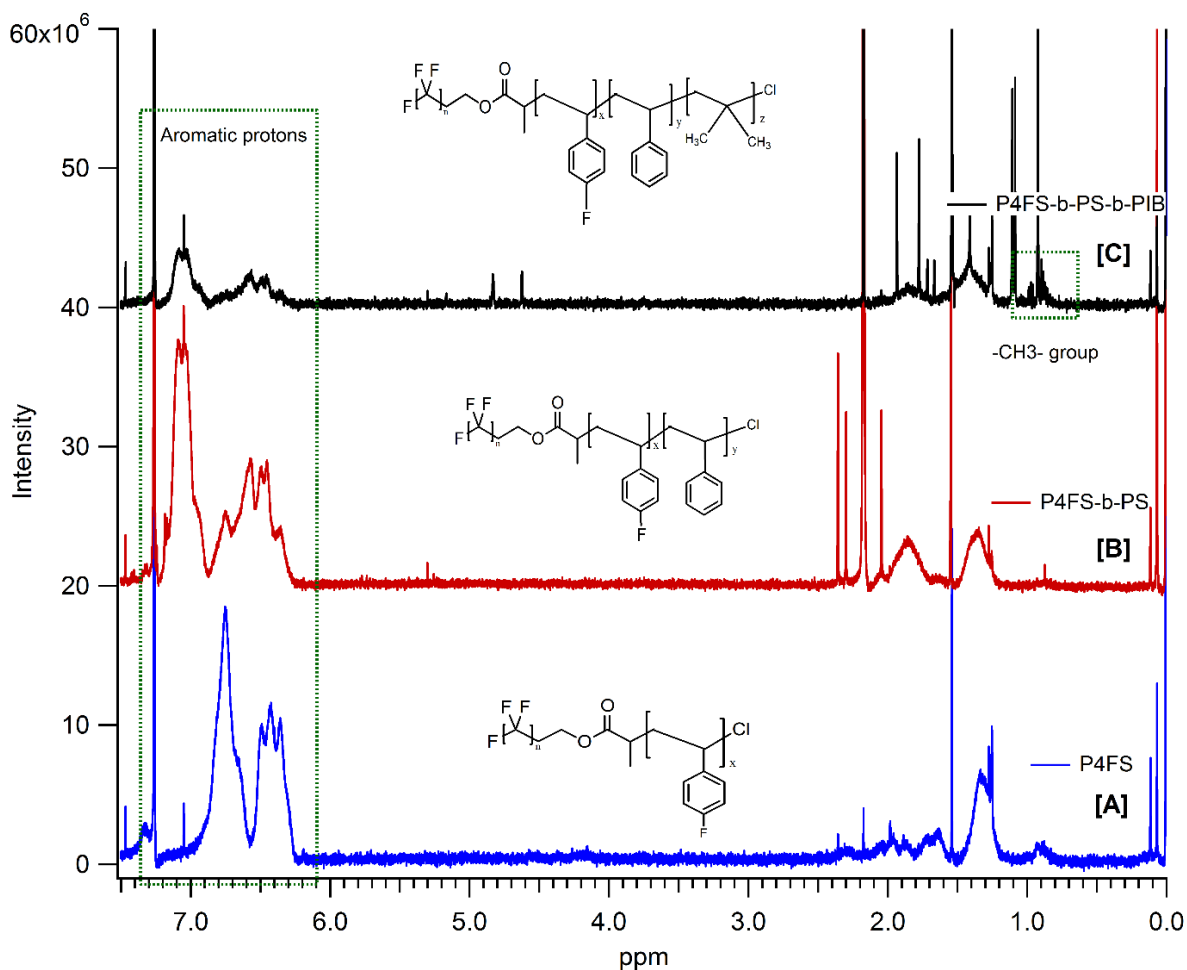


**Figure 4.1.** FTIR spectra for P4FS [A], P4FS-b-PS [B] and P4FS-b-PS-b-PIB [C].

#### 4.4.1.3. Nuclear Magnetic Resonance (NMR)

Liquid  $^1\text{H}$  NMR was employed in order to confirm the chemical composition of the synthesized homopolymer and fluoroblock copolymers. Figure 4.2 exhibits the  $^1\text{H}$  NMR spectra of P4FS, P4FS-b-PS and P4FS-b-PS-b-PIB. P4FS (Figure 4.2[A]) presented peaks at a large chemical shift around 6.5 ppm. These peaks were assigned to the typical band of the protons attached to the aromatic ring in P4FS. The peaks at 1.85 and 1.35 ppm are assigned to the methylene ( $-\text{CH}_2-$ ) and methine ( $-\text{CH}-$ ) absorptions in P4FS. Figure 4.2[B] shows the NMR spectra for P4FS-b-PS; this spectra presented an additional absorption around 7 ppm that represents the protons attached to the aromatic ring in PS. One additional peak appeared in P4FS-b-PS-b-PIB with respect to P4FS-b-PS 1 ppm (Figure 4.2[C]). This absorption is a characteristic chemical shift that corresponds to the

methyl group ( $-\text{CH}_3-$ ) attached to PIB. Both FT-IR and Liquid  $^1\text{H}$  NMR spectra confirm the chemical composition of the synthesized polymers using ATRP and cationic polymerization.

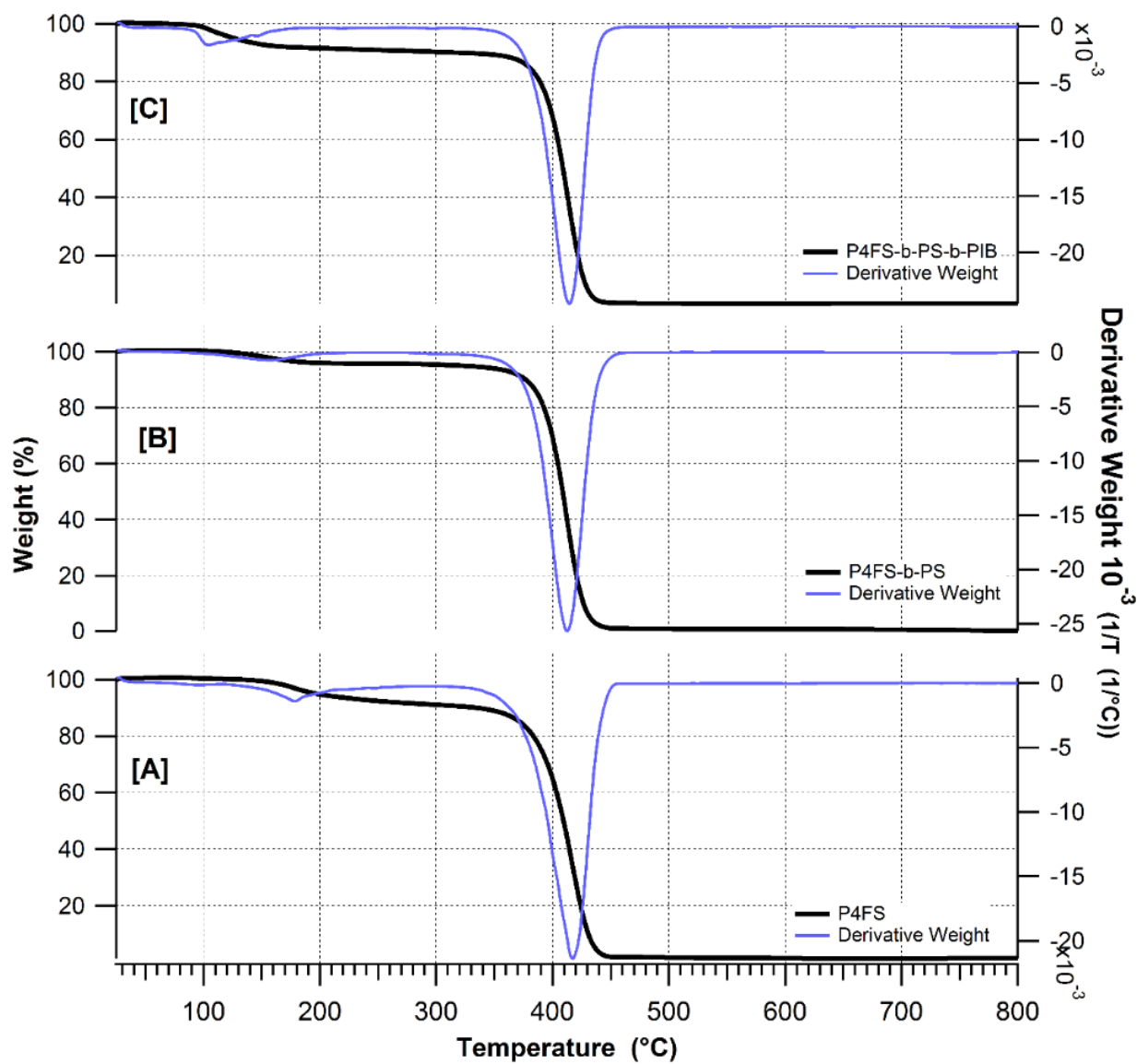


**Figure 4.2.** NMR spectra for P4FS [A], P4FS-b-PS [B] and P4FS-b-PS-b-PIB [C].

#### 4.4.1.4. Thermogravimetric Analysis (TGA)

The thermal degradation behavior for the block copolymers was determined by thermogravimetric analysis over a temperature range of 25–800°C under a  $\text{N}_2$  atmosphere. Figure 4.3 [A] shows the thermal degradation of P4FS. This polymer presented two different degradation. The first degradation was at 177.96°C with a weight loss percent of 7.35% and the second at 417.59°C. P4PS-b-PS (Figure 4.3 [B]) exhibited the degradation temperatures previously mentioned, however the thermal stability of this polymer was adversely affected when PIB was incorporated to the polymeric chain. The polymer suffered thermal degradation

below 110°C and the remaining polymer chain degraded at 414°C. In this weight loss step, PIB chain and all the P4FS-b-PS chain were overlapped (Figure 4.3[C]). Table 4.2 summarizes the degradation temperatures for the polymers.



**Figure 4.3.** TGA for P4FS [A], P4FS-b-PS [B] and P4FS-b-PS-b-PIB [C].

**Table 4.2.** Polymer degradation temperatures.

| Polymer         | 1 <sup>st</sup><br>Degradation<br>(°C) | 2 <sup>nd</sup><br>Degradation<br>(°C) |
|-----------------|----------------------------------------|----------------------------------------|
| P4FS            | 177.96                                 | 417.59                                 |
| P4FS-b-PS       | 157.1                                  | 420.33                                 |
| P4FS-b-PS-b-PIB | 105                                    | 414.30                                 |

#### 4.4.2. Polymer blend characterization

##### 4.4.2.1. Sulfonation Level, Ion Exchange Capacity (IEC) and Water Swelling

Table 4.3 shows the sulfonation level, IEC and water swelling comparison between SIBS SO<sub>3</sub>H and SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PIB SO<sub>3</sub>H. P4FS-b-PS-b-PIB SO<sub>3</sub>H exhibited higher sulfonation level than SIBS SO<sub>3</sub>H. The addition of the sulfonated fluoroblock copolymer to sulfonated SIBS increased the sulfonation level for the membranes studied. The IEC for SIBS SO<sub>3</sub>H/P4FS-b-PS-b-PIB SO<sub>3</sub>H increased 36% respect to SIBS SO<sub>3</sub>H. The percent of water swelling for SIBS SO<sub>3</sub>H/P4FS-b-PS-b-PIB SO<sub>3</sub>H is not available, because after 5 minutes submerged in water the membrane dissolved. This behavior was induced by the high sulfonation level and IEC for this membrane.

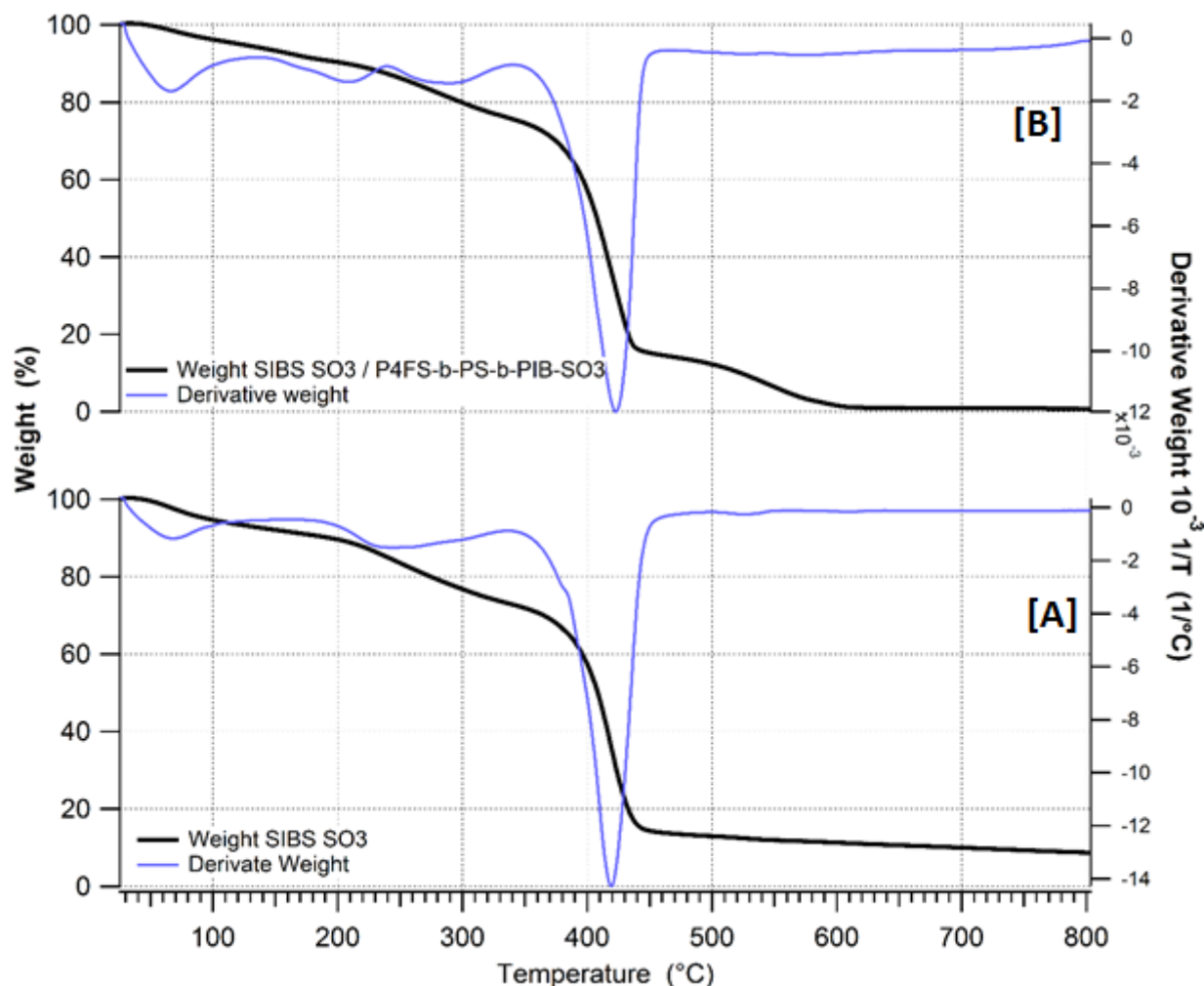
**Table 4.3.** Sulfonation percented, Ion Exchanged Capacity (IEC), water swelling for sulfonated SIBS / Fluoropolymer membranes.

| Membrana                                                   | Sulfonation level<br>(mol %) | IEC<br>(meq g <sup>-1</sup> ) | Water swelling<br>(%) |
|------------------------------------------------------------|------------------------------|-------------------------------|-----------------------|
| SIBS SO <sub>3</sub> H                                     | 84.0                         | 1.84                          | 608.14                |
| SIBS SO <sub>3</sub> H / P4FS-b-PS-b-PIB SO <sub>3</sub> H | 93                           | 2.50                          | Data not available    |

##### 4.4.2.2. Thermogravimetric Analysis (TGA)

The thermal degradation behavior for the sulfonated fluoroblock membrane was determined by thermogravimetric analysis over a temperature range of 25-800°C under a N<sub>2</sub> atmosphere. Figure 4.4 [A] shows the TGA curve for SIBS SO<sub>3</sub>. The TGA curve for this membrane exhibited three

degradation temperatures, the first one at 50 – 100°C corresponds to water absorbed inside the membrane, the second degradation region at 245°C represents the sulfonic group, and the third degradation at 419°C represent polymer backbones. Figure 4.4 [B] shows the TGA curve for SIBS-SO<sub>3</sub>H / P4FS-b-PS-b-PIB SO<sub>3</sub>H membrane. This membrane presents one region in the TGA that remained unchanged, however three additional weight losses are observed at 203°C, 274°C and 525°C respectively. In sulfonic group degradation region two of these additional degradations appeared. This results suggest that two different types of sulfonic domains coexist in the same polymer membrane. Ionic interactions with the sulfonic group suggest a new weight loss at higher temperatures in sulfonated SIBS membranes. Table 4.4 summarize the degradation temperatures for the polymeric blend membranes.



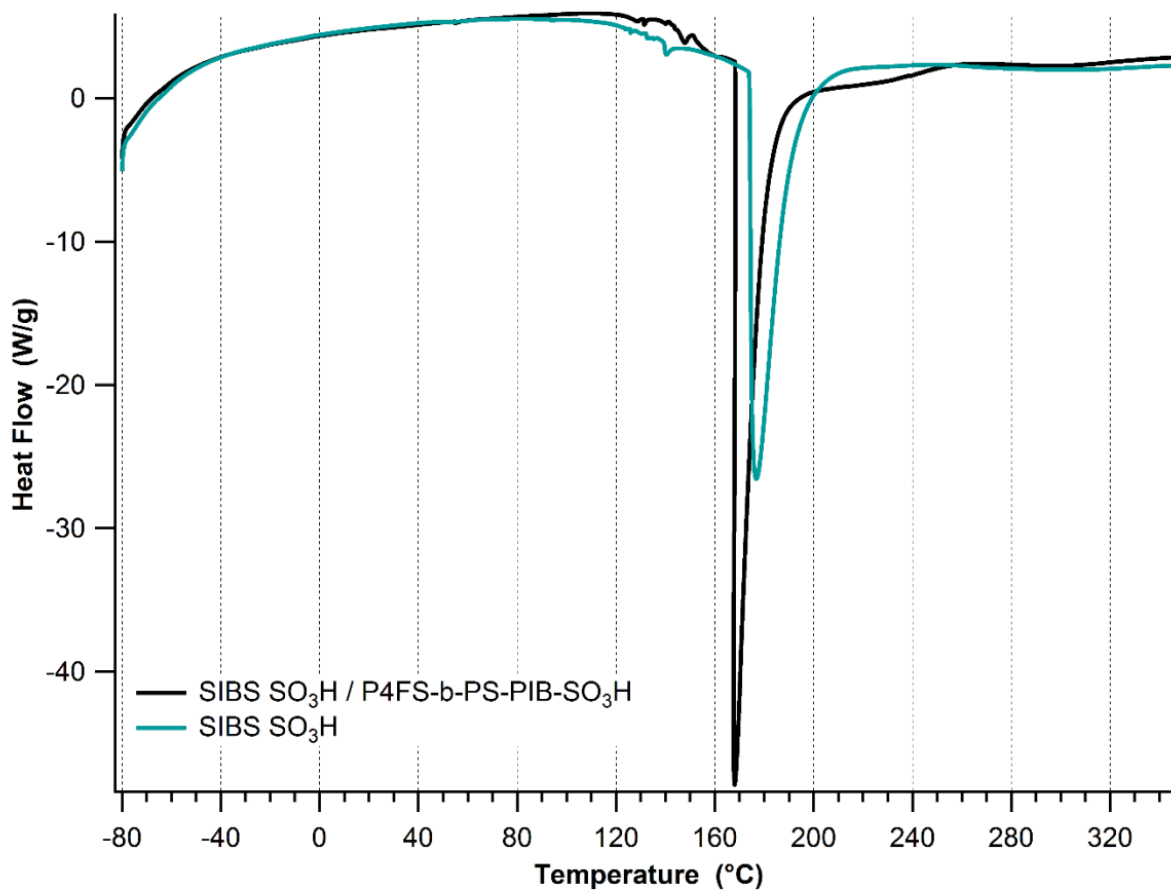
**Figure 4.4.** TGA for SIBS-SO<sub>3</sub>H / P4FS-b-PS-b-PIB SO<sub>3</sub>H and SIBS-SO<sub>3</sub>H membranes.

**Table 4.4.** Degradation temperatures for the polymeric blend membranes

| Membrane                                                  | 2 <sup>nd</sup><br>Degradation<br>(°C) | 3 <sup>rd</sup><br>Degradation<br>(°C) | 4 <sup>th</sup><br>Degradation<br>(°C) | 5 <sup>th</sup><br>Degradation<br>(°C) |
|-----------------------------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| SIBS SO <sub>3</sub> H                                    | 245                                    | Absent                                 | 419                                    | Absent                                 |
| SIBS SO <sub>3</sub> H /P4FS-b-PS-<br>b-SO <sub>3</sub> H | 203                                    | 274                                    | 423                                    | 525                                    |

#### 4.4.2.3. Differential Scanning Calorimetry (DSC)

Sulfonated SIBS presents (Figure 4.5 [B]) the two endothermic peaks induced by the sulfonation process; the first at 140°C and the second peak at 177°C. The incorporation of the sulfonated fluoroblock copolymer to SIBS SO<sub>3</sub>H membrane produced a unique DSC curve. SIBS SO<sub>3</sub>H/P4FS-b-PS-b-SO<sub>3</sub>H (Figure 4.5) presented a difference in both the energy and temperature required to produce the endothermic transitions. The endothermic transitions for the ionic cluster shifted towards a higher temperature; however, the endothermic transition for the crystalline region shifted towards a lower temperature. The changes in temperature are related to the energy needed to overcome the crystalline bonding forces and changes in the molecular conformation of the chains in the polymer.<sup>11</sup> The energy required to produce both transitions increased 25.31 and 25.24%, respectively. Table 6.5 summarizes the endothermic transition temperatures and their corresponding energies for the membranes studied.



**Figure 4.5.** DSC for SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PIB SO<sub>3</sub>H and SIBS-SO<sub>3</sub>H membranes.

**Table 4.5.** Endothermic transition temperatures for polymeric blend membranes

| Membrane                                              | First Transition |                                    | Second Transition |                                    |
|-------------------------------------------------------|------------------|------------------------------------|-------------------|------------------------------------|
|                                                       | T (°C)           | $\Delta H$<br>(J g <sup>-1</sup> ) | T (°C)            | $\Delta H$<br>(J g <sup>-1</sup> ) |
| SIBS SO <sub>3</sub> H                                | 140              | 1.58                               | 177               | 304.9                              |
| SIBS SO <sub>3</sub> H /P4FS-b-PS-b-SO <sub>3</sub> H | 147              | 1.98                               | 168               | 382                                |

#### 4.5. CONCLUSION

A sulfonated novel trifluoroblock copolymer was successfully synthesized using ATRP and cationic polymerization. The incorporation of this sulfonated fluoroblock copolymers into sulfonated SIBS have a significant impact on the thermal stability of the membrane. An additional degradation was observed around 203°C, and the sulfonic group degradation was improved 29°C. These results suggest two different ionic domains that influenced the morphology, which influenced the EIC, the sulfonation level, and the water swelling. The incorporation of a sulfonated fluoropolymer to sulfonated SIBS induced an improvement in the IEC of 36%, and the sulfonation level increased from 84% to 93%. These results induced higher water absorption in the membrane; therefore, the membrane was dissolved after submerged in water. Different polymer percent of P4FS-*b*-PS-*b*-SO<sub>3</sub>H should be added to SIBS SO<sub>3</sub>H, and should further be investigated for DMFC application.

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## CHAPTER 5

# Influence of Different Esterified Initiators on Fluorinated Block Copolymers and Transport Properties of Sulfonated Membranes

### 5.1. ABSTRACT

This investigation studied the synthesis of ionic membranes composed of a sulfonated poly(styrene-isobutylene-styrene) with a novel fluoroblock copolymers. These fluoroblock copolymers were synthesized using three different initiators by Atom Transfer Radical Polymerization (ATRP); two fluoroinitiators were obtained from the esterification of 2-(perfluoroalkyl) ethanol or, octafluoro 4-4'-biphenol. The third initiator evaluated was 1-bromoethyl benzene. The resulting block copolymers were characterized using several techniques: Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet Spectroscopy (UV), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). Transport properties (e.g., proton conductivity and methanol permeability) were measured to evaluate their performance for direct methanol fuel cell (DMFC). The choice of ATRP initiator was found to have a profound impact on the thermal stability of the different homopolymers and block copolymers that were studied. In addition, the chemical nature and symmetry of the initiators can lead to different chemical and electronic configurations, which influence the performance of these ionic membranes in applications such as proton exchange membranes (PEM) for DMFC applications.

## 5.2. INTRODUCTION

Fluorinated polymers are used in numerous and diverse functional materials because they possess high thermal stability, enhanced chemical resistance, and low surface energy compared to their non-fluorinated analogs.<sup>1</sup> Applications for these polymers include: proton conducting materials<sup>2</sup>, stabilizers for emulsion polymerization<sup>3</sup>, additives in oil recovery and water treatment<sup>4</sup>, surfactants<sup>5</sup>, lubricants<sup>6</sup>, and ion conducting materials.<sup>7</sup> Proton exchange membranes (PEM's) for direct methanol fuel cells (DMFC) is another application where sulfonated fluoropolymers (e.g. Nafion®) are used, because they possess high proton conductivity and excellent thermal, mechanical and barrier properties.<sup>8-14</sup> Our group has worked with different PEM's for DMFC that explored different chemical functionalities<sup>15-16</sup> and processing approaches to influence morphology.<sup>17-18</sup> These studies have demonstrated the sensitivity of the transport properties to the resulting nanostructure and the electronic configuration inside the resulting ionic nano-channels. This electronic configuration could be sensitive to the polymerization technique and the type of initiator used.

Controlled radical polymerization (CRP) allows for the synthesis of advanced well-defined fluoropolymers with specific structures and low polydispersity. Morphology and the chemical structure contribute to the mechanical, physical, thermal and chemical properties in polymeric materials.<sup>19</sup> CRP methods generally rely on a reversible activation-deactivation process between dormant and active polymer chains, and as the double bond of monomers containing fluorine is additionally activated by the electron withdrawing group, this sometimes leads to considerably higher rates of polymerization.<sup>20</sup> Atom transfer radical polymerization (ATRP) is a CRP technique that uses an alkyl halide like initiator, a transition metal in the lower oxidation state, and a ligand to synthesize different fluoropolymers. Initiators for ATRP must have a halogen (Br or Cl) and a functional group that can stabilize the formed radical.<sup>21</sup> Chemical modification on terminal groups of fluoroalcohols,<sup>22-23</sup> and polymers like poly(ethylene glycol) (PEG)<sup>24</sup> have been synthesized with the aim to obtain novel ATRP initiators. A limited number of studies have evaluated the effect of different initiators on the thermal stability and resulting properties of the polymers. Even less investigations have focused on the thermal stability and transport properties (for DMFC applications), of fluoroblock copolymers made with different esterified initiators.

Howell et al.<sup>25</sup> evaluated the impact of the initiator's characteristics on the thermal stability of vinylidene chloride copolymers. In their study, the polymer was synthesized by a radical suspension technique using four different initiators with similar decomposition temperature. The results showed that the changes in the thermal stability of the copolymers were probably induced by the introduction either via end-group effects, or by attack of residual initiator fragments on the finished polymer during isolation and residual monomer stripping.<sup>25</sup> Jankova and Hvilsted<sup>26</sup> modified chemically dipentaerythritol using an esterification reaction in order to obtain an ATRP initiator. A hexa-arm star diblock copolymer of styrene and 2,3,4,5,6-pentafluorostyrene was synthesized. The thermal degradation for this polymer presented lower temperature degradation, suggesting that a thermal degradation involved scission of the ester linkages in the polymer.<sup>26</sup>

Esterified initiators seem to have a strong influence on the thermal stability of block copolymers. Therefore, the first goal of this investigation was to evaluate the effect of different esterified initiators on the thermal properties of four novel fluoro diblock copolymers and their homopolymers synthesized by ATRP. The block copolymers were based on polystyrene (PS) and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HEMA). The initiators studied were obtained from the esterification of 2-(perfluoroalkyl) ethanol (Zonyl®) and octafluoro 4-4'-biphenol (octo). The third initiator studied was the conventional 1-bromo ethyl benzene (EtIB) for ATRP reactions. Since this communication compared different homopolymers and diblock copolymers, the nomenclature for the different polymers studied starts with the initiator, followed by the polymer or block copolymer studied. For example, Zonyl®-b-poly(PS)-b-poly(HEMA) represents the block copolymer poly(styrene) with poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) initiated with esterified 2-(perfluoroalkyl).

Esterified Zonyl® was evaluated based on a previous study,<sup>22</sup> where well-defined methacrylic copolymers were synthesized, but lacked the evaluation of the thermal stability and the polymerization of other blocks with different chemical structure, like styrene. In addition, it lacked the connection with transport properties for DMFC applications. The resulting homopolymer and diblock copolymers were chemically characterized using NMR and FTIR. Thermal properties were analyzed by TGA and DSC. Molecular weights were obtained by GPC,

and the electronic configuration was analyzed using UV spectroscopy. In addition, the transport properties of ionic membranes composed of a sulfonated poly(styrene-isobutylene-styrene) (SIBS SO<sub>3</sub>H) with novel fluoropolymer based on poly(styrene) were investigated. Therefore, the second goal of this investigation was to evaluate the influence of the initiator on the resulting transport properties of these membranes for DMFC applications.

### **5.3. EXPERIMENTAL**

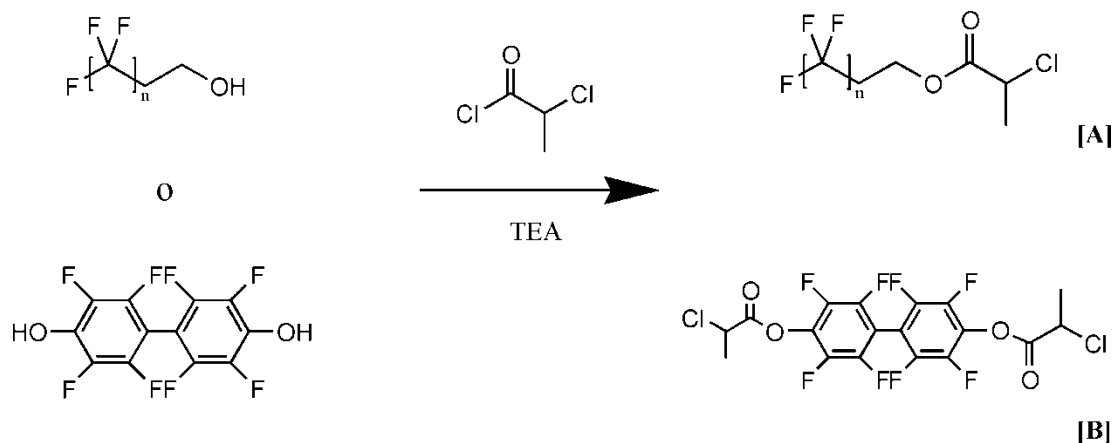
#### **5.3.1. Material**

Zonyl® BA-L Fluorotelomer intermediate (70 wt.%) Mn~443 was acquired from Sigma-Aldrich. Octafluoro-4-4'-biphenol was acquired from Tokyo Chemical Industry CO., LTD. Toluene ACS reagent (99%) and dichloromethane (99.9%) were acquired from Fisher Scientific. Other chemicals used include: 1-bromo ethyl benzene (Acros-Organics, 97%), triethylamine, (Acros-Organics, 99%), 4-dimethylamino pyridine, (Acros Organics, 99%), 2-chloropropionyl chloride, (Acros-Organics, 95%), 2, 2'-dipyridyl – Bipy - (Acros Organics, extra pure, 99%), calcium hydride -CaH<sub>2</sub>- (Acros-Organics, 93%), and copper (I) chloride (Acros-Organics, 99%). All chemicals were employed as received. The monomers used included: 2,2,3,4,4,4-hexafluorobutyl methacrylate (HEMA) (Alfa Aesar 96% inhibited with monomethyl ether hydroquinone –MEHQ-) and styrene (PS) (Across Organics, 99% inhibited with 4-tert-butyl catechol). Both HEMA and PS were passed through an inhibitor remover (disposable column from Sigma-Aldrich). After this process both monomers and the solvent were stored over CaH<sub>2</sub> and then vacuum-distilled before polymerization. Nafion® 117 was obtained from Ion Power, Inc.

#### **5.3.2. Esterification of 2-perfluoroalkyl ethanol and octafluoro-4-4'-biphenol**

2-(perfluoroalkyl) ethanol (Zonyl®) and, octafluoro 4-4'-biphenol were chemically modified using an esterification reaction, with the purpose of obtaining esterified compounds capable of initiating a polymeric reaction in an ATRP process. Scheme 5.1 shows the esterification pathway in order to synthesize esterified (Zonyl®) and esterified octafluoro 4-4'-biphenol initiators. Zonyl® and 4-dimethylamino pyridine were dissolved in toluene at 60°C. Triethylamine and 2-chloropropionyl chloride were added and the reaction was stopped after 24 h.<sup>22</sup> Toluene was

removed by rotary evaporation. The obtained product was dissolved using dichloromethane and washed with a saturated  $\text{NaHCO}_3$  solution, 1 M HCl, and distilled water. The solvents were removed by rotary evaporation.



**Scheme 5.1.** Esterification reaction for (perfluoroalkyl)ethanol (Zonyl®) [A] and octafluoro 4-4'-biphenol [B].

### 5.3.3. ATRP homopolymerization using esterified initiators and 1-bromo ethyl benzene

In a characteristic homopolymerization by ATRP, a Schlenk tube was charged with the initiator (e.g. esterified Zonyl® or 1-bromo ethyl benzene), copper chloride ( $\text{CuCl}$ ), and the ligand (2, 2'-dipyridyl [bipy]). The molar ratio of initiator: $\text{CuCl}$ :bipy was kept 1:1:2.<sup>27</sup> The monomer was added, and the system was degassed three times by freezing and thawing; then heating to the desired temperature ( $110^\circ\text{C}$ ) under a nitrogen atmosphere. Upon completion of the experiment, the polymerization mixture was diluted with THF. The solution was filtered (to remove the catalyst) and then precipitated in methanol, where the polymer appeared as a fluffy white material that was recovered after vacuum drying.

#### 5.3.4. ATRP copolymerization

In a typical block copolymerization by ATRP, a Schlenk tube was charged with the macroinitiator, copper chloride (CuCl) and the ligand (2, 2'-dipyridyl). The molar ratio of initiator:CuCl:bipy was kept 1:1:2.<sup>27</sup> The system was degassed three times minimum by freezing and thawing. After three freeze-thaw cycles, the mixture was heated (110 °C) for 24 h under a nitrogen atmosphere. The block copolymer solution was filtered and then precipitated in methanol.

#### 5.3.5. Characterization

FTIR was employed to identify the chemical nature of the polymers and the membranes analyzing the vibrational band of the functional groups. An attenuated total reflectance (ATR) cell was used with an FT-IR (Varian 800 FT-IR) to characterize the homopolymer, diblock copolymers and the polymeric membranes. The sample was clamped on the ATR cell and all infrared spectra were collected using 64 scans, 4 cm<sup>-1</sup> resolution and a range of 600 – 4000 cm<sup>-1</sup>.

The homopolymers and the block copolymers were characterized by <sup>1</sup>H NMR, using a NMR Bruker 500 MHz spectrometer with d-chloroform as a solvent.

A UV-VIS spectrophotometer equipment (Shimadzu UV-2401 P) was used to characterize the homopolymer and diblock copolymers. The sample was placed in quartz ultramicrocell for measurement. Ultraviolet spectra were collected using 1 nm intervals and a range of 200 – 600 nm, THF was used as the solvent.

GPC was performed on a Waters GPC system equipped with a mixed column (PLgel 5µm MIXED-C, Varian Inc.) and a differential refractometer (BI-DNDC, Brookhaven Instruments). THF HPLC solvent was used as the mobile phase with a flow rate of 0.5 ml/min. Molecular weight distributions were obtained with reference to polystyrene standards (Varian Inc.).

The thermal degradation behavior for each homopolymer, diblock copolymer and membranes was determined using TGA. A Mettler Toledo 851e instrument was used for this purpose. In each experiment, polymer samples weighting approximately 5-10 mg were used. Degradation temperatures were determined after heating the polymer samples to 800°C at 10°C/min under a nitrogen atmosphere.

Thermo-physical properties were determined using DSC. A Texas Instrument DSC Q2000 unit was used for this purpose. In each experiment, polymer samples weighting approximately 5-10 mg were used. Phase transitions (T<sub>g</sub>) and melting temperatures for each polymer were determined after heating the polymer samples from -80°C to 350°C at 10°C/min under a nitrogen atmosphere.

### 5.3.6. Blend preparation

Poly(styrene-isobutylene-styrene) (SIBS) was sulfonated using acetyl sulfate as the sulfonating agent. The sulfonation process is described in more detail elsewhere.<sup>16</sup> Sulfonated SIBS (SIBS SO<sub>3</sub>H) was used to prepare polymer blends with the fluoropolymers. The preparation of physical blends consisted of mixing SIBS SO<sub>3</sub>H (86wt.%) and unsulfonated fluoropolymer (14 wt.%) [EtIB-Poly (PS), Zonyl®-b-poly(PS) or Octo-poly(PS)]. SIBS SO<sub>3</sub>H and the fluoropolymer were dissolved in a solution (85/15) (v/v) of toluene and hexyl alcohol with a polymer concentration of 5 wt.%. SIBS SO<sub>3</sub>H/fluoropolymer membranes were solvent casted in Teflon® Petri dishes for 96 h at room temperature as the solvent evaporated; then dried at 60°C for 24 h to remove the residual solvent.

### 5.3.7. Methanol liquid-phase permeability

The methanol liquid-phase permeability was measured using a side-by-side glass diffusion cell discussed in detail elsewhere.<sup>17</sup> One side contained the permeant (*e.g.*, methanol) in a 2 M methanol-water solution, while the other side only contained deionized water. The concentration of the compound that permeated through the membrane was determined using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (Shimadzu GC-8). First a calibration curve was created, then measurements were determined after different times. The liquid permeability was obtained from the continuity equation for diffusion in plane geometry<sup>28</sup> (Equation 2.1)

$$C_B(t) = \frac{PC_{AA}}{V_b L} \left( t - \frac{L^2}{6D} \right) \quad (2.1)$$

where,  $C_A$  {mol/cm<sup>3</sup>} is the methanol concentration (permeant),  $C_B$  {mol/cm<sup>3</sup>} is the concentration of the compound that permeated through the membrane after different times,  $L$  is the membrane thickness {cm},  $V_b$  the volume of the receptor compartment {0.39 cm<sup>3</sup>},  $A$  the diffusional cross-sectional area of the membrane {0.64 cm<sup>2</sup>} and  $P$  the permeability {cm<sup>2</sup>/s}. The permeability ( $P$ ) was determined from the slope of the concentration  $C_B(t)$  versus time.<sup>29</sup>

#### 5.3.8. Proton conductivity

The proton conductivity ( $\sigma$ ) [S / cm] of each membrane was carried out on a Fuel Cell Test System (850e Multi Range) equipped with an 885 Fuel Cell Potenciostat from Scribner Associate Incorporated. The range of frequency and the AC amplitude used were from 0.1 Hz to 100,000 Hz and 0.1 Amps respectively at 40°C and 100% relative humidity. The membranes were first immersed in an excess of deionized water at 25°C before the experimentation during 24 hours. The proton conductivity was calculated from the impedance data, using the following relation (equation 2.2).<sup>30</sup>

$$\sigma = \frac{L}{R_{\Omega} A} \quad (2.2)$$

where  $L$  {cm} and  $A$  {cm<sup>2</sup>} are the membrane thickness and the area respectively.  $R_{\Omega}$  {1/ S} was obtained from the low intersect of the high frequency semicircle (Nyquist plot) on the complex impedance plane with the real component of the impedance axis ( $Re(z)$ ).

#### 5.3.9. Water swelling

Water absorption or water swelling in the membranes was measured immersing each membrane in an excess of deionized water at 25°C. The weight of the sample initially dried at 60°C for 24 hours in an oven was originally recorded, as well as the weight of the membrane after immersion

in water. The weights of the wet membranes were measured after different time intervals until swelling equilibrium was reached. Each reported result represents the average of at least three repetitions.

#### **5.3.10. Ion Exchange Capacity (IEC)**

IEC was measured immersing a specific amount of the membrane in a 1.0 M solution of NaCl for 24 h. After removing the membrane, the solution was titrated using a 0.01 M solution of NaOH until the pH was neutral. The IEC was calculated from the moles of ion substituted divided by the initial dry mass of the membrane.

#### **5.3.11. Small angle X-ray scattering (SAXS)**

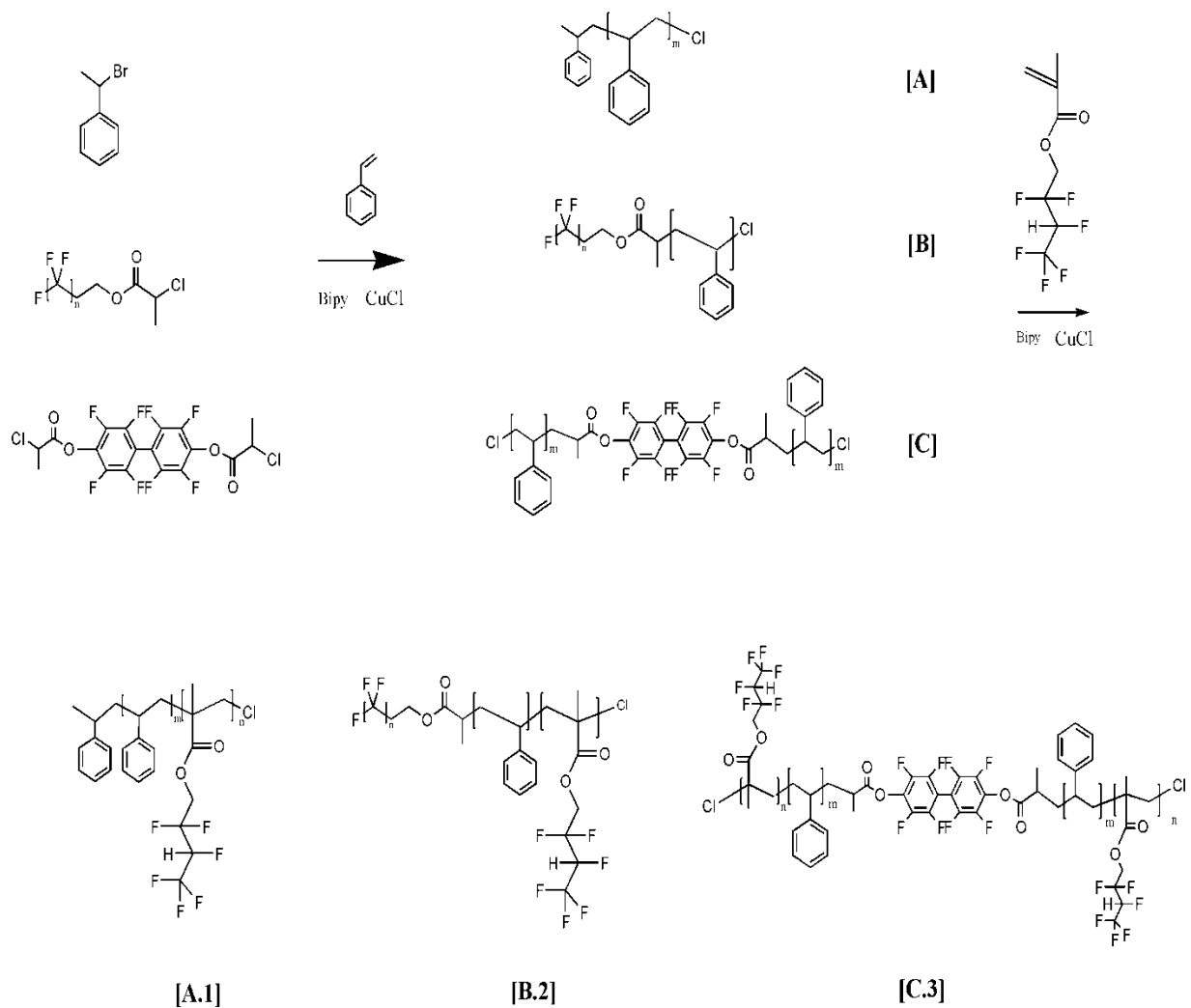
The morphology of the membranes was carried out on an Anton Paar SAXSpace. Two-dimensional scattering patterns were collected on a pinhole-collimated system using image plates and read by a Cyclone® Plus PerkinElmer image plate reader. The SAXSQuant software® was used to reduce two dimensional data to one-dimensional intensity versus scattering vector (Q) plots. The X-ray wavelength employed was 1.54 Å. The calibration standard was silver behenate and the height of the beam stop was 0.3 mm.

### **5.4. RESULTS AND DISCUSSIONS**

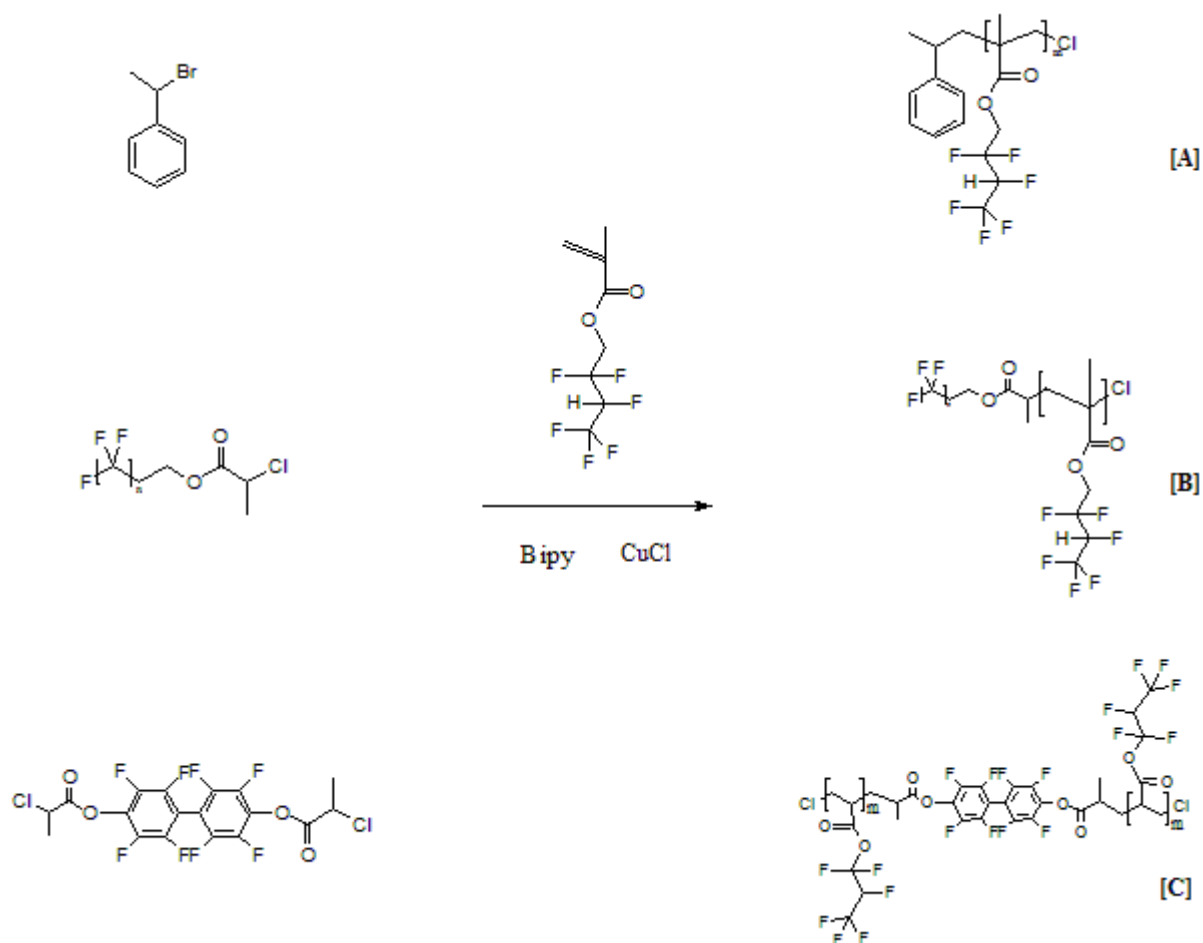
#### **5.4.1. Polymer Characterization**

##### *5.4.1.1. FTIR spectroscopy*

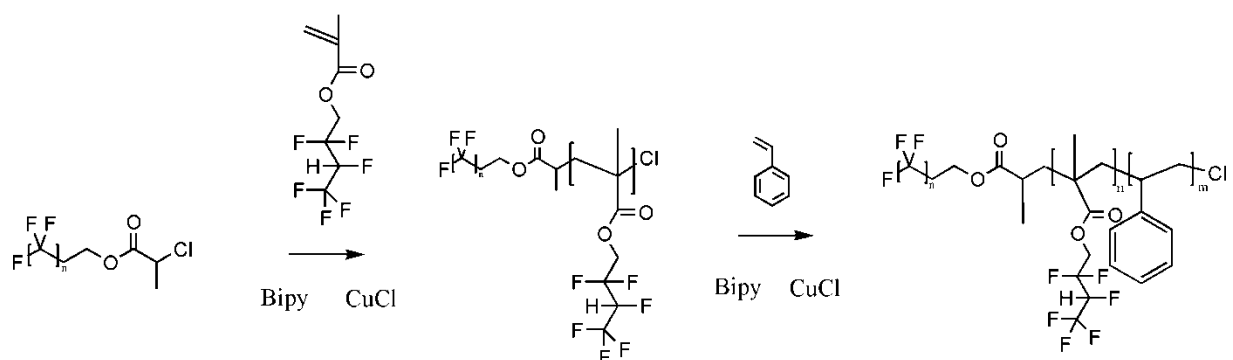
Figure 5.1 [A] and 5.1 [B] present the FTIR spectrum of Zonyl® and esterified Zonyl®; two distinctive bands were exhibited, the first band (\*2) is attributed to stretching vibration of the carbonyl group that appears around  $1755\text{ cm}^{-1}$ . The second band (\*1) corresponds to the polymer backbone (-CF<sub>2</sub>-) a strong band from  $1100\text{ to }1300\text{ cm}^{-1}$ , induced by the stretching vibration of the C – F groups. All the polymerization reactions for the homopolymer and diblock copolymers are presented in schemes 5.2, 5.3 and 5.4.



**Scheme 5.2.** Polymerization reaction for poly(PS)-b-poly(HEMA) [A.1], Zonyl®-b-poly(PS)-b-poly(HEMA) [B.2] and octo-poly(PS)-b-poly(HEMA) [C.3].

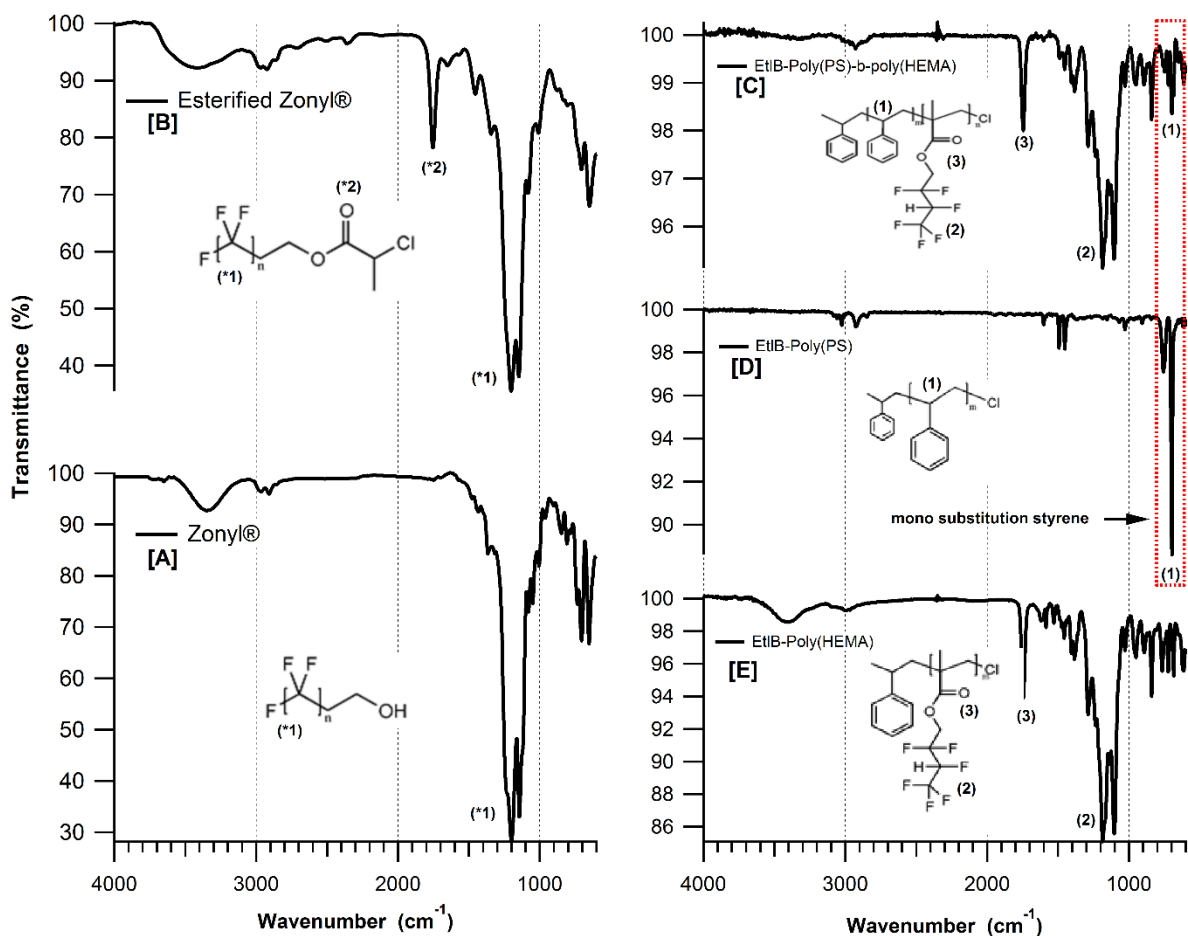


**Scheme 5.3.** Polymerization reaction for poly(HEMA) [A], Zonyl®-b-poly(HEMA) [B] and octo-poly(HEMA) [C].



**Scheme 5.4.** Polymerization reaction for Zonyl®-b-poly(HEMA)-b-poly(PS).

Poly(PS) homopolymers were synthesized using the three different initiators via ATRP technique (Scheme 5.2), in order to obtain a series of diblock fluoropolymers of poly(PS)-b-poly(HEMA). The chemical composition of poly(PS) homopolymers and poly(PS)-b-poly(HEMA) diblock copolymer were confirmed by FTIR. Figure 5.1 [D] exhibits the FT-IR spectra of EtIB-poly(PS); two distinctive regions are observed in this figure. A mono-substitution band corresponding to the styrene group is present at  $700\text{ cm}^{-1}$  (1). The second band corresponds to overtone absorptions induced by the aromatic ring; these bands appear between  $2000$  and  $1667\text{ cm}^{-1}$ .



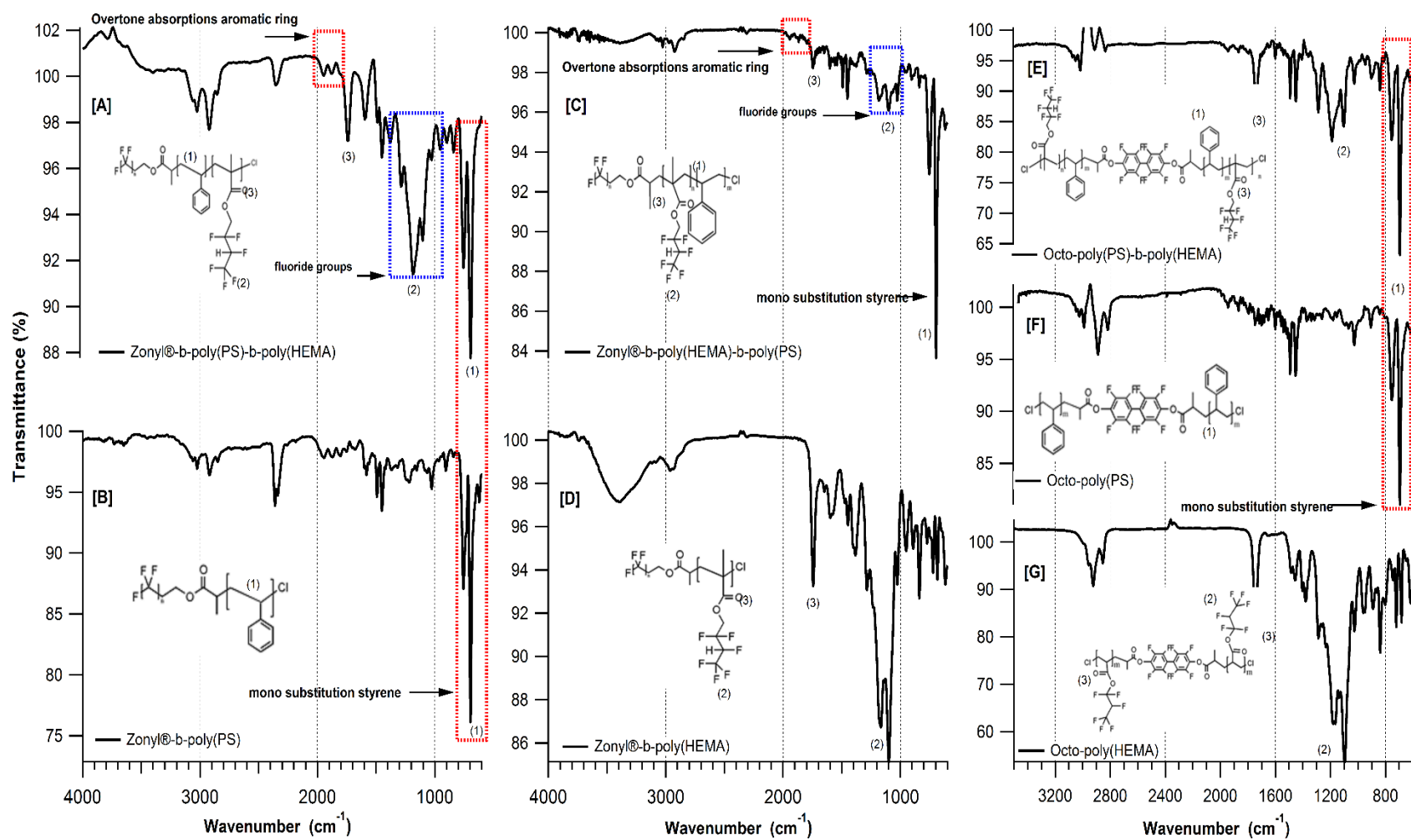
**Figure 5.1.** FTIR spectra for Zonyl® [A], esterified Zonyl® [B], EtIB-poly(PS)-b-poly(HEMA) [C], EtIB-poly(PS) [D] and EtIB-poly(HEMA) [E].

Figure 5.1[E] shows the FT-IR spectra of EtIB-poly(HEMA). This polymer possessed a characteristic peak around  $1750\text{ cm}^{-1}$  (3), that is ascribed to the stretching vibration of the carbonyl group

attributed to the C=O bond attached to HEMA. Other important band appears from 1100 to 1300  $\text{cm}^{-1}$  (2), this band corresponds to the stretching vibration induced by the chemical presence of the fluoride groups incorporated by the polymerization reaction of HEMA. EtIB-Poly(PS)-b-poly(HEMA) (Figure 5.1[C]) exhibited the stretching vibration of the carbonyl group attributed to the C=O bond attached to HEMA around 1750  $\text{cm}^{-1}$ . Other important band corresponds to the stretching vibration induced by the chemical presence of the fluoride groups appears from 1100 to 1300  $\text{cm}^{-1}$ . The chemical presence of polystyrene was confirmed by the mono-substitution band corresponding to this chemical group at 700  $\text{cm}^{-1}$ . These results indicate the presence of PS and HEMA into the homopolymers and diblock fluoropolymer.

Figure 5.2 shows the FTIR spectra for Zonyl®-b-poly(PS)-b-poly(HEMA), Zonyl®-b-poly(HEMA)-b-poly(PS), octo-poly(PS)-b-poly(HEMA) and their respective homopolymers. Zonyl®-b-poly(PS) (Figure 5.2[B]) exhibited the monosubstitution band related to the styrene group and overtone absorptions induced by the aromatic ring appeared between 2000 and 1800  $\text{cm}^{-1}$ . Zonyl®-b-poly(PS)-b-poly(HEMA) (Figure 5.2[A]) exhibited the same bands previously observed. Additionally, the vibration of the carbonyl group attributed to the C=O bond appeared around 1750  $\text{cm}^{-1}$  (3) and the fluoride group bands appeared from 1100 to 1300  $\text{cm}^{-1}$  (2). Figure 5.2[D] shows the FT-IR spectra of Zonyl®-b-poly(HEMA). The characteristic peak of the carbonyl group appeared around 1750  $\text{cm}^{-1}$  (3) and the bands corresponding to the fluoride groups appeared from 1100 to 1300  $\text{cm}^{-1}$  (2). Zonyl®-b-poly(HEMA)-b-poly(PS) (Figure 5.2[C]) presented similar chemical behavior to that of Zonyl®-b-poly(PS)-poly(HEMA). Differences between 5.2A and 5.2C could be due to the different block composition. Figure 5.2[C] displays the overtone absorptions induced by the aromatic ring and the fluoride groups attached to HEMA. These bands evidence the chemical presence of PS and HEMA in the diblock copolymer.

Figure 5.2 presents the FTIR spectra for octo-poly(PS)-b-poly(HEMA) [E], octo-Poly(PS) [F] and octo-poly(HEMA) [G]. These polymers also exhibited the characteristic bands of PS and HEMA in the range of wavenumbers previously mentioned.



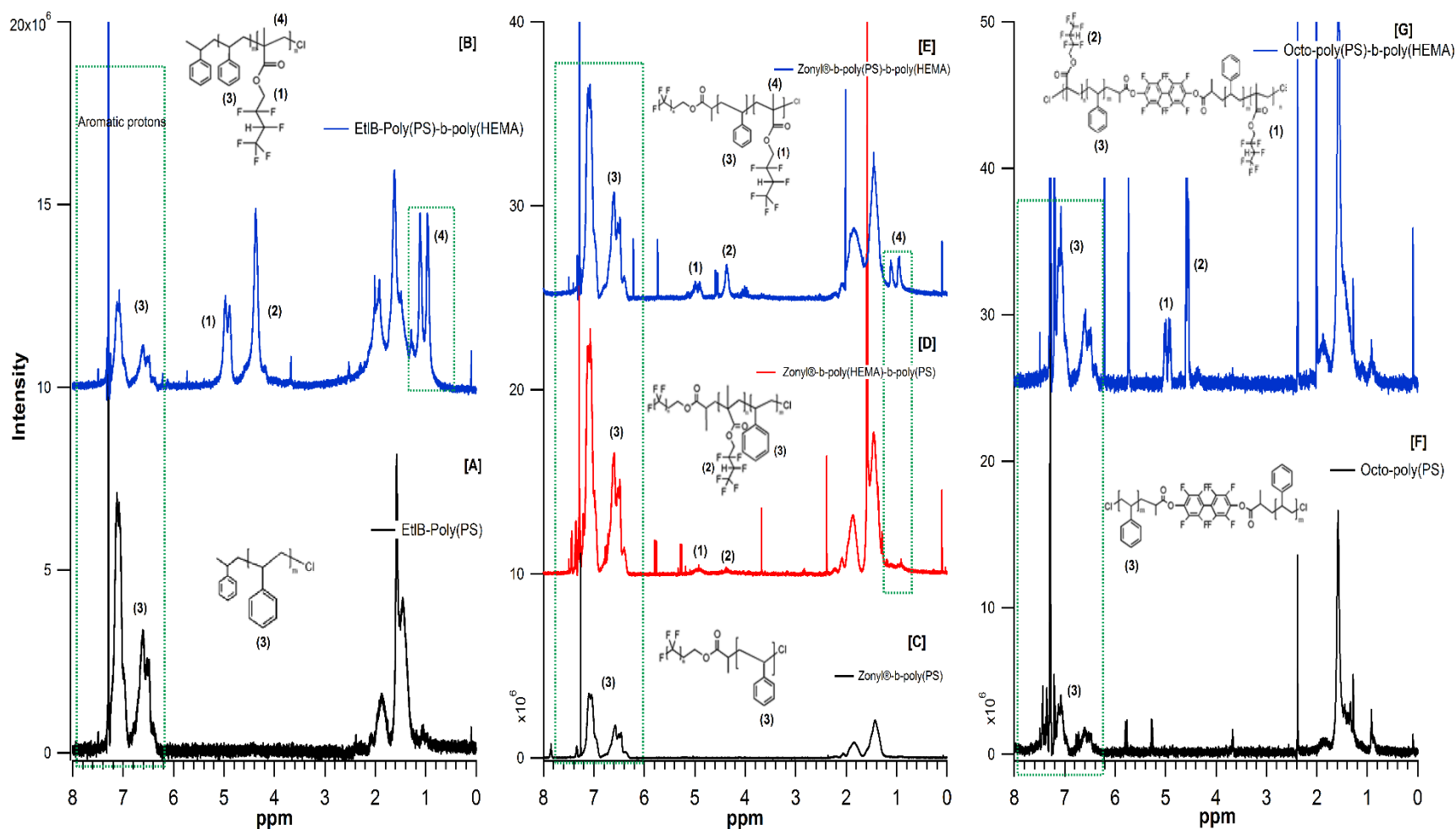
**Figure 5.2.** FTIR spectra Zonyl®-b-poly(PS)-b-poly(HEMA) [A], Zonyl®-b-poly(PS) [B], Zonyl®-b-poly(HEMA)-b-poly(PS) [C], Zonyl®-b-poly(HEMA) [D], octo-poly(PS)-b-poly(HEMA) [E], octo-poly(PS) [F] and octo-poly(HEMA) [G]

#### 5.4.1.2. Nuclear Magnetic Resonance (NMR)

$^1\text{H}$  NMR was employed in order to confirm the chemical composition of the synthesized homopolymer and diblock fluoropolymers. Figure 5.3 exhibits the  $^1\text{H}$  NMR spectra of etlB-poly(PS)-b-poly(HEMA) (Figure 5.3 [A]) and etlB-Poly(PS) (Figure 5.3 [B]). EtlB-Poly(PS) presented peaks at a large chemical shift around 7 ppm. These peaks (3) were assigned to the typical band of the protons attached to the aromatic ring in polystyrene. The peaks at 1.85 and 1.5 ppm are assigned to the methylene (-CH<sub>2</sub>-) and methine (-CH-) absorptions in Poly(PS). Three additional peaks appeared in etlB-poly(PS)-b-poly(HEMA) respect to poly(PS) at 4.95, 4.4 and 1 ppm, not previously present in PS. The absorption at 4.95 ppm is a characteristic chemical shift that corresponds to the hydrogens deshielded by the anisotropy of the adjacent C = O and fluorine groups, induced by the presence of poly(HEMA) in the diblock copolymer (1). The chemical shift at 4.4 ppm represents the proton attached to the same carbon as a fluorine group in HEMA (2). Methyl groups (-CH<sub>3</sub>-) peaks appeared at 1 ppm (4).

Zonyl®-b-poly(HEMA)-b-poly(PS) and, Zonyl®-b-poly(PS)-b-poly(HEMA) (Figure 5.3[D] and 5.3[E]) exhibited four similar characteristic peaks: a large chemical shift at 7 ppm related to the aromatic protons in PS, the hydrogens deshielded by the anisotropy of the adjacent C = O and fluorine groups at 4.95 ppm (1), the proton attached to the same carbon as a fluorine group in HEMA (2) and, the methyl groups (-CH<sub>3</sub>-) at 1 ppm.

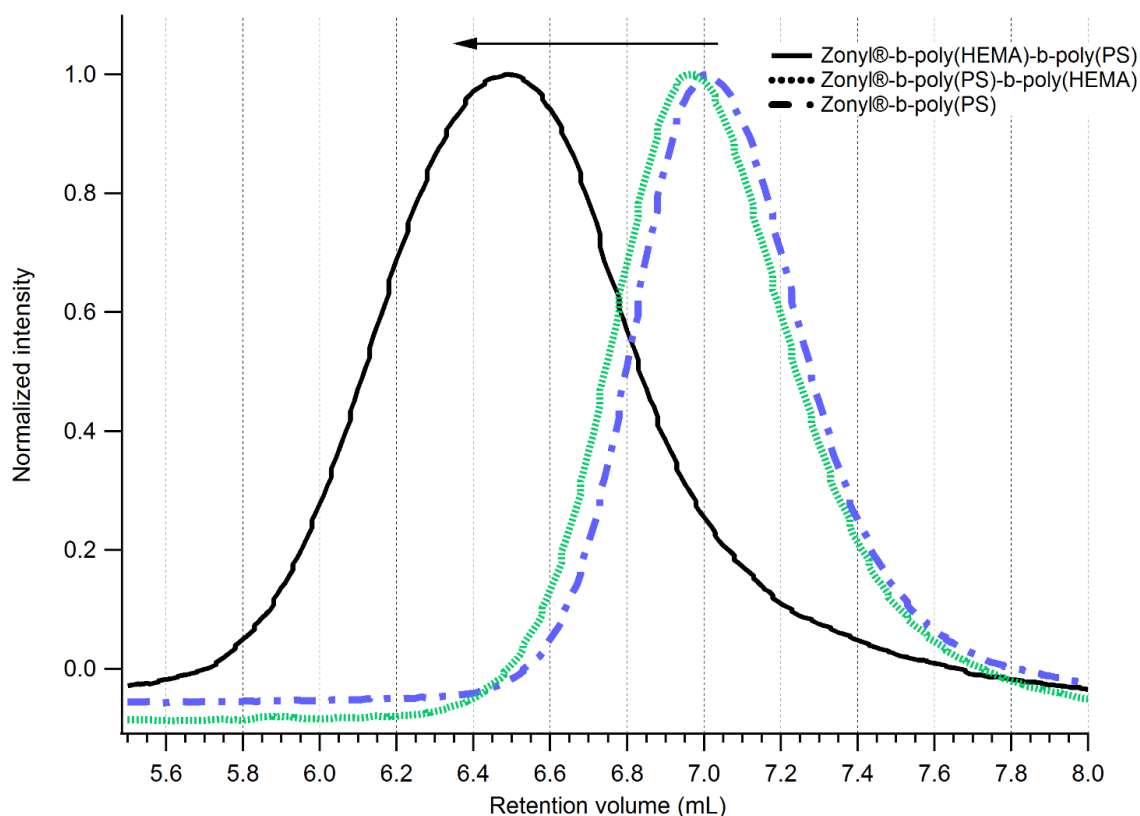
Figure 5.3[F] and 5.3[G] present the NMR spectra for octo-poly(PS)-b-poly(HEMA) and octo-Poly(PS) respectively. The homopolymer and diblock copolymer synthesized presented the chemical shift, previously mentioned, and attributed to PS and HEMA. Both FT-IR and  $^1\text{H}$  NMR spectra confirm that poly(PS) synthesized using three different initiators and their respective diblockfluoro polymers were successfully synthesized.



**Figure 5.3.** NMR spectra EtIB-poly(PS)-b-poly(HEMA) [A], EtIB-poly(PS) [B], Zonyl®-b-poly(PS) [C], Zonyl®-b-poly(HEMA)-b-poly(PS) [D], Zonyl®-b-poly(PS)-b-poly(HEMA) [E], octo-poly(PS)-b-poly(HEMA) [F] and octo-Poly(PS) [G].

#### 5.4.1.3. Gel permeation Chromatography (GPC)

The molecular weight of diblock copolymers were determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene as calibration standards. The GPC trace for Zonyl®-b-poly(PS)-b-poly(HEMA), possess a higher retention volume that Zonyl®-b-Poly(ST) (Figure 5.4); therefore, the diblock copolymer was obtained. The molecular weight for this block copolymer increased 11.3% with respect to Zonyl®-b-Poly(PS). The other homopolymers and diblock copolymers were successfully synthesized. The molecular weight, polydispersities ( $M_w/M_n$ ) and the polymer composition results and are shown in Table 5.1A and 5.1B.



**Figure 5.4.** GPC traces of Zonyl®-b-poly(HEMA)-b-Poly(PS) (Straight line), Zonyl®-b-poly(PS)-b-poly(HEMA) (Short dot line), Zonyl®-b-Poly(PS) (Short dash dot line).

**Table 5.1A.** Molecular weight characterization for homopolymer and block copolymers prepared by ATRP (using polystyrene standards).

| Sample                         | Initiator                                  | Mn x<br>E-3 | Mw x<br>E-3 | Mw/Mn |
|--------------------------------|--------------------------------------------|-------------|-------------|-------|
| EtIB-Poly(PS)                  | 1-bromo ethyl benzene                      | 3.68        | 5.19        | 1.41  |
| EtIB-Poly(PS)-b-poly(HEMA)     | EtIB-Poly(PS)                              | 24.9        | 48.2        | 1.94  |
| Zonyl®-b-poly(PS)              | Esterified Zonyl®                          | 10.6        | 14.9        | 1.4   |
| Zonyl®-b-poly(PS)-b-poly(HEMA) | Zonyl-b-poly(PS)                           | 11.8        | 16.9        | 1.44  |
| Zonyl®-b-poly(HEMA)-b-poly(PS) | Zonyl-b-poly(HEMA)                         | 36.5        | 65.7        | 1.8   |
| Octo-poly(PS)                  | Esterified<br>octafluoro-4-4'-<br>biphenol | 24.6        | 42.3        | 1.7   |
| Octo-poly(PS)-b-poly(HEMA)     | Octo-poly(PS)                              | 26.6        | 44.85       | 1.68  |

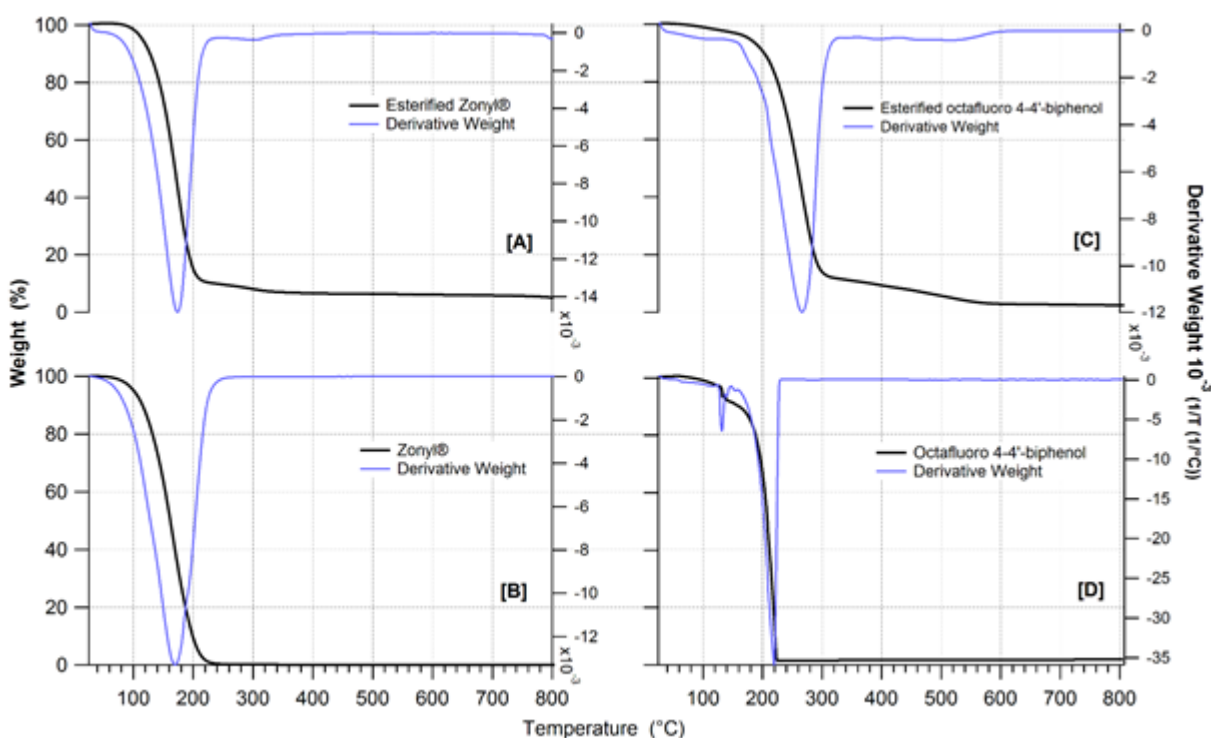
**Table 5.1B.** Polymer composition (wt%).

| Sample                         | Initiator<br>[wt%] | PS<br>[wt%] | HEMA<br>[wt%] |
|--------------------------------|--------------------|-------------|---------------|
| EtIB-Poly(PS)                  | 3                  | 97          | Absent        |
| EtIB-Poly(PS)-b-poly(HEMA)     | 0.44               | 14.28       | 85.27         |
| Zonyl®-b-poly(PS)              | 13.89              | 86.11       | Absent        |
| Zonyl®-b-poly(PS)-b-poly(HEMA) | 8.98               | 55.52       | 35.50         |
| Zonyl®-b-poly(HEMA)            | 2.99               | Absent      | 97.01         |
| Zonyl®-b-poly(HEMA)-b-poly(PS) | 0.73               | 75.62       | 23.65         |
| Octo-poly(PS)                  | 10.81              | 89.19       | Absent        |
| Octo-poly(HEMA)                | 8.75               | Absent      | 91.25         |
| Octo-poly(PS)-b-poly(HEMA)     | 7.32               | 60.41       | 32.26         |

#### 5.4.1.4. Thermogravimetric Analysis (TGA)

Figure 5.5[B] shows that unesterified Zonyl® only possessed one degradation temperature at 169.73°C, this degradation corresponds to the polymer backbone (-CF<sub>2</sub>-) degradation. The esterification reaction modified the degradation curve, shifting the degradation temperature towards a higher temperature (173.73°C). One additional small degradation was observed

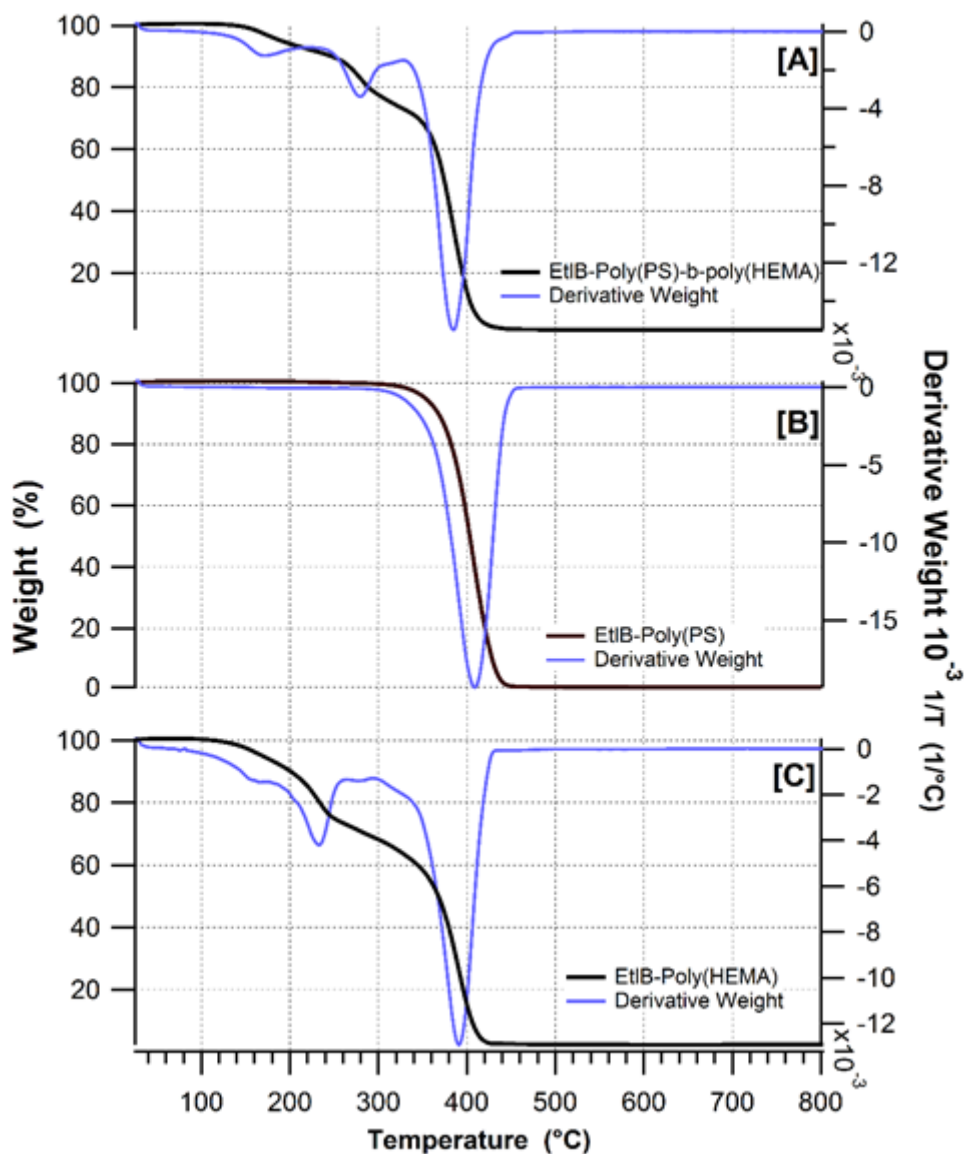
around 297.47°C (Figure 5.5[A]). Considering that Zonyl® suffered only one chemical modification, induced by the esterification reaction, we could conclude that the weight loss at 297.47°C was due to the incorporation of the ester group to Zonyl®. Esterified octafluoro 4-4'-biphenol was analyzed using the same procedure. The thermal behavior of octafluoro 4-4'-biphenol exhibited two degradation temperatures: one at 130°C and the second one at 220°C (Figure 5.5 [D]). The thermal stability of octafluoro 4-4'-biphenol significantly improved after the esterification reaction. Figure 5.5[C] exhibits the thermal behavior for esterified octafluoro 4-4'-biphenol. This compound shows its first degradation started at 190°C, additional degradations occurred above 300°C.



**Figure 5.5.** TGA for esterified Zonyl® [A], Zonyl® [B], esterified octafluoro 4-4'-biphenol [C] and octafluoro 4-4'-biphenol [D].

The thermal degradation of etIB-poly(PS) is shown in Figure 5.6[B]. The TGA curve for this polymer only presented one degradation temperature at 408.86°C that corresponds to the polystyrene backbone. Figure 5.6[C] presented the TGA curve for EtIB-poly(HEMA). This polymer exhibited two degradation temperatures at 166.69 and 233.24°C. Previous studies<sup>31,32</sup> have show

that methacrylic acid ester polymers suffered degradation at lower temperatures. These studies suggest that the degradation mechanism at lower temperatures is related to the bond cleavage in the ester group (between the carbonyl group and oxygen)<sup>33</sup> and, that the polymeric backbone degraded at higher temperatures.

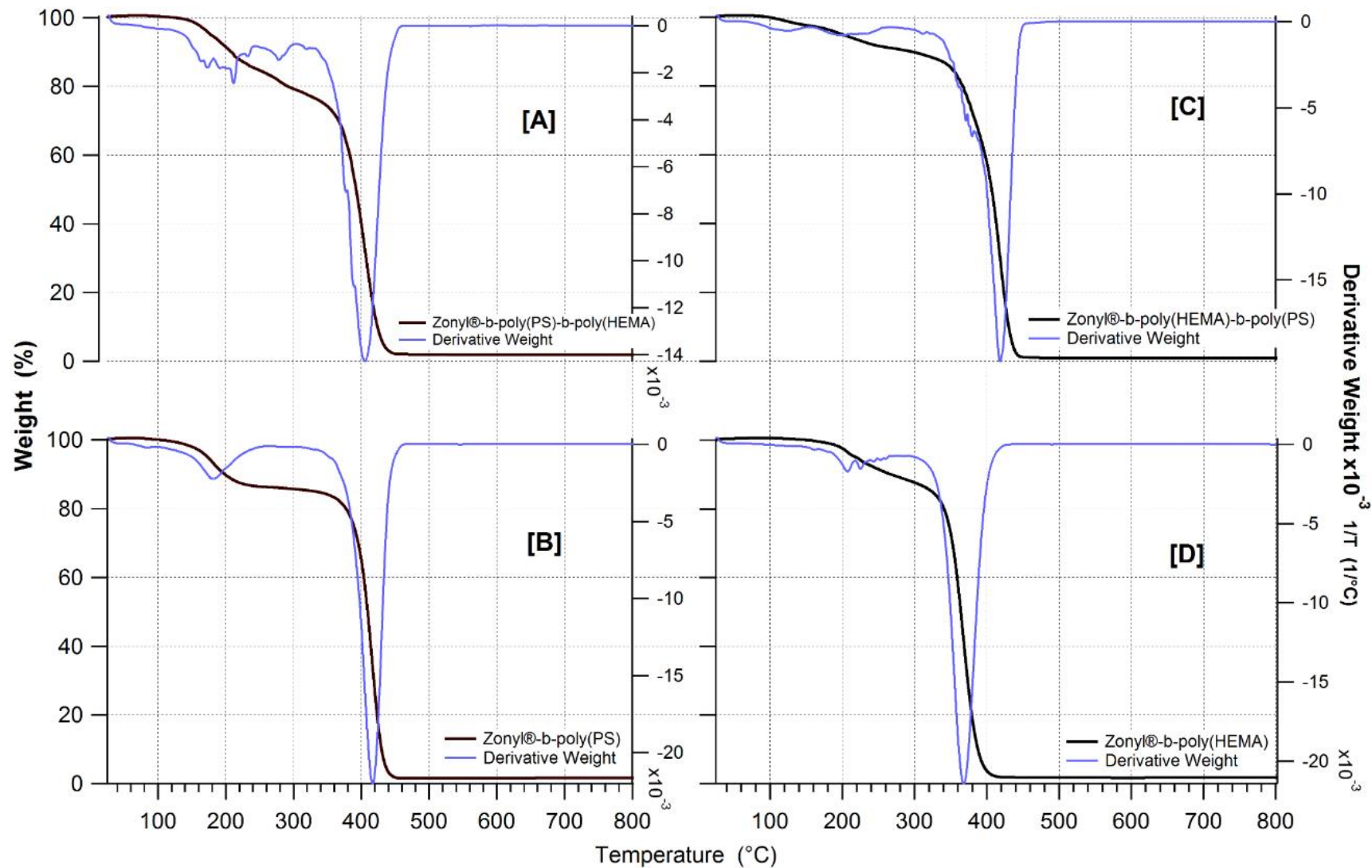


**Figure 5.6.** TGA for EtIB-Poly(PS)-b-poly(HEMA) [A], EtIB-poly(PS) [B] and EtIB-poly(HEMA) [C].

Figure 5.6[A] shows the TGA curve for EtIB-Poly(PS)-b-poly(HEMA). The thermal stability of poly(PS) was adversely affected when HEMA was incorporated to the polymeric chain. Part of the fluorocarbon polymer group (ester group) suffered thermal degradation below 300°C and the remaining polymer chain was degraded in the range from 350 to 450°C. In this weight loss step, the remaining of polymeric chain of HEMA and all the PS chain were overlapped.

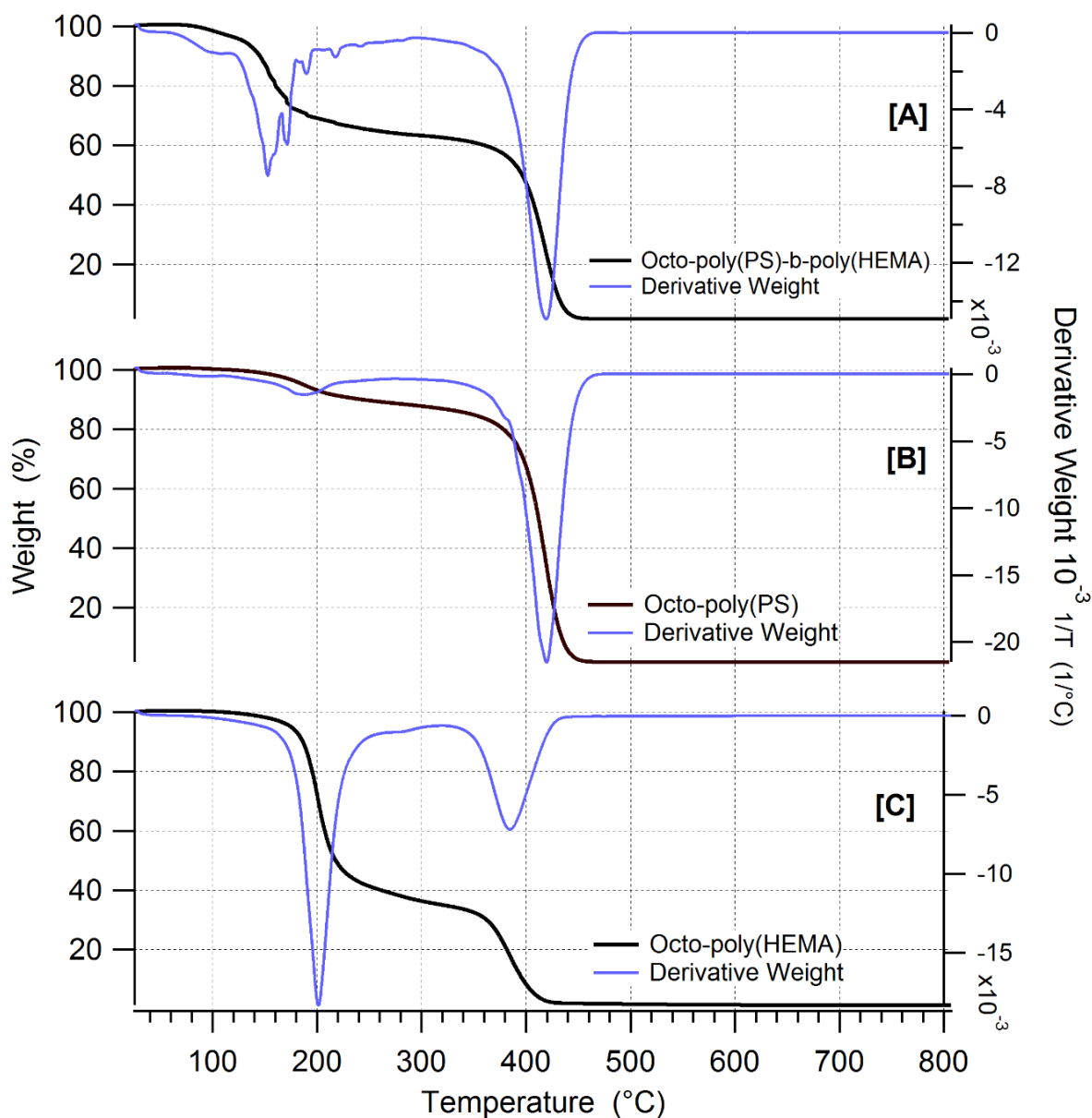
Figure 5.7 [B] exhibits poly(PS) initiated with esterified Zonyl®. This polymer presented two different degradation temperatures. The first degradation was at 181.79°C with a weight loss percent of 13.84% and the second at 416.69°C. Zonyl®-b-poly(PS)-b-poly(HEMA) (Figure 5.7 [A]) exhibited changes with respect to Zonyl®-b-poly(PS); three different degradation temperatures were identified: at 211.69°C with 14.96% weight loss, 278.62°C with 8.86% weight loss and finally 405.22°C with 75.05% of weight loss.

The incorporation of HEMA to Zonyl®-b-poly(PS) also affected adversely the thermal stability; however, Zonyl®-b-poly(PS)-b-poly(HEMA) started its degradation at a lower temperature than poly(PS)-b-poly(HEMA). Figure 5.7[D] shows the TGA for Zonyl®-b-poly(HEMA). This polymer presents one difference with respect to EtIB-poly(HEMA): Zonyl®-b-poly(HEMA) exhibited only one degradation at a lower temperature, from 200 to 300°C, while EtIB-poly(HEMA) exhibited two different degradations in the same range. The remaining polymeric back-bone degrades at similar degradation temperature for both polymers. The incorporation of PS to this polymer (Figure 5.7[C]) improved the thermal stability at higher temperatures; however, the weight loss at lower temperatures (corresponding to HEMA), was still present.



**Figure 5.7.** TGA for Zonyl®-b-poly(PS)-b-poly(HEMA) [A], Zonyl®-b-poly(PS) [B], Zonyl®-b-poly(HEMA)-b-poly(PS) [C] and Zonyl®-b-poly(HEMA) [D].

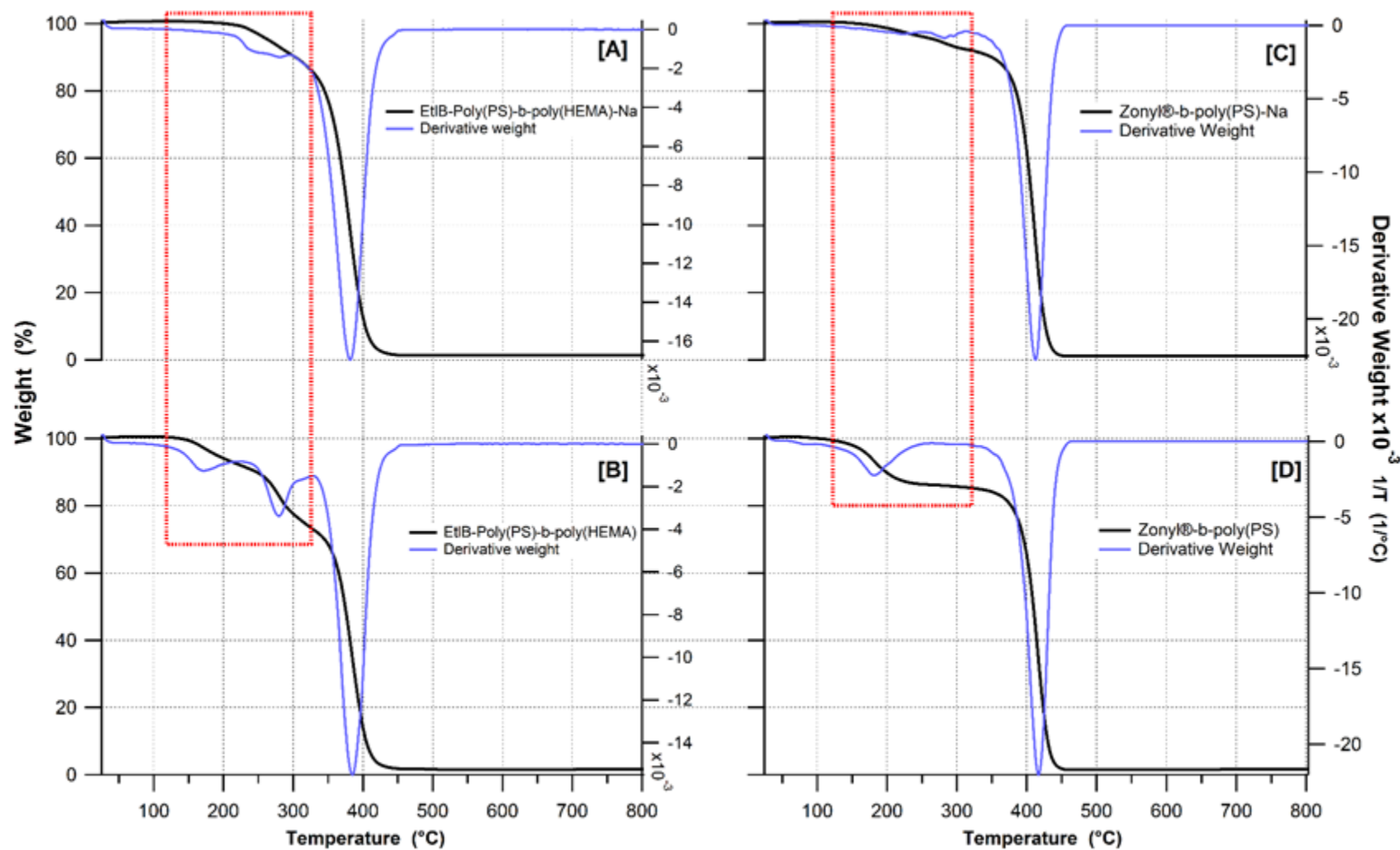
Octo-poly(PS) (Figure 5.8[B]) presented two different degradation temperatures. The first was observed at 181.79°C with a weight loss percent of 10.81% and the second at 419.74°C. Octo-poly(HEMA) (Figure 5.8[C]) exhibited changes in the TGA curve with respect to poly(HEMA) and Zonyl®-b-poly(HEMA).



**Figure 5.8.** TGA for octo-poly(PS)-b-poly(HEMA) [A], octo-poly(PS) [B] and octo-poly(HEMA) [C].

A large weight loss of 58% was identified at 200°C and another degradation at 385°C with 41% of weight loss. This suggests that the degradation behavior remarkably depends on the initiator; esterified octafluoro 4-4'-biphenol and HEMA possess a significant weight loss around 200°C. The combination of these chemical groups produced a unique TGA behavior for poly(HEMA) with a higher weight loss at lower temperature. Figure 5.8 [A] presents the TGA curve for octo-poly(PS)-b-poly(HEMA); a large weight loss of 36.67% was identified from 125 to 300°C and, another degradation at 420.01°C with 61.67% of weight loss. These results agree with the previously observed results that the incorporation of HEMA to octo-poly(PS) produce a unique thermal behavior with a higher weight loss at lower temperature. These results suggest that the incorporation of esterified Zonyl® or esterified octafluoro 4-4'-biphenol to poly(PS) or poly(HEMA) unstabilize the polymeric chain, presenting an additional weight loss at lower temperature with respect to the homopolymer initiated with 1-bromo ethyl benzene.

In order to improve the thermal stability of EtIB-poly(PS)-b-poly(HEMA) and Zonyl®-b-poly(PS), they were exchanged with a solution 0.1 M of NaOH for 48 hours. Studies suggest that the interactions of the counter-ion with a specific group, like ethers<sup>18</sup> or the sulfonic group<sup>15-16,34</sup>, improve the polymer stability. A unique feature was observed for EtIB-poly(PS)-b-poly(HEMA) exchanged with Na<sup>+</sup> (Figure 5.9[A]). Although the polymer structure degraded at 383°C, the first degradation region, (corresponding to the ester group), was absent. For this counter-ion, the second degradation (related also to ester group) suffered 12.5% of weight loss, instead of 18.3% without the cation-substitution. This suggests that sodium interacts directly with the ester group improving the thermal stability of this polymer. A similar procedure was used with Zonyl®-b-poly(PS); the thermal stability of this polymer significantly improved (78°C) after the counter-ion substitution with sodium (Figure 5.9[C]). This results suggest that the counter-ion inhibited the bond cleavage in the ester group contained in the esterified Zonyl®. Other experiments are presented ahead to understand the impact of the initiator on the thermal stability of these polymers. Table 5.2 summarizes the degradation temperatures for all the synthesized polymers.



**Figure 5.9.** TGA for EtIB-poly(PS)-b-poly(HEMA)-Na [A], EtIB-poly(PS)-b-poly(HEMA) [B], Zonyl®-b-poly(PS)-Na [C] and Zonyl®-b-poly(PS) [D].

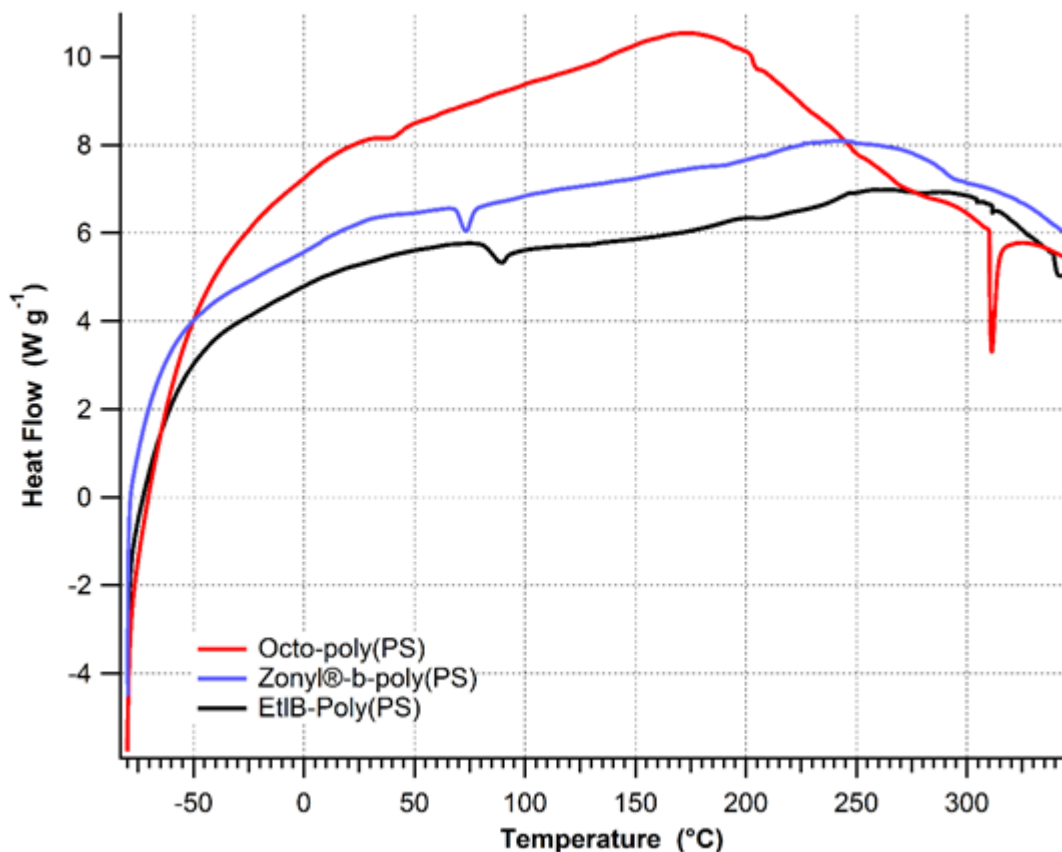
**Table 5.2.** Polymer and initiators degradation temperatures.

| Polymer                             | 1 <sup>st</sup>     | weight<br>[%] | 2 <sup>nd</sup>     | weight<br>[%] | 3 <sup>rd</sup>     | weight<br>[%] | Residue<br>[%] |
|-------------------------------------|---------------------|---------------|---------------------|---------------|---------------------|---------------|----------------|
|                                     | degradation<br>(°C) |               | degradation<br>(°C) |               | degradation<br>(°C) |               |                |
| Zonyl®-b-poly(PS)-b-poly(HEMA)      | 211.69              | 14.96         | 278.62              | 8.867         | 402                 | 75.05         | 1.11           |
| Zonyl®-b-poly(PS)                   | 181.79              | 13.89         | *                   | *             | 416.69              | 84.81         | 1.28           |
| Zonyl®-b-poly(PS)-Na                | 260                 | 9.48          | *                   | *             | 412                 | 89.35         | 1.16           |
| Zonyl®-b-poly(HEMA)-poly(PS)        | 124.35              | 2.99          | 199.21              | 6.72          | 419.21              | 89.40         | 0.88           |
| Zonyl®-b-poly(HEMA)                 | 207.64              | 12.2          | *                   | *             | 368.22              | 86.57         | 1.18           |
| Esterified Zonyl®                   | 173.73              | 89.30         | 297.47              | 3.93          | *                   | *             | 6.75           |
| Zonyl®                              | 169.73              | 99.85         | *                   | *             | *                   | *             | 0.15           |
| Octo-poly(PS)-b-poly(HEMA)          | 152.80              | 36.67         | *                   | *             | *                   | 61.67         | 1.66           |
| Octo-poly(PS)                       | 187.99              | 10.81         | *                   | *             | 419.74              | 88.02         | 1.17           |
| Octo-poly(HEMA)                     | 202                 | 58.09         | *                   | *             | 385                 | 40.8          | 1.11           |
| Esterified octafluoro-4-4'-biphenol | 265                 | 89            | *                   | *             | 450                 | 10            | 1              |
| Octafluoro-4-4'-biphenol            | 130                 | 8             | 220                 | 91            | *                   | *             | 1              |
| EtIB-Poly(PS)-b-poly(HEMA)          | 171.64              | 7.93          | 279.50              | 18.28         | 384.82              | 72.2          | 1.57           |
| EtIB-Poly(PS)-b-poly(HEMA)-Na       | *                   | *             | 280                 | 12.54         | 382                 | 86            | 1.45           |
| EtIB-Poly(PS)                       | *                   | *             | *                   | *             | 408.86              | 99.84         | 0.16           |
| EtIB-Poly(HEMA)                     | 166.69              | 9.25          | 233.24              | 23.18         | 391.04              | 65.24         | 2.32           |

\* Absent

#### 5.4.1.5. Differential Scanning Calorimetry (DSC)

Figure 5.10 presents the DSC comparison between octo-poly(PS), Zonyl®-b-poly(PS) and EtIB-poly(PS). The incorporation of different initiators to the polymeric chain of poly(PS) produced different DSC curves for each of the initiators studied. EtIB-poly(PS) exhibited a thermal transition at 92°C. The glass transition temperature of polystyrene has been investigated and different values for this transition were found in a range from 90 to 100°C.<sup>35-37</sup> Zonyl®-b-poly(PS) presented the same transition shifted towards lower temperatures (70°C). Octo-poly(PS) showed the transition at 45°C, which is even at a lower temperature as compared to poly(PS) and Zonyl®-b-poly(PS).



**Figure 5.10.** DSC comparison between octo-Poly(PS), Zonyl®-b-poly(PS) and EtIB-poly(PS).

#### 5.4.1.6. UV Spectroscopy

In order to investigate the role of the initiators on the electronic transitions and thermal stability of the polymers, UV spectroscopy was performed first at room temperature.

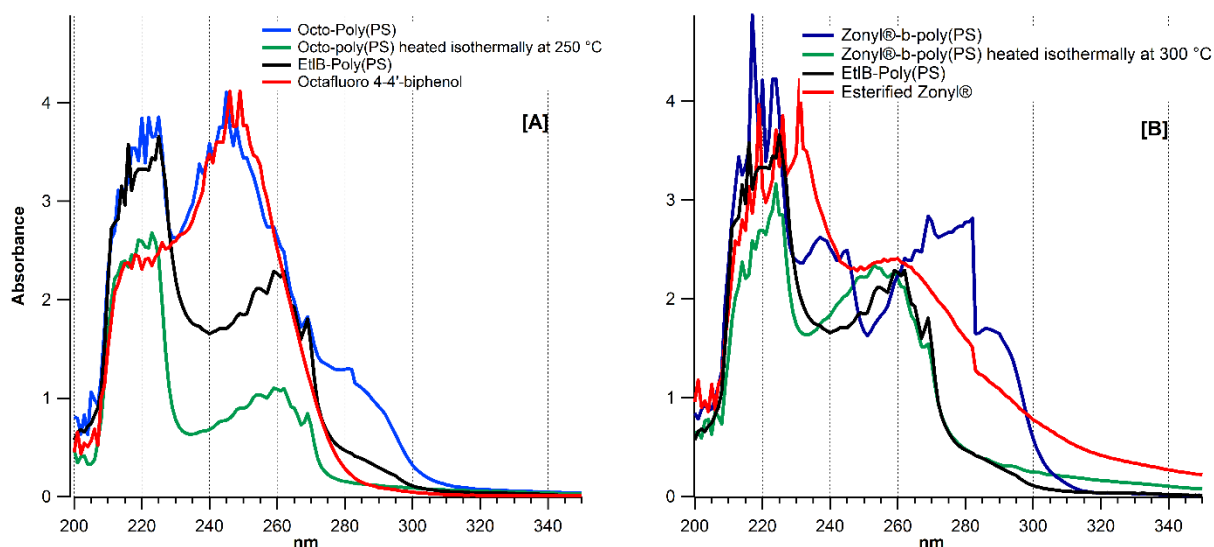
They were heated isothermally at a specific temperature (e.g. 250 or 300°C) during two and a half hours, the resulting polymers were dissolved in THF and then the UV spectra were recorded. The UV spectrum of octafluoro-4-4'-biphenol, EtIB-poly(PS) and octo-poly(PS) isothermally heated to 250 °C are presented in Figure 5.11[A]. This figure also shows the UV spectrum for octo-poly(PS) for comparison purposes. As shown in this figure, octafluoro-4-4'-biphenol exhibited a lambda maximum at 247 nm, which corresponds to the secondary band of the aromatic rings attached to the diphenol group. The 220-nm band is less intense, and it corresponds to a forbidden transition of the aromatic ring.<sup>38</sup> Poly(PS) initiated with 1-bromo ethyl benzene (Figure 5.11[A]), presented two typical transitions related to the aromatic ring present in styrene. The band at 260 nm corresponds to the transition related to the secondary bands of the aromatic ring; another band at 225 nm is associated with the primary bands of this chemical group attached into this polymer.

The incorporation of octafluoro-4-4'-biphenol into the polymeric chain of poly(PS) produced a unique and different UV spectrum than poly(PS) initiated with 1-bromo ethyl benzene. Octo-poly(PS) presented a lambda maxima at 245 nm, this band corresponds to the transition related to the secondary band of the aromatic ring attached to the diphenol group presented in the initiator. The observed spectrum of this polymer has an additional absorption band around 280-290 nm, this band is attributed to the  $n - \pi^*$  transition of the carbonyl group<sup>38-40</sup> attached to the octafluoro-4-4'-biphenol after the esterification reaction. The bands corresponding to the polystyrene group in this polymer are overlapped at 260 nm with the band related to the diphenol group present in the initiator.

Octo-poly(PS) was heated isothermally at 250°C, after this process, the UV spectra was recorded. The observed spectrum for this polymer shows that the heat treatment removed the bands attributed to the  $n - \pi^*$  transition of the carbonyl group attached in the initiator. In addition, the

band at 245 nm assigned to diphenol group in the initiator disappeared. These results suggests that the first weight loss of octo-poly(PS) presented in the TGA curve correspond to the esterified octafluoro-4-4'-biphenol.

Similarly poly(PS) initiated with esterified Zonyl® was analyzed. Figure 5.11 [B] presents the UV spectra for esterified Zonyl®, EtIB-poly(PS) and Zonyl®-b-poly(PS) heated isothermally to 300°C. As shown in this figure, Zonyl®-b-poly(PS) exhibited an absorption band around 280-290 nm; this band is also attributed to the  $n - \pi^*$  transition of the carbonyl group attached to this initiator.

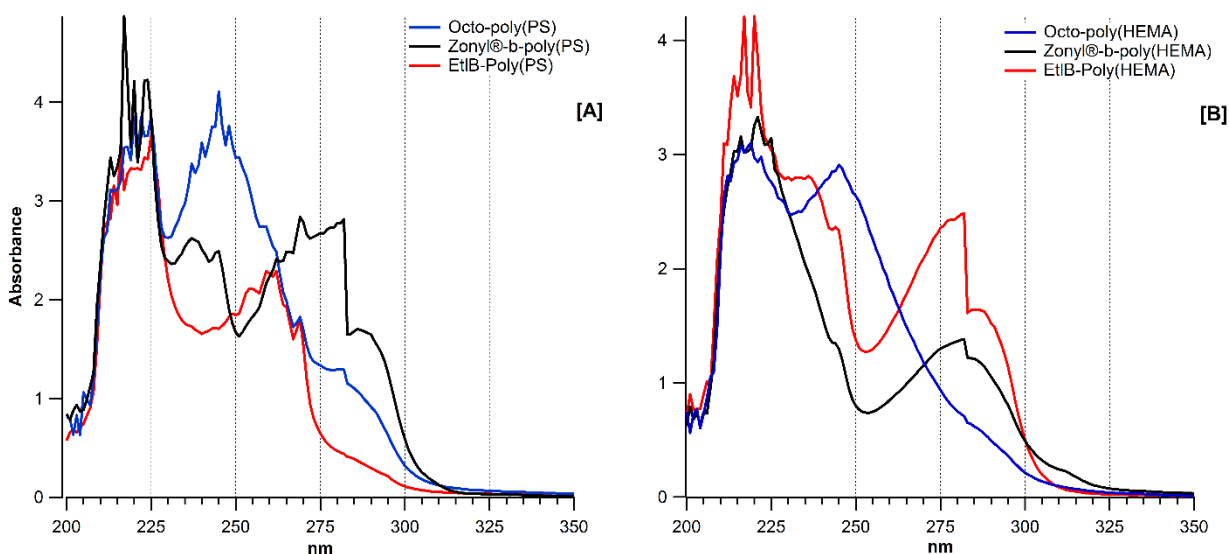


**Figure 5.11.** UV comparison between octo-poly(PS), octo-poly(PS) heated isothermally at 250 °C during 2.5 h, EtIB-poly(PS), octafluoro 4-4'-biphenol [A] and Zonyl®-b-poly(PS), Zonyl®-b-poly(PS) heated isothermally at 300 °C during 2.5 h, poly(PS) and esterified Zonyl® [B]. All the UV spectra were measured at room temperature.

The poly(PS) group exhibited a band at 260 nm related to the aromatic ring. A similar procedure was used in order to understand the thermal effect of the esterified Zonyl® on poly(PS): it was heated isothermally at 300°C during two and a half hours; after this process the UV spectra was recorded. The UV spectrum exhibited that the heat treatment also removed the bands attributed to the  $n - \pi^*$  transition of the carbonyl group attached to the initiator; additional to this, the

bands at 235 and 245 nm disappeared. The spectrum obtained after the heat treatment shows a similar trend to that observed for poly(PS). These results suggest that the first weight loss of Zonyl®-b-poly(PS) presented in the TGA curve corresponds to the esterified Zonyl®.

Figure 5.12 exhibited the comparison between the initiators used to polymerize poly(PS) (5.12[A]) and poly(HEMA) (5.12[B]). As shown in this figure, octo-poly(PS) and octo-poly(HEMA) for example, exhibited a strong absorption at 245 nm, this absorption was related to the esterified octafluoro 4-4'-biphenol in the polymer. The bands corresponding to PS and HEMA were overlapped by this absorption. These results suggest that the initiator produced unique UV spectra for this polymer depending on the chemical properties of the initiator. Table 5.3 summarizes the UV transitions for all the synthesized polymers.



**Figure 5.12.** UV spectra for octo-poly(PS), Zonyl®-b-poly(PS) , EtIB-poly(PS) [A] and octo-poly(HEMA), Zonyl®-b-poly(HEMA) , EtIB-poly(HEMA) [B].

**Table 5.3.** UV parameters.

| Polymer                                         | $\lambda 1$<br>[nm] | $\lambda 2$<br>[nm] | $\lambda 3$<br>[nm] | $\lambda 4$<br>[nm] | $\lambda 5$<br>[nm] |
|-------------------------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| EtIB-Poly(PS)                                   | 220                 | *                   | *                   | 260                 | *                   |
| EtIB-Poly(PS)-b-poly(HEMA)                      | 220                 | 237.5               | 245                 | 260                 | 282                 |
| Zonyl®-b-poly(PS)                               | 220                 | 237.5               | 245                 | 260                 | 282                 |
| Zonyl®-b-poly(PS) heated isothermally at 300 °C | 220                 | *                   | *                   | 255                 | *                   |
| Zonyl®-b-poly(PS)-b-poly(HEMA)                  | 220                 | 237.5               | 245                 | 260                 | 282                 |
| Esterified Zonyl®                               | 220                 | 232                 | *                   | 258                 | 282                 |
| Zonyl®                                          | 220                 | 232                 | *                   | 258                 | *                   |
| Octo-poly(PS)-b-poly(HEMA)                      | 220                 | 237.5               | 245                 | *                   | 282                 |
| Octo-poly(PS)                                   | 220                 | *                   | 245                 | *                   | 282                 |
| Octo-poly(PS) heated isothermally at 250 °C     | 220                 | *                   | *                   | 260                 | *                   |
| Esterified octafluoro-4-4'-biphenol             | 220                 | *                   | 247                 | *                   | 282                 |
| Octafluoro-4-4'-biphenol                        | 220                 | *                   | 247                 | *                   | *                   |

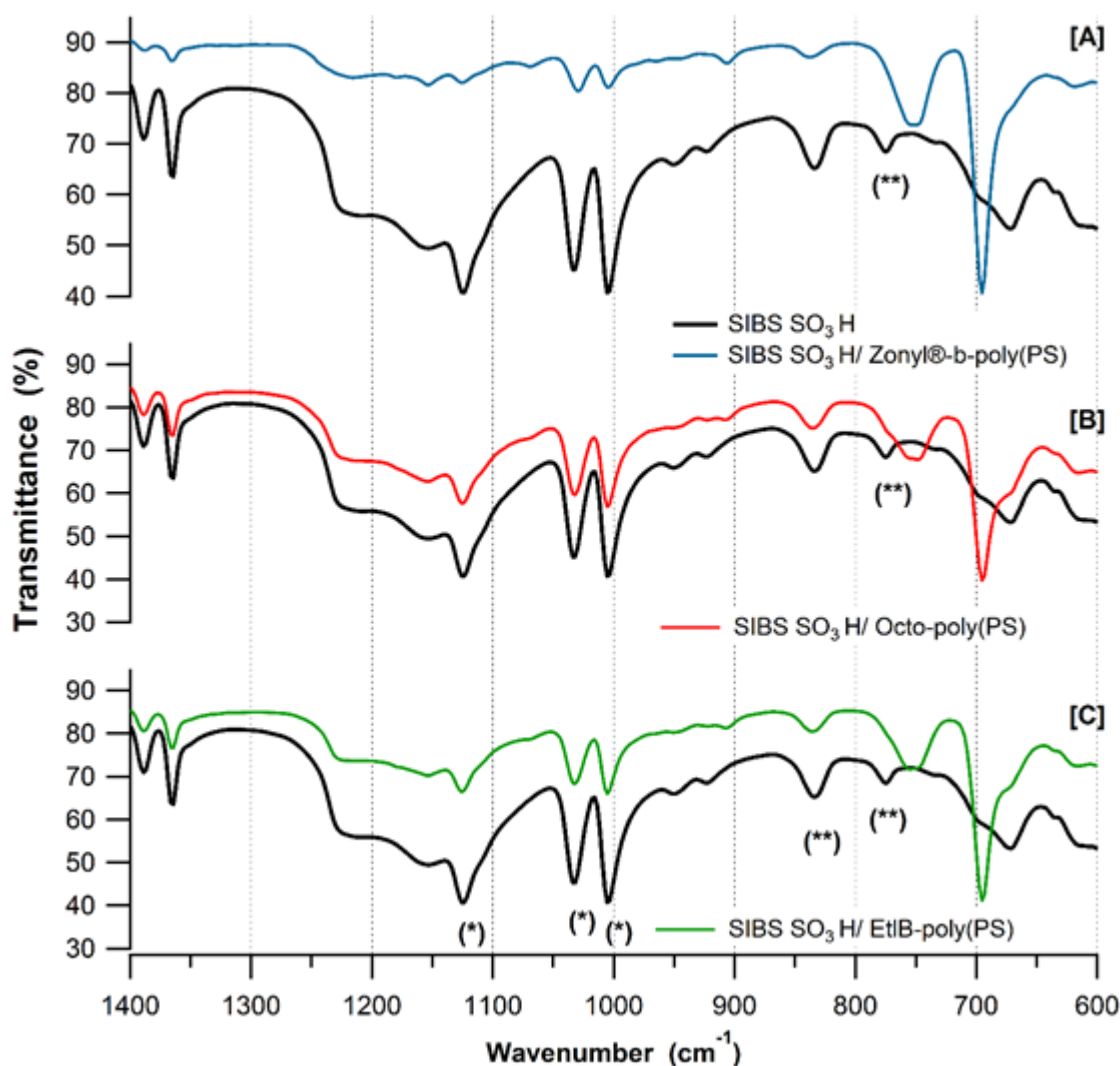
\* Absent

## 5.4.2. Polymer blend characterization

### 5.4.2.1. FTIR spectroscopy

Figure 5.13[A] shows the FT-IR spectrum of SIBS SO<sub>3</sub>H and SIBS SO<sub>3</sub>H/Zonyl®-b-poly(PS) membranes. SIBS SO<sub>3</sub>H membrane exhibited three distinctive bands at 1124, 1034, 1007(\*) cm<sup>-1</sup> associated to the sulfonic group.<sup>15</sup> The band at 1034 cm<sup>-1</sup> was caused by an symmetric stretching vibration of the sulfonated group attributed to the S=O bond. Other important bands correspond to the para-substitution of the sulfonic group at 830 cm<sup>-1</sup> (\*\*\*) and the mono-substitution of the aromatic ring in poly(styrene) at 770 cm<sup>-1</sup> (\*\*). This figure also shows the FTIR for SIBS SO<sub>3</sub>H / Zonyl®-b-poly(PS) membrane, the addition of this polymer to SIBS SO<sub>3</sub>H membrane shifts the symmetric stretching vibration of the S=O group towards lower wavenumbers. However, the band corresponding to the mono-substitution disappeared. These results suggest that the Zonyl®-b-poly(PS) is interacting with the sulfonic group and the aromatic ring. Therefore, a change of energy is required to produce the bands at those specific wavenumbers.

Figure 5.13 [B] shows the FT-IR spectrum of SIBS SO<sub>3</sub> and SIBS SO<sub>3</sub> / Octo-poly(PS) membranes. The incorporation of this polymer to SIBS SO<sub>3</sub> membrane also shifted the symmetric stretching vibration of the S=O group and the mono-substitution band, suggesting an interaction between the sulfonic group and the aromatic ring with Octo-poly(PS). The incorporation of EtIB-poly(PS) to SIBS SO<sub>3</sub> membranes presented the same behavior previously mentioned, the polymer changed the symmetric vibration of the sulfonic group towards lower wavenumber. (Figure 5.13 [C]). Other experiments are presented ahead to understand the impact of the incorporation of these polymers in SIBS SO<sub>3</sub> membranes. Table 5.4 compiles the wavenumber changes for the symmetric stretching vibration of the sulfonic group.



**Figure 5.13.** FTIR spectra for SIBS-SO<sub>3</sub> / Zonyl®-b-poly(PS) [A], SIBS-SO<sub>3</sub> / octo-poly(PS) [B] and SIBS-SO<sub>3</sub> / EtIB-poly(PS) [C].

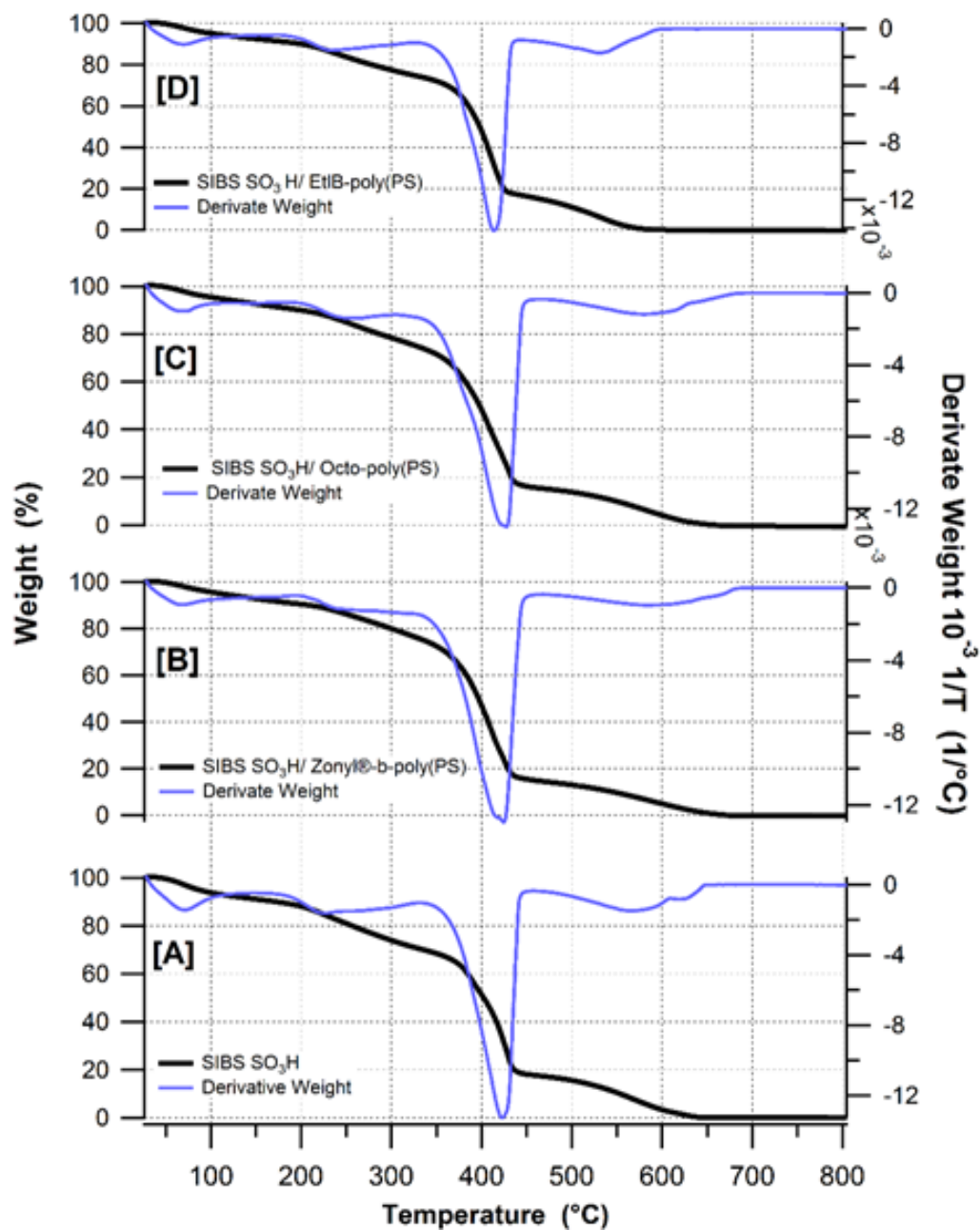
**Table 5.4.** FTIR stretching vibration bands for polymeric blends membranes.

| Membrane                                 | FTIR bands (cm <sup>-1</sup> ) |      |      |
|------------------------------------------|--------------------------------|------|------|
| SIBS-SO <sub>3</sub>                     | 1124                           | 1034 | 1005 |
| SIBS-SO <sub>3</sub> / EtIB-Poly(PS)     | 1126                           | 1032 | 1005 |
| SIBS-SO <sub>3</sub> / Zonyl®-b-poly(PS) | 1126                           | 1027 | 1005 |
| SIBS-SO <sub>3</sub> / Octo-poly(PS)     | 1126                           | 1032 | 1005 |

#### 5.4.2.2. Thermogravimetric Analysis (TGA)

Figure 5.14 [A] shows the TGA curve for SIBS SO<sub>3</sub>H. The TGA curve for this membrane exhibited four degradation temperatures, the first one at 50 – 100°C corresponds to water absorbed inside the membrane. The second degradation region at 245°C corresponds to the degradation of the sulfonic group. The third degradation at 419°C represents the polymer backbone degradation, as well as the last degradation at 565°C.<sup>16, 34</sup>

Figure 5.14 [B] shows the TGA curve for SIBS SO<sub>3</sub>/Zonyl®-b-poly(PS) membrane. The incorporation of this polymer to SIBS SO<sub>3</sub> improved 24 °C the sulfonic group degradation, 11°C the polymer backbone degradation and 56°C the last degradation. Ionic interactions with the sulfonic group in SIBS SO<sub>3</sub> membranes produced an improvement in the second and last degradation temperature in this membrane.<sup>16</sup> SIBS SO<sub>3</sub> / Octo-poly(PS) (Figure 5.14 [C]) and SIBS SO<sub>3</sub> / EtIB-poly(PS) (Figure 4.14 [D]) improved 38°C and 13°C the sulfonic group degradation and 22°C and 9°C the polymer backbone; however SIBS SO<sub>3</sub> / EtIB-poly(PS) reduced the last degradation 35°C. Table 5.5 summarized the degradation temperatures for the polymeric blend membranes.



**Figure 5.14.** TGA for SIBS-SO<sub>3</sub> [A], SIBS-SO<sub>3</sub> / Zonyl®-b-poly(PS) [B], SIBS-SO<sub>3</sub> / octo-poly(PS) [C] and SIBS-SO<sub>3</sub> / EtIB-poly(PS) [D].

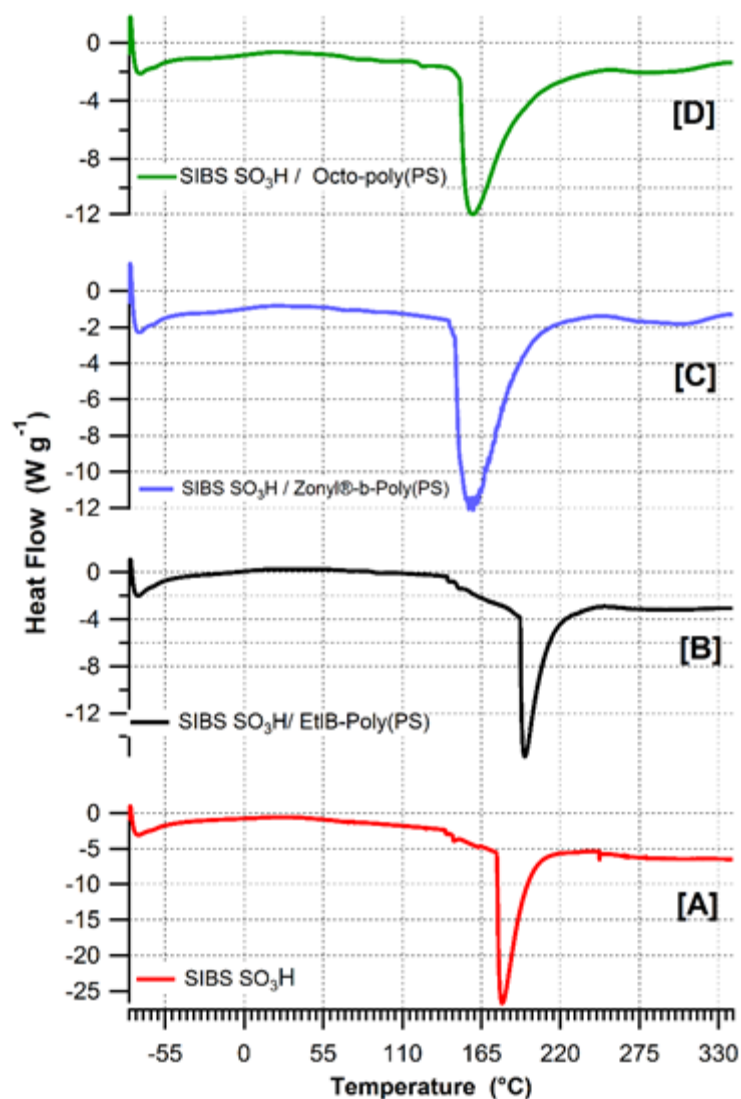
**Table 5.5.** Degradation temperatures for the polymeric blend membranes.

| Membrane                                             | 1 <sup>nd</sup> Degradation<br>(°C) | 2 <sup>nd</sup> Degradation<br>(°C) | 3 <sup>th</sup> Degradation<br>(°C) |
|------------------------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| SIBS-SO <sub>3</sub>                                 | 220                                 | 405                                 | 565                                 |
| SIBS-SO <sub>3</sub> / EtIB-Poly(PS)                 | 233                                 | 414                                 | 530                                 |
| SIBS-SO <sub>3</sub> /Zonyl <sup>®</sup> -b-poly(PS) | 244                                 | 425                                 | 586                                 |
| SIBS-SO <sub>3</sub> / Octo-poly(PS)                 | 258                                 | 427                                 | 580                                 |

#### 5.4.2.3. Differential Scanning Calorimetry (DSC)

Figure 5.15 [A] shows the DSC curve for SIBS SO<sub>3</sub>. Sulfonated SIBS presents the two endothermic peaks induced by the sulfonation process; the first at 140°C and the second peak at 177°C. The incorporation of the fluoroblock copolymer to the SIBS SO<sub>3</sub>H membrane produced unique DSC curves for each of the polymer studied. SIBS SO<sub>3</sub>H / EtIB-Poly(PS) (Figure 5.15 [B]) presented a difference in both the energy and temperature required to produce the endothermic transitions. The endothermic transitions for the ionic cluster dissapeared, however the endothermic transition for the crystalline region shifted towards higher temperature and the energy required for this transition was reduced. These changes in temperature, are related to the energy needed to overcome the crystalline bonding forces and changes in the molecular conformation of the chains in the polymer.<sup>41</sup>

DSC results for sulfonated membranes show that changes in the energy and temperature required to produce the endothermic transition for the ionic group and crystalline regions are associated to a new configuration for the ionic domain and the polymeric backbone.<sup>18</sup> SIBS SO<sub>3</sub> / Zonyl<sup>®</sup>-b-poly(PS) (Figure 5.15 [C]) also presented changes in the temperature and energy required to produce the endothermic transitions.



**Figure 5.15.** TGA for SIBS-SO<sub>3</sub> [A], SIBS-SO<sub>3</sub> / EtIB-poly(PS) [B], SIBS-SO<sub>3</sub> / Zonyl®-b-poly(PS) [C] and SIBS-SO<sub>3</sub> / octo-poly(PS) [D].

This membrane required more energy to produce the endothermic transition for the crystalline region than SIBS SO<sub>3</sub> and SIBS SO<sub>3</sub> / EtIB-Poly(PS), however the transition for the ionic domain disappeared. SIBS SO<sub>3</sub> / Octo-poly(PS) (Figure 5.15 [D]) exhibits the ionic and the crystalline transitions. However, both transitions were shifted to lower temperatures than SIBS SO<sub>3</sub>. These results are related to the changes induced by the incorporation of the polymer on the molecular conformation of the polymeric chains and sulfonic group in the membrane showed in the FTIR

and TGA experiments. Table 5.6 summarizes the endothermic transition temperatures and their corresponding energies for the membranes studied.

**Table 5.6.** Endothermic transition temperatures for polymeric blend membranes.

| Membrane                                | First Transition |                                 | Second Transition |                                 |
|-----------------------------------------|------------------|---------------------------------|-------------------|---------------------------------|
|                                         | T (°C)           | $\Delta H$ (J g <sup>-1</sup> ) | T (°C)            | $\Delta H$ (J g <sup>-1</sup> ) |
| SIBS-SO <sub>3</sub>                    | 146              | 1.30                            | 180               | 208.5                           |
| SIBS-SO <sub>3</sub> / EtIB-Poly(PS)    | *                | *                               | 195               | 149.1                           |
| SIBS-SO <sub>3</sub> /Zonyl®-b-poly(PS) | *                | *                               | 159               | 221.6                           |
| SIBS-SO <sub>3</sub> /Octo-poly(PS)     | 123              | 0.40                            | 159               | 208.9                           |

\* Absent

#### 5.4.2.4. Ion Exchange Capacity (IEC) and Water Swelling

Figure 5.16 presents IEC and water swelling for the polymer membranes studied. SIBS SO<sub>3</sub>H had the highest IEC and water swelling. Upon the incorporation of PS with different initiators, the amount of water remained constant, although lower than SIBS SO<sub>3</sub>H. The IEC for the octo-initiated PS was significantly higher than with the other initiators. Das et al.,<sup>42</sup> explained a reduction in the IEC of sulfonated fluorinated polymers with the formation of cross-linked chemical groups. Moukheiber et al.,<sup>43</sup> studying perfluoro sulfonic membranes found-out that IEC changed with the distance between the ionic domains and the polymer length. Elabd et al.,<sup>44</sup> suggested that morphological changes can also lead to changes in IEC.

Our results for SIBS SO<sub>3</sub>H/ EtIB-poly(PS) and SIBS SO<sub>3</sub>H/Zonyl®-b-poly(PS) show a significant reduction in IEC, perhaps due to the additional phase segregation upon the incorporation of the PS that perhaps led to the cross-linking of the sulfonic domains. SIBS SO<sub>3</sub>H/ Octo-poly(PS) showed a much lower reduction in IEC from SIBS SO<sub>3</sub>H, and significantly higher than the other initiated PS perhaps due to the chemical nature of the esterified octo initiator that allowed

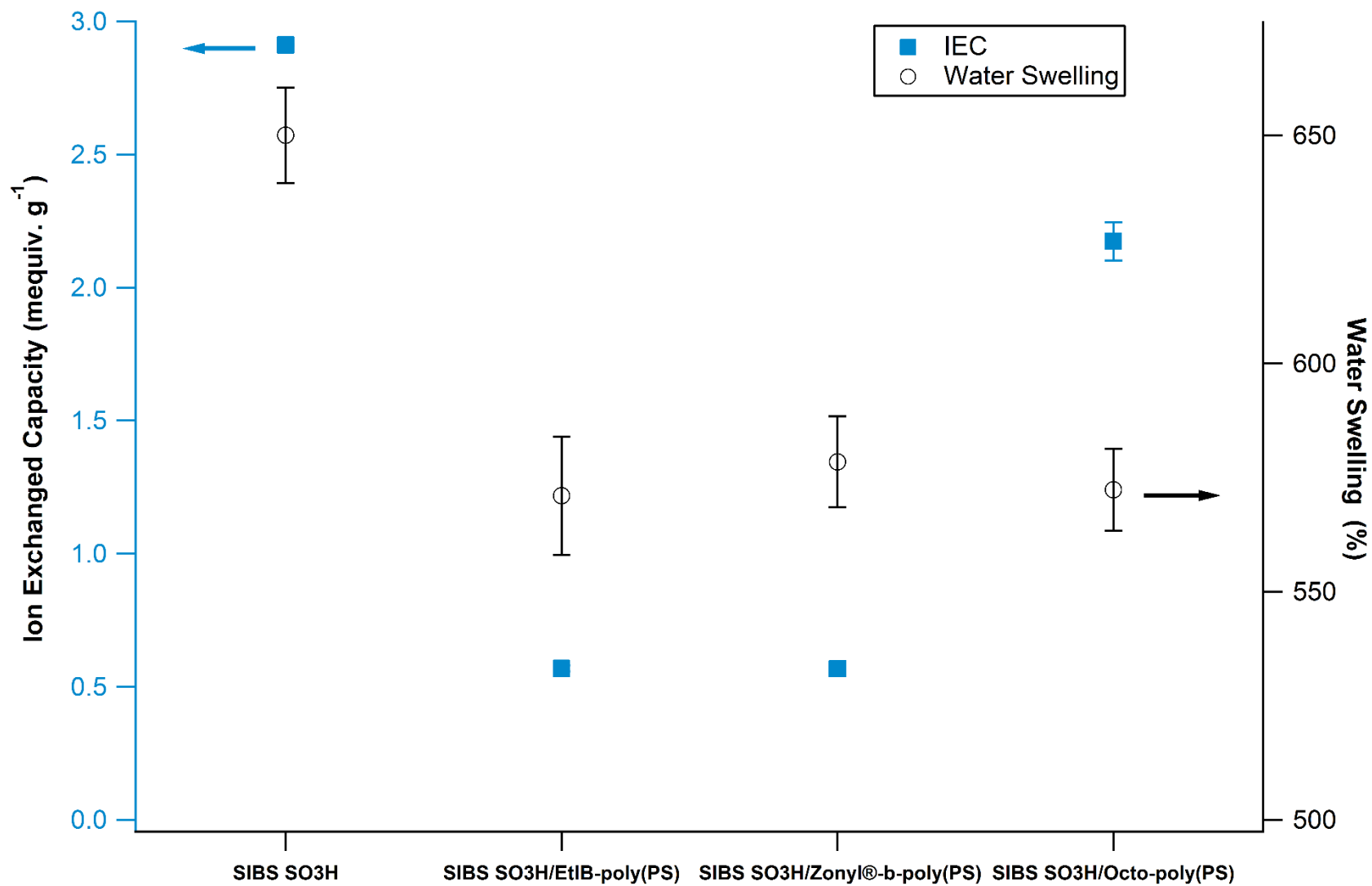
polymerization from the center in both directions. In addition, since our UV results point-out a significant electronic configuration for the octo-initiated polymer, this can lead to an improved electron mobility as suggested by Dutta et al.<sup>45</sup>

#### 5.4.2.5. Small angle X-ray Scattering (SAXS)

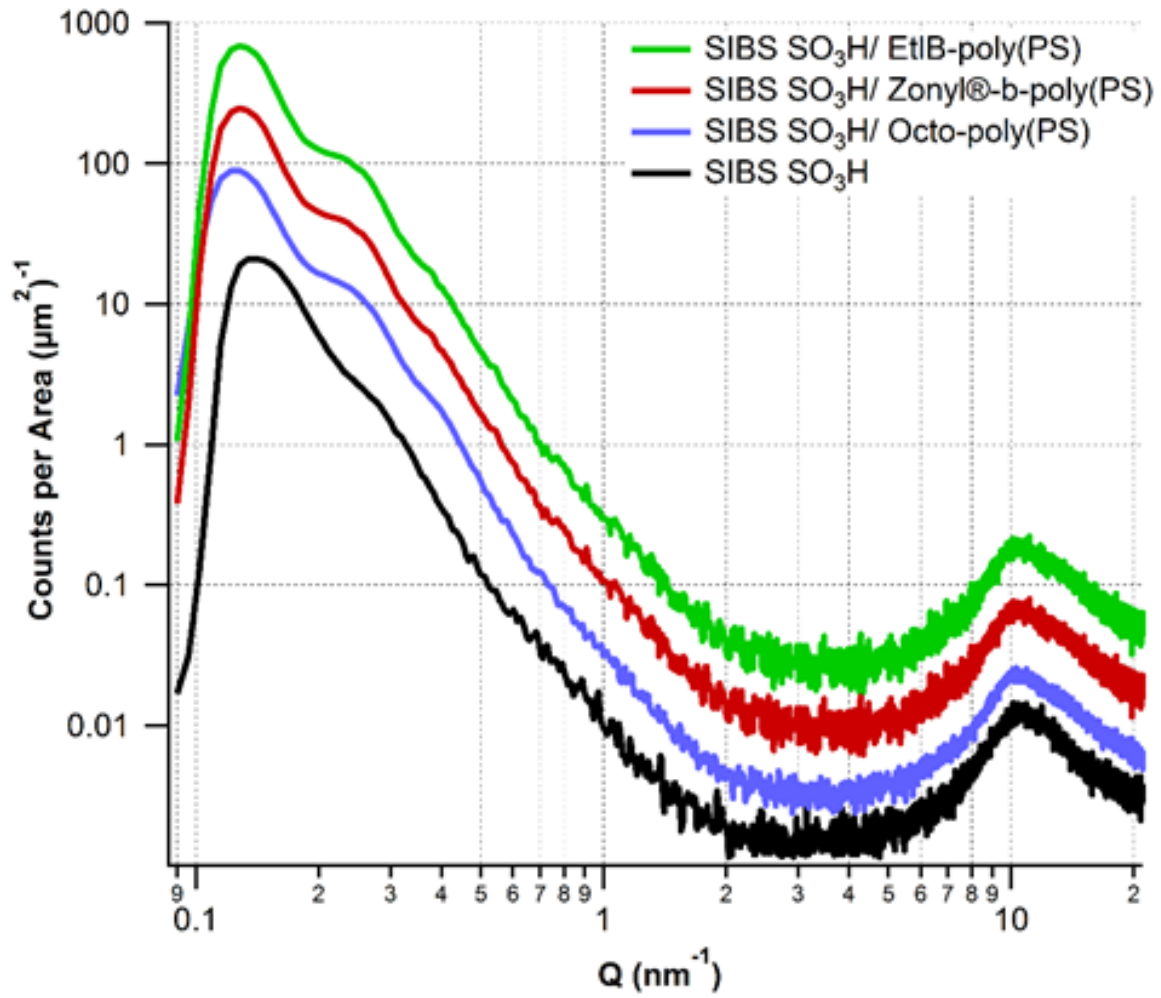
SAXS profiles for the polymeric membranes are shown in Figure 5.17. SIBS SO<sub>3</sub> exhibited a first-order reflection at  $Q = 0.138 \text{ nm}^{-1}$ , however sulfonated SIBS shows a nonperiodic morphology at higher ion content (above  $1 \text{ mequiv g}^{-1}$ ) at lower  $Q$  vectors.<sup>36</sup> The incorporation of the fluoroblock copolymer to the SIBS SO<sub>3</sub> membrane produced unique SAXS profile for each of the polymer studied. SIBS SO<sub>3</sub> / EtIB-Poly(PS) presented a first-order reflection at  $Q = 0.118 \text{ nm}^{-1}$ . Combining Bragg's law with the scattering vector ( $Q$ ) obtained from the SAXS plot, the interstitial was determined from the maximum in the first-order reflection. Table 5.7 shows the values for the Bragg's distance calculated for all the membranes studied. The Bragg distance increases with the incorporation of the polymer from 45.53 to 53.24 nm. The incorporation of the polymer to SIBS SO<sub>3</sub>, results in large clusters, which impacts in the polymer blend morphology. This results agree with the previously presented DSC results, where a new configuration was obtained depending on the initiator selected.

**Table 5.7.** Scattering vector and Bragg distance for the polymeric membranes.

| Membrane                                 | $Q_{\text{Bragg}}$<br>( $\text{nm}^{-1}$ ) | $d_{\text{Bragg}}$<br>(nm) |
|------------------------------------------|--------------------------------------------|----------------------------|
| SIBS-SO <sub>3</sub>                     | 0.138                                      | 45.53                      |
| SIBS-SO <sub>3</sub> / EtIB-Poly(PS)     | 0.118                                      | 53.24                      |
| SIBS-SO <sub>3</sub> / Zonyl®-b-poly(PS) | 0.118                                      | 53.24                      |
| SIBS-SO <sub>3</sub> / Octo-poly(PS)     | 0.118                                      | 53.24                      |



**Figure 5.16.** Ion Exchanged Capacity and Water Swelling for polymeric membran



**Figure 5.17.** A log-log SAXS profile for polymeric membranes.

Another important parameter that was obtained from the SAXS data is the radius of gyration (Rg). For polymers, this parameter represents the dimension of a polymer chain and can be used to evaluate changes with the variables studied. This parameter was obtained using the Guinier equation, which provides the relation between Rg, the intensity in a SAXS profile and the scattering vector (Q). Rg was estimated using the slope of the linear relationship between  $\ln(I(Q))$  and  $Q^2$ .<sup>46</sup> The incorporation of polymer into the SIBS SO<sub>3</sub>H membrane produced unique Rg's. The incorporation of EtIB-poly(PS) and Zonyl®-b-poly(PS) increased this parameter 19%, however Octo-poly(PS) increased this parameter only 14% and was the lowest Rg for all the membranes studied.

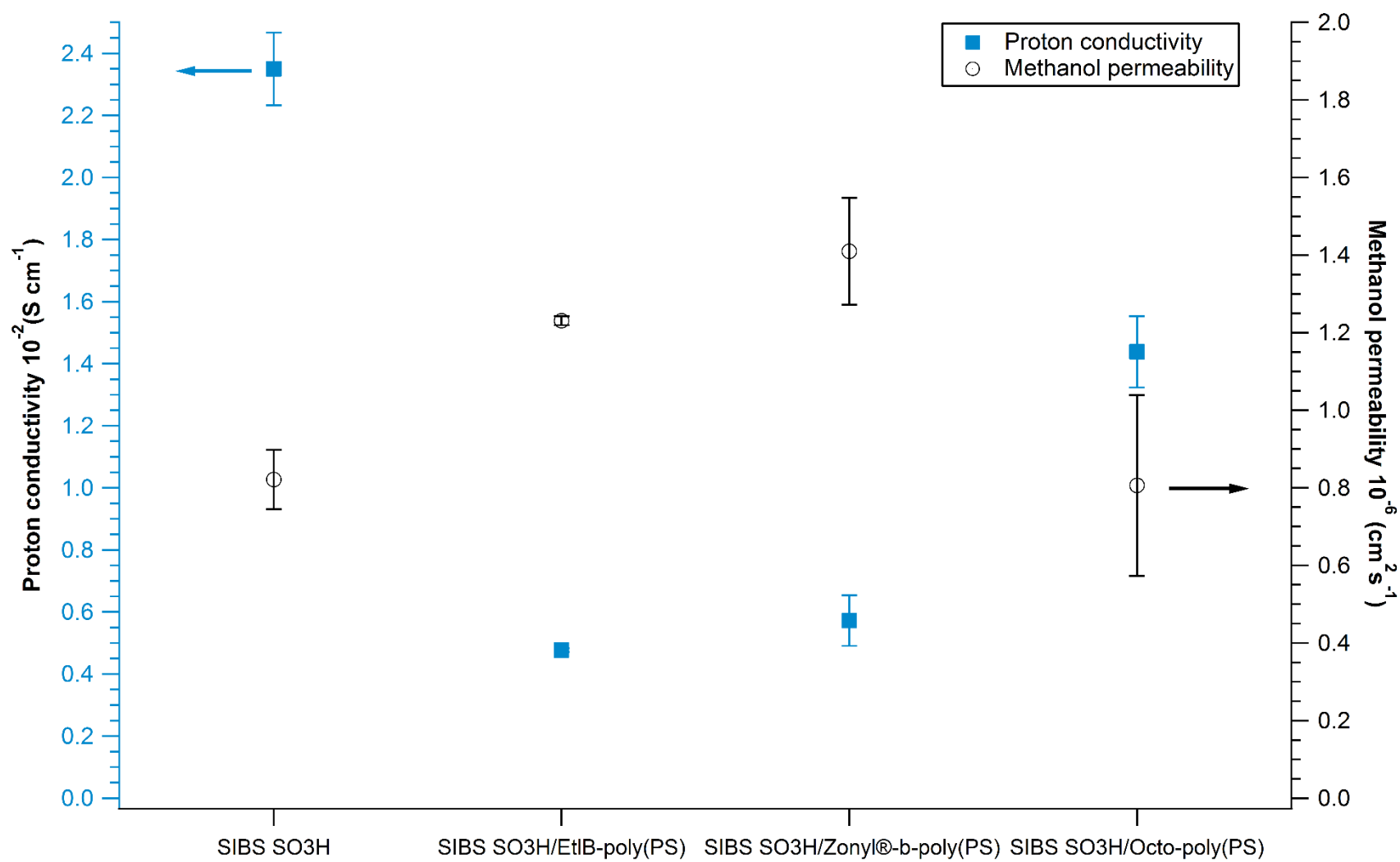
#### 5.4.2.6. *Methanol permeability and proton conductivity*

Proton conductivity and methanol permeability for SIBS SO<sub>3</sub>H, SIBS SO<sub>3</sub>H/EtIB-poly(PS), SIBS SO<sub>3</sub>H/Zonyl®-b-poly(PS) and SIBS SO<sub>3</sub>H /Octo-poly(PS) membranes are presented in figure 18. SIBS SO<sub>3</sub>H / Octo-poly(PS) presents the highest value of proton conductivity (three times higher) for the three different initiators evaluated, even though its water swelling was very similar to the other initiators. SIBS SO<sub>3</sub>H / Octo-poly(PS) however, had the highest IEC among the initiators studied, suggesting that the initiator octo influenced new ionic conformations that improved the transport of protons through the membrane. The transport of protons used the hydrated sulfonic groups in the polymeric membrane; the predominant mechanism consists in a series of Eigen-Zundel-Eigen or Zundel-Zundel transformations that depend on the sulfonic group,<sup>47</sup> the type of water<sup>48</sup> and the morphology.<sup>49</sup> These results agree with other proton conductivity results, where proton conductivity is related with IEC.<sup>50-52</sup> The incorporation of the polymer produced a reordering of polymeric chains and the ionic domain for SIBS SO<sub>3</sub>H membranes. The polymer interacts with the ionic domains that inhibit the complex formation between the proton, water and the sulfonic group described above.

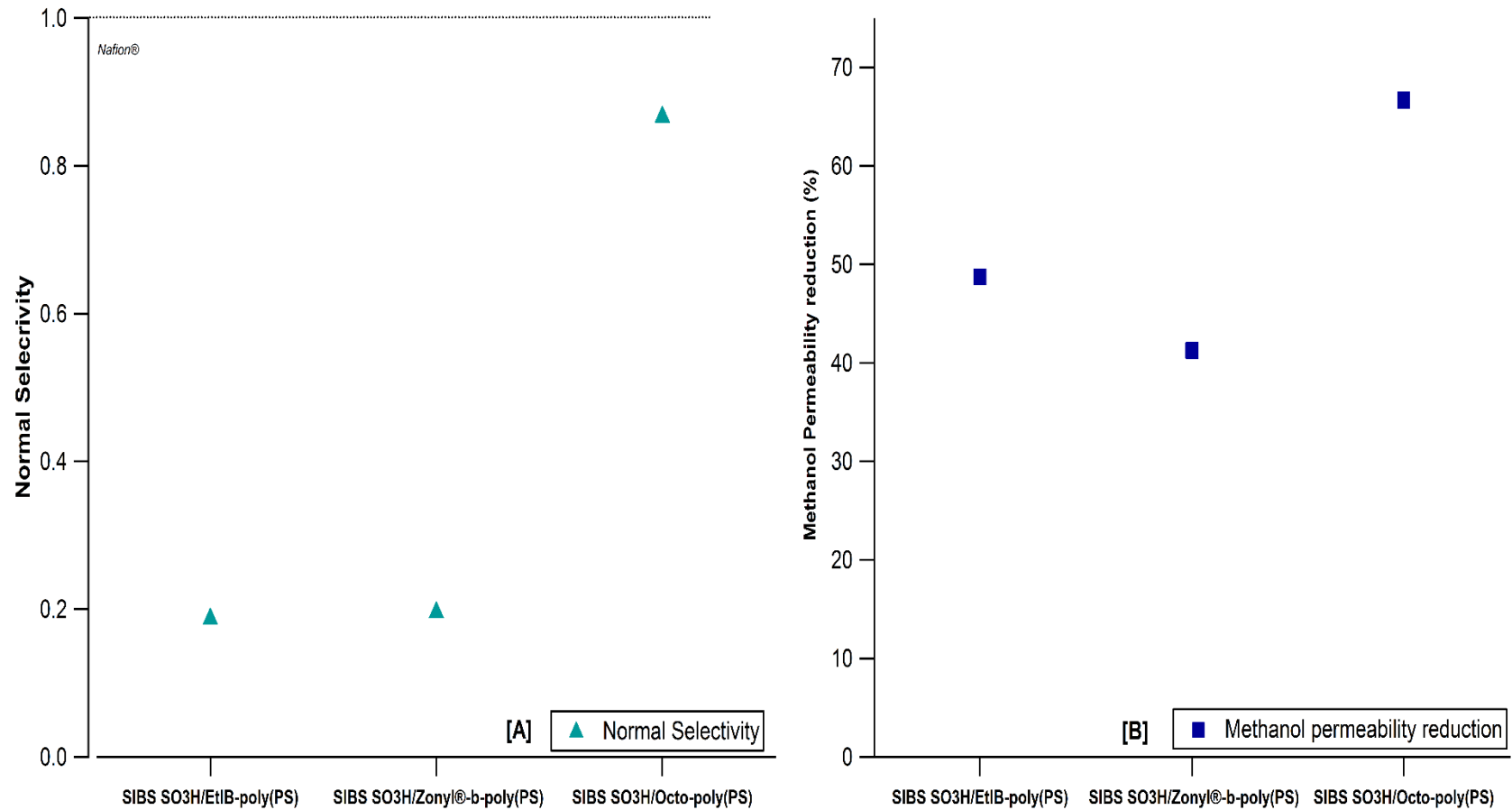
The methanol permeability of the polymeric blend membranes are also presented in figure 5.18. The methanol permeability for SIBS SO<sub>3</sub>H/EtIB-poly(PS), SIBS SO<sub>3</sub>H/Zonyl®-b-poly(PS) and SIBS SO<sub>3</sub>H/Octo-poly(PS) increased or remain the same in comparison with SIBS SO<sub>3</sub>H. One possible

explanation for this behavior could be related to the increase in free volume, concluded from the SAXS results ( $R_g$ ). The methanol permeability in an ionic polymeric membrane is influenced by the capacity of the compound to move through the free volume available,<sup>53</sup> the morphology<sup>44, 50</sup> and the sulfonic group configuration.<sup>15-18, 28</sup> These results agree with the previously presented DSC, FTIR, TGA, IEC and SAXS results, where the variation of the proton conductivity and methanol permeability for each membrane is related to the interaction between the fluoroblock copolymer with SIBS  $\text{SO}_3\text{H}$ , the changes in the sulfonic group conformation, and changes in morphology (related to its free volume) induced by the different initiators used.

To evaluate the effect of each initiator on the transport properties of protons and methanol, and to compare the changes with respect to the state-of-the-art Nafion<sup>®</sup>, a normalized selectivity was calculated. Figure 5.19[A] presents the normalized selectivities (Proton Conductivity / Methanol Permeability) for the blend membranes (normalized with the values for Nafion<sup>®</sup>). The results show that the highest selectivity, corresponds to SIBS  $\text{SO}_3\text{H}$ /Octo-poly(PS) membrane; this selectivity although slightly lower than Nafion<sup>®</sup> (13.4% lower), is comparable. In addition, figure 5.19 [B] shows a significant reduction in the methanol permeability from Nafion<sup>®</sup> and the significant variations with the choice of initiator for DMFC applications.



**Figure 5.18.** Proton conductivity and methanol permeability for polymeric membranes.



**Figure 5.19.** Normalized Selectivities (Proton Conductivity / Methanol Permeability) for polymeric blends with different initiators (Normalized with selectivity of Nafion®) [A] and methanol permeability reduction [B].

## 5.5. CONCLUSIONS

Four novel diblock fluoropolymers and their homopolymers were successfully synthesized using two fluorinated initiators (esterified Zonyl® and esterified octafluoro 4-4'-biphenol) and 1-bromo ethyl benzene by ATRP. The selection of the esterified initiators have a significant impact on the thermal stability of poly(PS), poly(HEMA) and the diblock copolymers. The thermal stability of PS was reduced upon polymerization with esterified initiators. In addition, an additional degradation was observed with the new esterified initiator around 150 °C. This degradation temperature was absent when 1-bromo ethyl benzene was used. Additional to this, each initiator produced a unique UV spectra for poly(styrene) and poly(2,2,3,4,4,4-hexafluorobutylmethacrylate), suggesting a unique electronic configuration. The use of different esterified initiators with sulfonated SIBS influenced the ionic domains uniquely, which influenced the IEC, the water swelling, the morphology, and the transport of protons and methanol through the membrane. Therefore, the proton conductivity and methanol permeability of these membranes is limited by the nature of the initiator, the resulting free-volume and the interaction of the chemical blocks with the sulfonic domain.

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## CHAPTER 6

### Correlation between Morphology and the Transport Properties of Sulfonated Fluoro Block Copolymer Blend Membranes

#### 6.1. ABSTRACT

The transport and morphological changes of ionic blend membranes composed of sulfonated copolymers with four different fluoroblock copolymers were studied. Two novel fluoroblock copolymers composed of poly(styrene)-*b*-poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) [PS-*b*-P5FS-*b*-PHFBM] and poly(4-fluorostyrene)-*b*-poly(styrene)-*b*-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) [P4FS-*b*-PS-*b*-PHFBM] were synthesized using Atom Transfer Radical Polymerization (ATRP). The block copolymer properties were measured using different characterization techniques such as Gel Permeation Chromatography (GPC), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The chemical composition was monitored with Fourier Transform Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. Additionally, a difluoroblock copolymer composed of PS-*b*-PHFBM and a homopolymer composed of PHFBM were evaluated. The resulting block copolymers were incorporated into an elastomeric matrix; therefore, physical blends of sulfonated poly(styrene-isobutylene-styrene) (SIBS SO<sub>3</sub>H) and the unsulfonated fluoroblock copolymers were cast and analyzed. The developed fluoro-membranes were characterized with Ion Exchanged Capacity (IEC), Small Angle X-Ray scattering (SAXS), Atomic Force Spectroscopy (AFM) and with the previous techniques. In addition, proton conductivity and methanol permeability were measured to understand transport properties throughout the membrane for direct methanol fuel cell (DMFC) applications. The proton conductivity of these membranes was limited by the chemical and fluoropolymer composition, the blend morphology and the interaction of the fluoroblock polymer with the sulfonic groups.

## 6.2. INTRODUCTION

Non-fluorinated ionic polymers, like sulfonated poly(styrene-isobutylene-styrene)<sup>1</sup>, sulfonated aromatic poly(etheretherketone)<sup>2</sup>, sulfonated polyarylenethioether sulfones, poly(arylene ether sulfone)<sup>3</sup> and fluorinated polymers like poly(arylene ether benzonitrile) containing hexafluoroisopropylidene diphenol<sup>4</sup> have been studied as proton exchange membranes (PEMs) for direct methanol fuel cell (DMFC) applications. Unfortunately, even today most of these PEMs have either low proton conductivity ( $\sigma$ ) or high methanol permeability limiting their performance in DMFC. Nafion<sup>®</sup> is a sulfonated fluoropolymer which is commonly used in DMFC. This membrane consists of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by a sulfonated ionic group.<sup>5</sup> Nafion<sup>®</sup> remains the standard in DMFC, because has high proton conductivity and excellent thermal and mechanical properties; unfortunately, it also has higher than desired methanol permeability leading to the well-known methanol cross-over limitation.<sup>6</sup>

Morphology and chemical-physical interaction are very important parameters being investigated to obtain membranes with higher proton conductivity and low methanol permeability.<sup>7</sup> Polymer blends emerged like an alternative to obtain membranes with a controlled morphology in order to improve the proton conductivity. The use of well-ordered fluoroblock copolymers in blends membranes is an additional approach that has been investigated to modify the membrane's final morphology. G.J.D Kalaw et al.<sup>8</sup> studied polymeric blends compound of hydrophilic and hydrophobic perfluorocyclobutyl (PFCB) polymers. Blending these polymers, the membrane obtained a proton conductivity of 0.015 S/cm induced by a nanophase-separated morphology. J. Hou et al.<sup>9</sup> enhanced the proton conductivity of polyelectrolyte-fluoropolymer blends membranes changing the phase homogeneity increasing the degree of tetrabutylammonium hydroxide. Controlled radical polymerization (CRP) allows the synthesis of advanced well-defined fluoropolymers with specific structures and lower polydispersity.<sup>10</sup> The polymer structure contribute to mechanical, physical, thermal and chemical properties in polymeric materials. CRP methods generally rely on a reversible activation-deactivation process between dormant and active polymer chains, and as the double bond of monomers containing fluorine is additionally activated by the electron withdrawing group, this sometimes leads to considerably higher rates

of polymerization.<sup>11</sup> Atom transfer radical polymerization (ATRP) is a CRP technique that used an alkyl halide like initiator, a transition metal in the lower oxidation state and a ligand to synthesize different fluoropolymers like, perfluoroalkyl ethyl methacrylate and fluoropolymers with polyether blocks as examples. Initiators for ATRP must have a halogen (Br or Cl) and a functional group that can stabilize the formed radical.<sup>12</sup>

Fluoropolymer seems to have a strong influence in the morphology and transport properties of blend membranes. Therefore, the goal of this studied was to evaluate the transport and morphological changes of ionic membranes composed of sulfonated copolymers with four different fluoroblock copolymers. Two fluoroblock copolymers composed of poly(styrene)-b-poly(2,3,4,5,6-Pentafluorostyrene)-b-poly(2,2,3,4,4,4-Hexafluorobutyl methacrylate) [PS-b-P5FS-b-PHFBM] and poly(4-fluorostyrene)-b-poly(styrene)-b-poly(2,2,3,4,4,4-Hexafluorobutyl methacrylate) [P4FS-b-PS-b-PHFBM] were synthesized by ATRP. Additionally, a difluoroblock copolymer composed of PS-b-PHFBM and a homopolymer composed of PHFBM were used. Sulfonated poly(styrene-isobutylene-styrene) and these fluoroblock copolymers were blended; the resulting polymer blend membranes were characterized for methanol permeability and proton conductivity, while water swelling, and additional materials characterization techniques (*e.g.*, FT-IR, GPC, IEC, TGA, SAXS, AFM) were used to explain the results.

### **6.3. EXPERIMENTAL**

#### **6.3.1. Materials**

Zonyl® BA-L Fluorotelomer intermediate (70 wt.%)  $M_n \sim 443$  was acquired from Sigma-Aldrich. SIBS was purchased from Kaneka® (30 wt % polystyrene and  $M_n \sim 65,000$  g/mol). Sulfuric acid (Sigma Aldrich, 95–98%), acetic anhydride (Aldrich Chemical, 99+%), hexyl alcohol (Acros Organics, 98%, extra pure), methanol (Fisher Scientific, 99.9%), toluene ACS reagent (99%) and Dichloromethane were acquired from Fisher Scientific. Other chemicals used include: 1-bromo ethyl benzene (Acros-Organics, 97%), triethylamine, (Acros-Organics, 99%), 4-dimethylamino pyridine, (Acros Organics, 99%), 2-chloropropionyl chloride, (Acros-Organics, 95%), 2, 2'-dipyridyl – Bipy - (Acros Organics, extra pure, 99%), calcium hydride - $\text{CaH}_2$ - (Acros-Organics, 93%), copper

(I) chloride (Acros-Organics, 99%) were employed as received. The monomers used: 2,2,3,4,4,4-hexafluorobutyl methacrylate (HEMA) (Alfa Aesar 96% inhibited with monomethyl ether hydroquinone –MEHQ-) and styrene (PS) (Across Organics, 99% inhibited with 4-*tert-butyl* catechol). Both HEMA and PS were passed through an inhibitor remover (Disposable column from Sigma-Aldrich), after this process both monomers and the solvent were stored over CaH<sub>2</sub> and then vacuum-distilled before polymerization.

#### **6.3.2. Esterification of 2-perfluoroalkyl ethanol.**

Zonyl® and 4-dimethylamino pyridine were dissolved using toluene at 60 °C. Triethylamine and 2-chloropropionyl chloride were added and the reaction was stopped completed after 24 h. Toluene was removed by rotary evaporation. The obtained product was dissolved using dichloromethane and washed with a saturated NaHCO<sub>3</sub> solution, 1 M HCl, and distilled water. The solvents were removed by rotary evaporation.

#### **6.3.3. ATRP homopolymerization using esterified initiator**

In a homopolymerization by ATRP, a Schlenk tube was charged with the initiator, copper chloride (CuCl), and the ligand (2, 2'-dipyridyl –bipy-). The molar ration of initiator: CuCl:bipy was kept 1:1:2. The monomer was added, and the system was degassed three times by freezing and thawing; then heated to the desired temperature (110 °C) under a nitrogen atmosphere. Upon completion of the experiment, the polymerization mixture was diluted with THF. The solution was filtered (to remove the catalyst) and then precipitated in methanol, where the polymer appeared as a fluffy white material that was recovered after vacuum drying.

#### **6.3.4. ATRP Copolymerization**

In a typical block copolymerization by ATRP, a Schlenk tube was charged with the macroinitiator, copper chloride (CuCl) and the ligand (2, 2'-dipyridyl). The molar ratio of initiator:CuCl:bipy was kept 1:1:2. The system was degassed three times minimum by freezing and thawing. After three freeze-thaw cycles, the mixture was heated (110°C) for 24 h under a nitrogen atmosphere. The block copolymer solution was filtered and then precipitated in methanol.

#### **6.3.5. Gel Permeation Chromatography (GPC)**

Gel Permeation Chromatography (GPC) was performed on a Waters GPC system equipped with a mixed column (PLgel 5 $\mu$ m MIXED-C, Varian Inc.) and a differential refractometer (BI-DNDC, Brookhaven Instruments). THF HPLC solvent was used as the mobile phase with a flow rate of 0.5 ml/min. Molecular weight distributions were obtained with reference to polystyrene standards (Varian Inc.).

#### **6.3.6. Nuclear Magnetic Resonance (NMR) Spectroscopy**

The initiator, macroinitiators and the block copolymers were characterized by liquid  $^1\text{H}$  NMR, using a NMR Bruker 500 MHz spectrometer with chloroform-d as a solvent.

#### **6.3.7. Fourier Transform Infrared Spectroscopy (FT-IR)**

Fourier Transform Infrared Spectroscopy (FT-IR) was employed to identify the chemical nature of the polymers analyzing the vibrational band of the functional groups expected after the polymerization. An attenuated total reflectance (ATR) cell was used with an FT-IR (Brucker Alpha Platinum-ATR) to characterize the homo, block copolymers and the membranes. The sample was clamped on the ATR cell and all infrared spectra were collected using 64 scans, 4  $\text{cm}^{-1}$  resolution and a range of 600 – 4000  $\text{cm}^{-1}$ .

#### **6.3.8. Ultraviolet Spectroscopy**

An UV-VIS spectrophotometer equipment (Shimatzu UV-2401 P) was used to characterize the homo and diblock copolymers. The sample was placed in a quartz ultramicrocells for measurement. Ultraviolet spectra were collected using 1 nm intervals and a range of 200 – 600 nm. THF was used as the solvent.

#### **6.3.9. Thermogravimetric Analysis (TGA)**

The thermal degradation behavior were determined using a Mettler Toledo 851e instrument. In each experiment, the samples weighting approximately 5-10 mg were used. Degradation temperatures were determined after heating the polymer samples to 800°C at 10°C/min under a nitrogen (99.9% purity) atmosphere.

#### **6.3.10. Differential Scanning Calorimetry (DSC)**

Thermo physical properties were determined using Differential Scanning Calorimetry (DSC). A Texas Instrument DSC Q2000 unit was used for this purpose. In each experiment, samples weighting approximately 5-10 mg were used. Phase transitions ( $T_g$ ) and melting temperatures for each polymer were determined after heating the polymer samples from -80°C to 350°C at 10°C/min under a nitrogen atmosphere.

#### **6.3.11. Blend Preparation**

Poly(styrene-isobutylene-styrene) (SIBS) was sulfonated using acetyl sulfate as the sulfonating agent. The sulfonation process is described in more detail elsewhere. The preparation of physical blends consisted of mixing sulfonated SIBS and unsulfonated [PS-*b*-P5FS-*b*-PHFBM] or [P4FS-*b*-PS-*b*-PHFBM]. Sulfonated SIBS and the fluoroblock copolymer were dissolved in a solution (85/15) (v/v) of toluene and hexyl alcohol with a polymer concentration of 5 wt%. Sulfonated SIBS/fluoropolymer membranes were solvent casted in Teflon® Petri dishes for 72 h at room temperature as the solvent evaporated; then dried at 60°C for 24 h to remove the residual solvent. Elemental Analysis (EA) was used to determine the exact amount of the mole percent of sulfonated styrene in the membrane. EA was conducted by Atlantic Microlab, Norcross, Georgia.

#### **6.3.12. Ion Exchange Capacity (IEC)**

IEC was measured immersing a specific amount of the membrane in a 1.0 M solution of NaCl for 24 h. After removing the membrane, the solution was titrated using a 0.1 M solution of NaOH until the pH was neutral. The IEC was calculated from the moles of ion substituted divided by the initial dry mass of the membrane.

### 6.3.13. Water Uptake and water content

Water absorption or water uptake in the membranes was measured immersing each membrane in an excess of deionized water at 25°C. The weight of the sample initially dried at 60°C for 24 hours in an oven was originally recorded, as well as the weight of the membrane after immersion in water. The weights of the wet membranes were measured after different time intervals until swelling equilibrium was reached. Each reported result represents the average of at least three repetitions.

The water content ( $\lambda$ ) represents the number of water per moles of ionic domains, was calculated using Equation 5.1:

$$\lambda = \frac{\text{Water uptake} * 10}{18 * IEC} \quad (5.1)$$

Where, IEC is the ion exchanged capacity (moles of ionic domain/grams of polymer)

### 6.3.14. Small angle X-ray scattering (SAXS)

The morphology of the membranes was carried out on an Anton Paar SAXSpace. Two-dimensional scattering patterns were collected on a pinhole-collimated system using image plates and read by a Cyclone® Plus PerkinElmer image plate reader. The SAXSQuant software® was used to reduce two dimensional data to one-dimensional intensity versus scattering vector (Q) plots. The X-ray wavelength employed was 1.54 Å. The calibration standard was silver behenate and the height of the beam stop was 0.3 mm.

### 6.3.15. Atomic Force Spectroscopy (AFM)

Atomic Force microscopy (AFM) was performed using an Agilent AFM 550 in AC imaging mode. The samples were measured at room temperature and without previous treatment. The images were recorded with resolution of 256 and the scanning speed was 1.99 lines/s.

### 6.3.16. Methanol Liquid-Phase Permeability

The liquid permeability was obtained from the continuity equation for diffusion in plane geometry (Equation 2.1):

$$C_B(t) = \frac{PC_A A}{V_b L} \left( t - \frac{L^2}{6D} \right) \quad (2.1)$$

where,  $C_A$  {mol/cm<sup>3</sup>} is the methanol concentration (permeant),  $C_B$  {mol/cm<sup>3</sup>} is the concentration of the compound that permeated through the membrane after different times,  $L$  is the membrane thickness {cm},  $V_b$  the volume of the receptor compartment {0.39 cm<sup>3</sup>},  $A$  the diffusional cross-sectional area of the membrane {0.64 cm<sup>2</sup>} and  $P$  the permeability {cm<sup>2</sup>/s}. The permeability ( $P$ ) was determined from the slope of the concentration  $C_B(t)$  versus time.<sup>29</sup>

### 6.3.17. Proton Conductivity

The proton conductivity ( $\sigma$ ) [S / cm] of each membrane was measured normal to the plane using AC electrochemical impedance spectroscopy (EIS). The measurements were carried out on a Fuel Cell Test System (850e Multi Range) equipped with an 885 Fuel Cell potentiostat from Scribner Associate Incorporated. The range of frequency and the AC amplitude used were from 0.1 Hz to 100,000 Hz and 0.1 Amps respectively at 40 °C and 100% relative humidity. The membranes were first immersed in an excess of deionized water at 25°C before the experimentation during 24 hours. The proton conductivity was calculated from the impedance data, using the following relation (equation 2.2):

$$\sigma = \frac{L}{R_{\Omega} A} \quad (2.2)$$

where  $L$  {cm} and  $A$  {cm<sup>2</sup>} are the membrane thickness and the area respectively.  $R_{\Omega}$  {1/ S} was obtained from the low intersect of the high frequency semicircle (Nyquist plot) on the complex impedance plane with the real component of the impedance axis ( $Re(z)$ ).

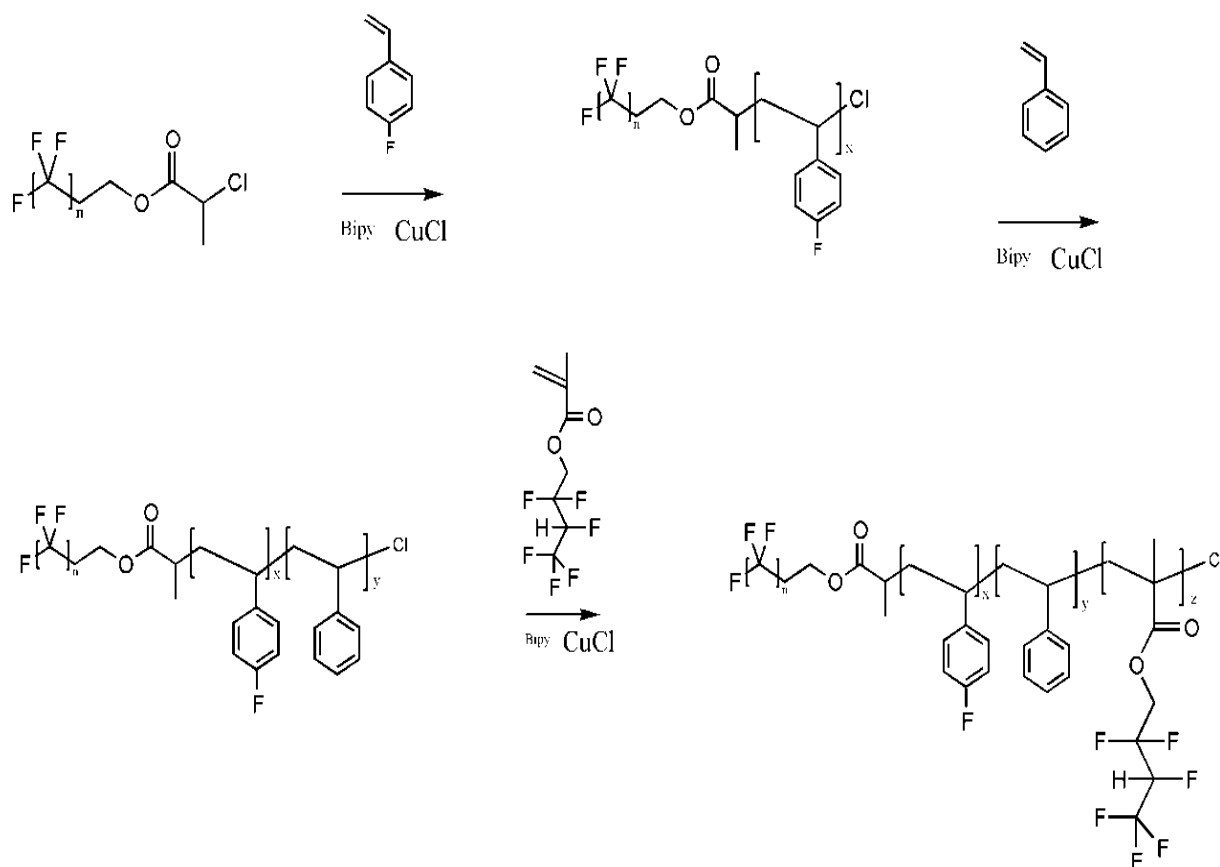
## 6.4. RESULTS AND DISCUSSIONS

### 6.4.1. Polymer Characterization

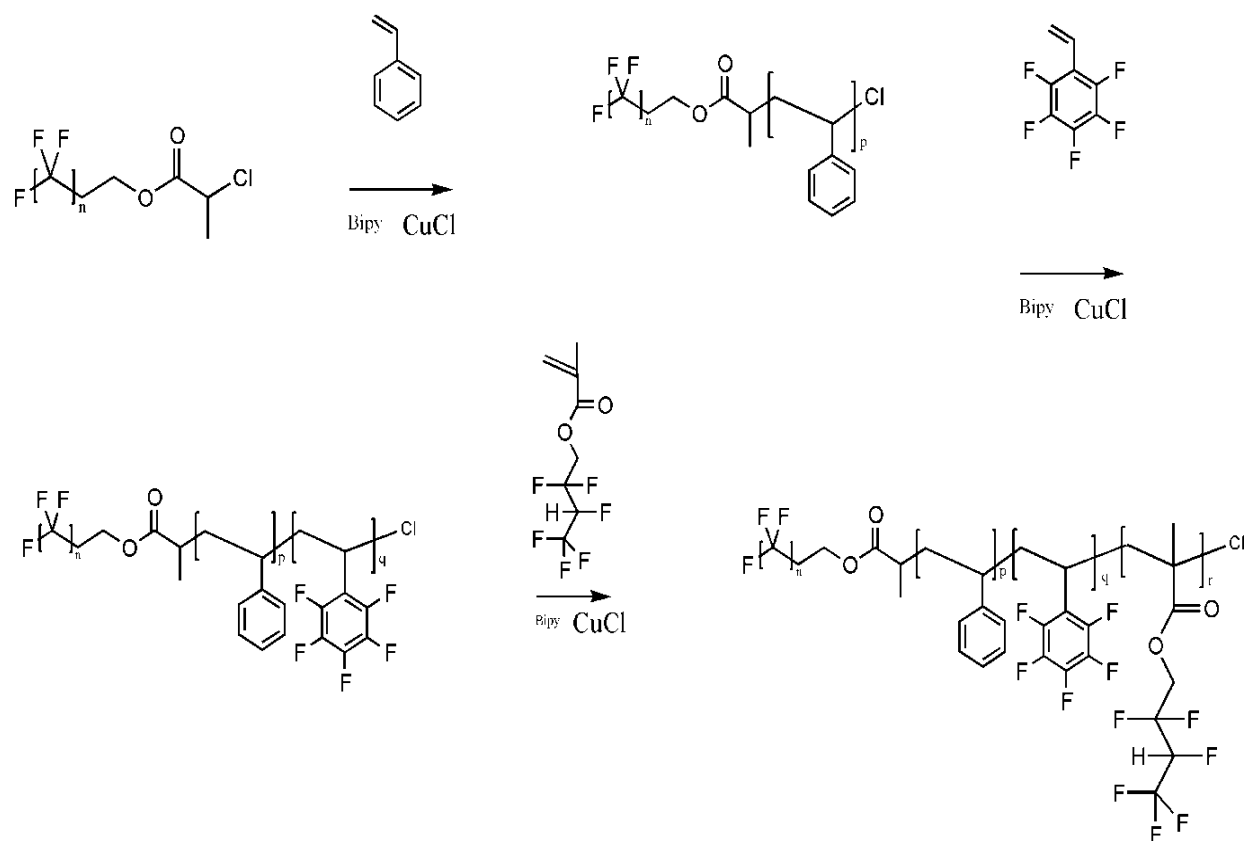
#### 6.4.1.1. FT-IR spectroscopy

The homopolymers were synthesized using the esterified Zonyl® via ATRP technique, in order to obtain a series of fluoroblock polymers of P4FS-b-PS-b-PHFBM or PS-b-P5FS-b-PHFBM. All the polymerization reactions for the homo and the block copolymers are presented in schemes 6.1 and 6.2. The chemical composition of P4FS, P4FS-b-PS and P4FS-b-PS-b-PHFBM were confirmed by FTIR. Figure 6.1 [A] exhibits the FT-IR spectra of P4FS, three distinctive regions were observed in this figure: A para-substitution band correspond to 4-fluorostyrene group was presented at 820 cm<sup>-1</sup> (1). The second bands correspond to overtone absorptions induced by the aromatic ring, these bands appeared between 2000 and 1667 cm<sup>-1</sup>. An additional band appears between 1300 and 1000 cm<sup>-1</sup>, this band corresponds to the C – F group attached to 4FST. Figure 6.1 [B] shows the FT-IR spectra of P4FS-b-PS; two distinctive regions were observed in this figure. A mono-substitution band corresponding to the styrene group was presented at 700 cm<sup>-1</sup> (2). The second band corresponds to a para-substitution band correspond to 4-fluorostyrene group presented at 820 cm<sup>-1</sup>. Figure 6.1 [C] shows the FT-IR spectra of P4FS-b-PS-b-PHFBM. This polymer possessed a characteristic peak around 1750 cm<sup>-1</sup> (3), that was ascribed to the stretching vibration of the carbonyl group attributed to the C=O bond attached to HFBM. Other important bands appeared from 1100 to 1300 cm<sup>-1</sup> (4), these bands corresponded to the stretching vibration induced by the chemical presence of the fluoride groups incorporated by the polymerization reaction of HFBM. These results indicate the presence of 4FS, PS and HFBM into the fluoroblock copolymer.

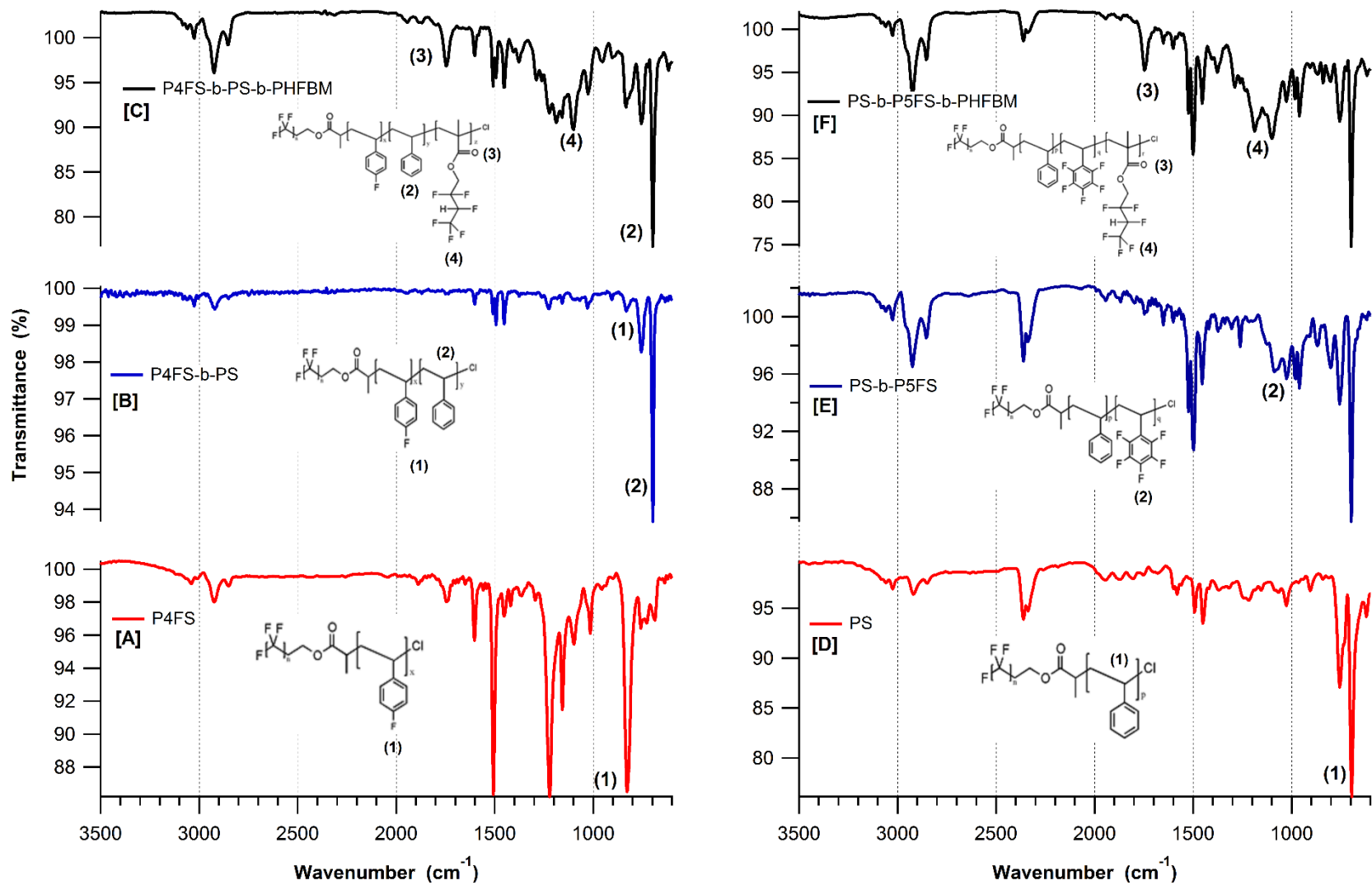
PS (Figure 6.1 [D]) exhibits two distinctive regions; a mono-substitution band corresponding to the styrene group was presented at  $700\text{ cm}^{-1}$  (1) and the overtone absorptions induced by the aromatic ring. These bands appeared between  $2000$  and  $1667\text{ cm}^{-1}$ . PS-b-P5FS (Figure 6.1 [E]) presented an additional band between  $1100$  and  $1000\text{ cm}^{-1}$ . These bands correspond to the C – F group attached to 5FST. PS-b-P5FS-b-PHFBM (Figure 6.1 [F]) exhibited the same bands previously observed; additionally, the vibration of the carbonyl group attributed to the C=O bond appeared around  $1750\text{ cm}^{-1}$  (3) and the fluoride group bands appeared from  $1100$  to  $1300\text{ cm}^{-1}$  (4).



**Scheme 6.1.** Polymerization reaction for P4FS-b-PS-b-PHFBM.



**Scheme 6.2.** Polymerization reaction for PS-b-P5FS-b-PHFBM.

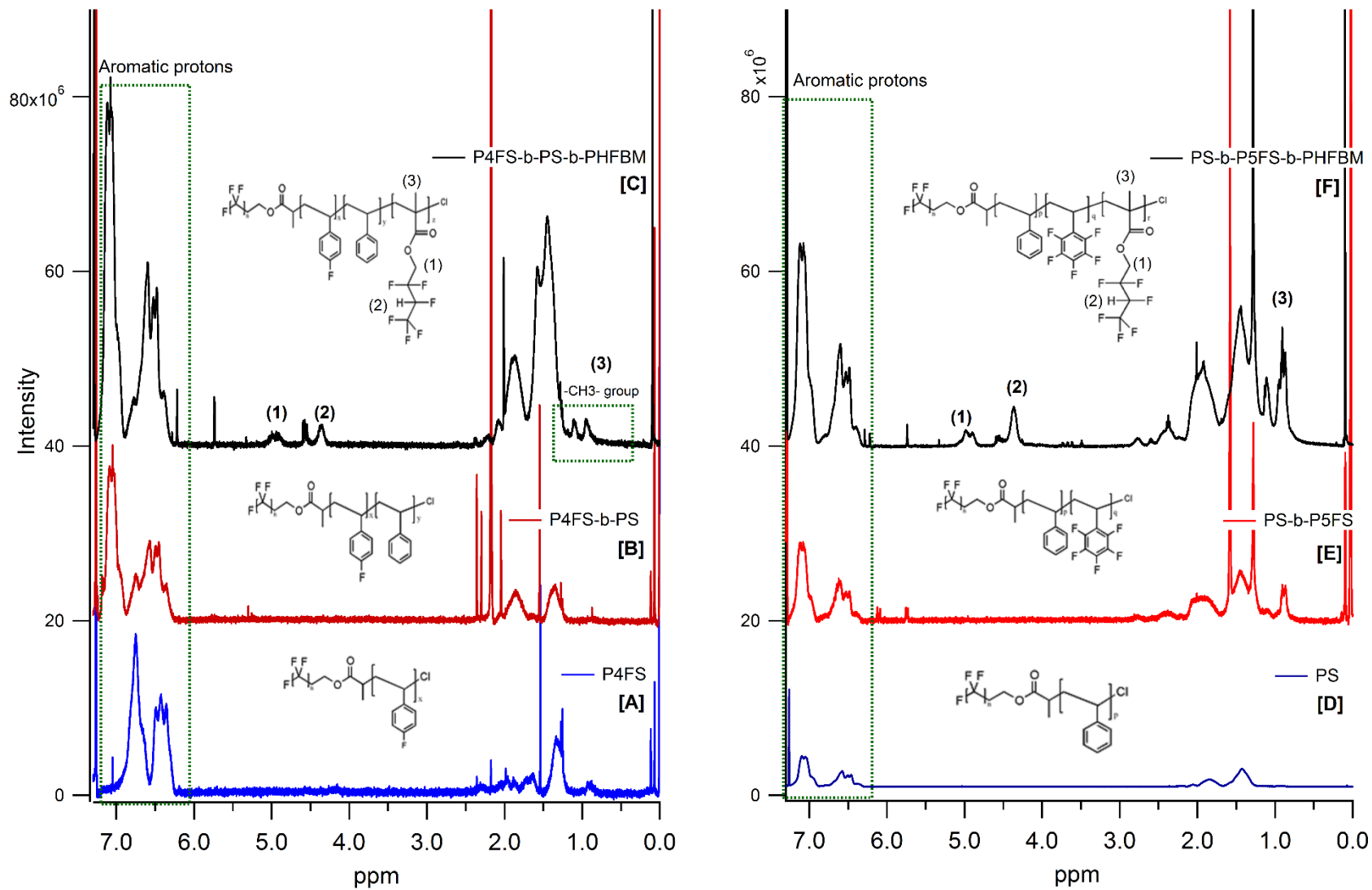


**Figure 6.1.** FTIR spectra for P4FS [A], P4FS-b-PS [B], P4FS-b-PS-b-PHFBM [C], PS [D], PS-b-P5FS [E] and PS-b-P5FS-b-PHFBM [F].

#### 6.4.1.2. Nuclear Magnetic Resonance (NMR)

Liquid  $^1\text{H}$  NMR was employed in order to confirm the chemical composition of the synthesized homo and fluoroblock copolymers. Figure 6.2 exhibits the  $^1\text{H}$  NMR spectra of P4FS, P4FS-b-PS and P4FS-b-PS-b-PHFBM. 4FPS (Figure 6.2[A]) presented peaks at a large chemical shift around 6.5 ppm. These peaks were assigned to the typical band of the protons attached to the aromatic ring in 4FS. The peaks at 1.85 and 1.35 ppm are assigned to the methylene ( $-\text{CH}_2-$ ) and methine ( $-\text{CH}-$ ) absorptions in 4FS. Figure 6.2[B] shows the NMR spectra for P4FS-b-PS, this spectra presented an additional absorption around 7 ppm that represents the protons attached to the aromatic ring in PS. Three additional peaks appeared in P4FS-b-PS-b-PHFBM with respect to P4FS-b-PS at 4.95, 4.4 and 1 ppm (Figure 6.2[C]). The absorption at 4.95 ppm is a characteristic chemical shift that corresponds to the hydrogens deshielded by the anisotropy of the adjacent  $\text{C}=\text{O}$  and fluorine groups, induced by the presence of PHFBM in the fluoroblock copolymer (1). The chemical shift at 4.4 ppm represents the proton attached to the same carbon as a fluorine group in HFBM (2). Methyl groups ( $-\text{CH}_3-$ ) peaks appeared at 1 ppm (3). Figure 6.2[D], 6.2[E] and 6.2[F] shows the  $^1\text{H}$  NMR spectra for PS, PS-b-P5FS and PS-b-P5FS-b-PHFBM respectively. PS presented peaks at a large chemical shift around 7 ppm. These peaks were assigned to the typical band of the protons attached to the aromatic ring in polystyrene.

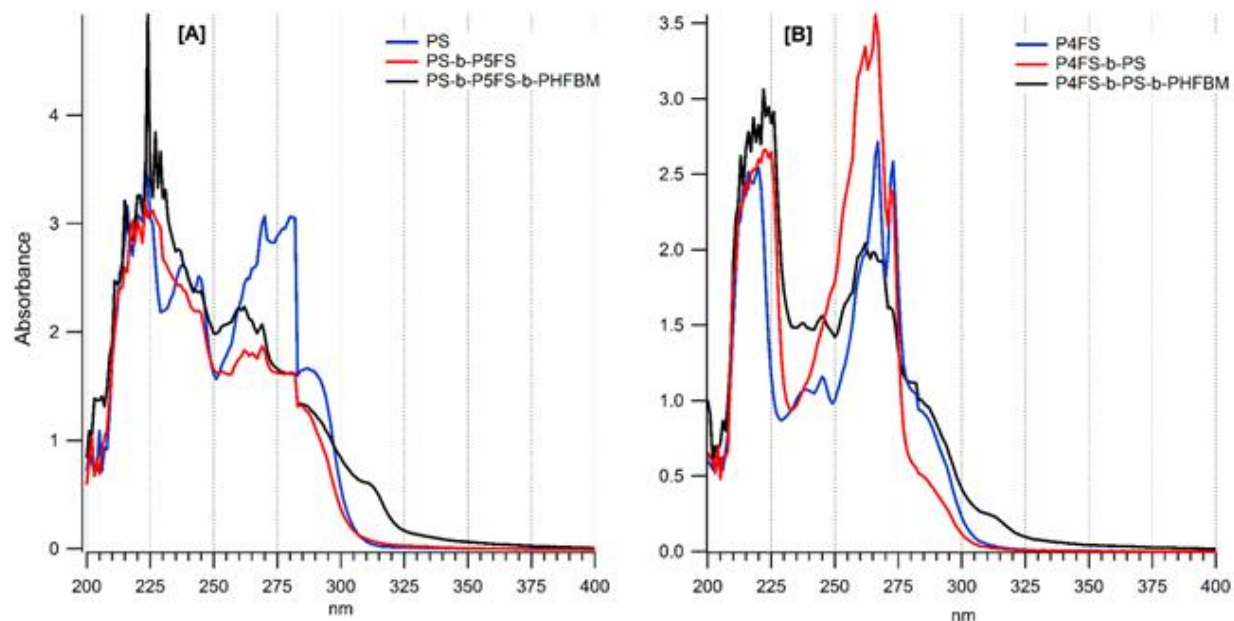
The peaks at 1.85 and 1.5 ppm are assigned to the methylene ( $-\text{CH}_2-$ ) and methine ( $-\text{CH}-$ ) absorptions in this polymer. PS-b-P5FS shows peaks at 2.35 and 2.65 ppm are assigned to the methylene ( $-\text{CH}_2-$ ) and methine ( $-\text{CH}-$ ) absorptions in this polymer deshielded by the anisotropy of the adjacent fluorine groups in the aromatic ring. PS-b-P5FS-b-PHFBM exhibited additional peaks with respect to PS-b-P5FS: the hydrogens deshielded by the anisotropy of the adjacent  $\text{C}=\text{O}$  and fluorine groups at 4.95 ppm (1), the proton attached to the same carbon as a fluorine group in HFBM (2) and the methyl groups ( $-\text{CH}_3-$ ) at 1 ppm. Both FT-IR and Liquid  $^1\text{H}$  NMR spectra confirm the chemical composition of the synthesized polymers using the esterified Zonyl®.



**Figure 6.2.** NMR spectra for P4FS [A], P4FS-b-PS [B], P4FS-b-PS-b-PHFBM [C], PS [D], PS-P5FS [E] and PS-P5FS-PHFBM [F].

#### 6.4.1.3. UV Spectroscopy

In order to investigate the electronic transitions of the polymers, studied UV spectroscopy was performed, starting with the homopolymers. The resulting homopolymers were dissolved in THF and, then UV spectra was obtained. The UV spectrum for PS, PS-b-P5FS, PS-b-P5FS-b-PHFBM, P4FS, P4FS-b-PS, P4FS-b-PS-b-PHFBM are presented in Figure 6.3[A] and 6.3[B]. As shown in Figure 6.3[A], PS exhibited a band at 220 nm, which corresponds to a forbidden transition of the aromatic ring.<sup>13</sup> The observed spectrum has an additional absorption band around 280-290 nm, this band is attributed to the  $n - \pi^*$  transition of the carbonyl group attached to the Zonyl® after the esterification reaction. The bands corresponding to the polystyrene group in this polymer are overlapped at 260 nm with the band related to the initiator. PS-b-P5FS exhibited the bands aforementioned however, PS-b-P5FS-b-PHFBM exhibited three additional bands at 230, 245 and 315 nm induced by the incorporation of HFBM to PS-b-P5FS. Figure 6.3 [B] presents the UV spectra for P4FS. As shown in this figure, P4FS exhibited an absorption band around 280-290 nm, this band is also attributed to the  $n - \pi^*$  transition of the carbonyl group attached to this initiator. P4FS exhibited a shift in the absorbance band of the aromatic ring; this chemical group showed and absorption band at 270 nm, however PS presented the absorption at 260 nm. P4FS shows a band corresponds to a forbidden transition of the aromatic ring at 215 nm. P4FS-b-PS exhibited the band corresponds to a forbidden transition of the aromatic ring at 220 nm, however the bands corresponding to the aromatic ring of PS and P4FS were overlapped at 270 nm. P4FS-b-PS-b-PHFBM exhibited three additional bands at 237, 245 and 315 nm induced by the incorporation of HFBM to P4FS-b-PS.



**Figure 6.3.** UV spectra for PS, PS-b-P5FS, PS-b-P5FS-b-PHFBM [A] and P4FS, P4FS-b-PS, P4FS-b-PS-b-PHFBM [B].

#### 6.4.1.4. Gel Permeation Chromatography (GPC)

The molecular weight of fluoroblock copolymers were determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene as calibration standards. PS-b-P5FS-b-PHFBM was synthesized in three steps; PS was polymerized first; the number average molecular weight was 13.6E3 g/mol with a polydispersity of 1.31. PS-b-PFS was synthesized and finally PS-b-P5FS-b-PHFBM was obtained with a  $M_n$  of 18E3 g/mol and a polydispersity of 1.35. Similarly P4FS-b-PS-b-PHFBM was analyzed; the molecular weight, polydispersities ( $M_w/M_n$ ) and the polymer composition results and are shown in Table 6.1A and 6.1A.

**Table 6.1A.** Molecular weight characterization for homopolymer and block copolymers Prepared by ATRP (using polystyrene standards)

| Sample            | Initiator         | Mn x e-3 | Mw x e-3 | Mw/Mn |
|-------------------|-------------------|----------|----------|-------|
| PS                | Esterified Zonyl® | 13.6     | 17.9     | 1.31  |
| PS-b-P5FS         | PS                | 17.4     | 23.3     | 1.34  |
| PS-b-P5FS-b-PHFBM | PS-b-P5FS         | 18.0     | 24.3     | 1.35  |
| P4FS              | Esterified Zonyl® | 9.77     | 13.3     | 1.36  |
| P4FS-b-PS         | P4FS              | 35.8     | 64.6     | 1.81  |
| P4FS-b-PS-b-PHFBM | P4FS-b-PS         | 42.2     | 74.6     | 1.77  |

**Table 6.1B.** Polymer composition (wt%).

| Sample            | Zonyl®<br>[wt%] | PS<br>[wt%] | P4FS<br>[wt%] | P5FS<br>[wt%] | PHFBM<br>[wt%] |
|-------------------|-----------------|-------------|---------------|---------------|----------------|
| PS                | 13.89           | 86.11       | *             | *             | *              |
| PS-b-P5FS         | 9.34            | 57.93       | *             | 32.72         | *              |
| PS-b-P5FS-b-PHFBM | 6.93            | 42.87       | *             | 24.21         | 25.99          |
| P4FS              | 7.35            | *           | 92.65         | *             | *              |
| P4FS-b-PS         | 0.73            | 90.09       | 9.18          | *             | *              |
| P4FS-b-PS-b-PHFBM | 0.51            | 62.60       | 6.38          | *             | 30.51          |

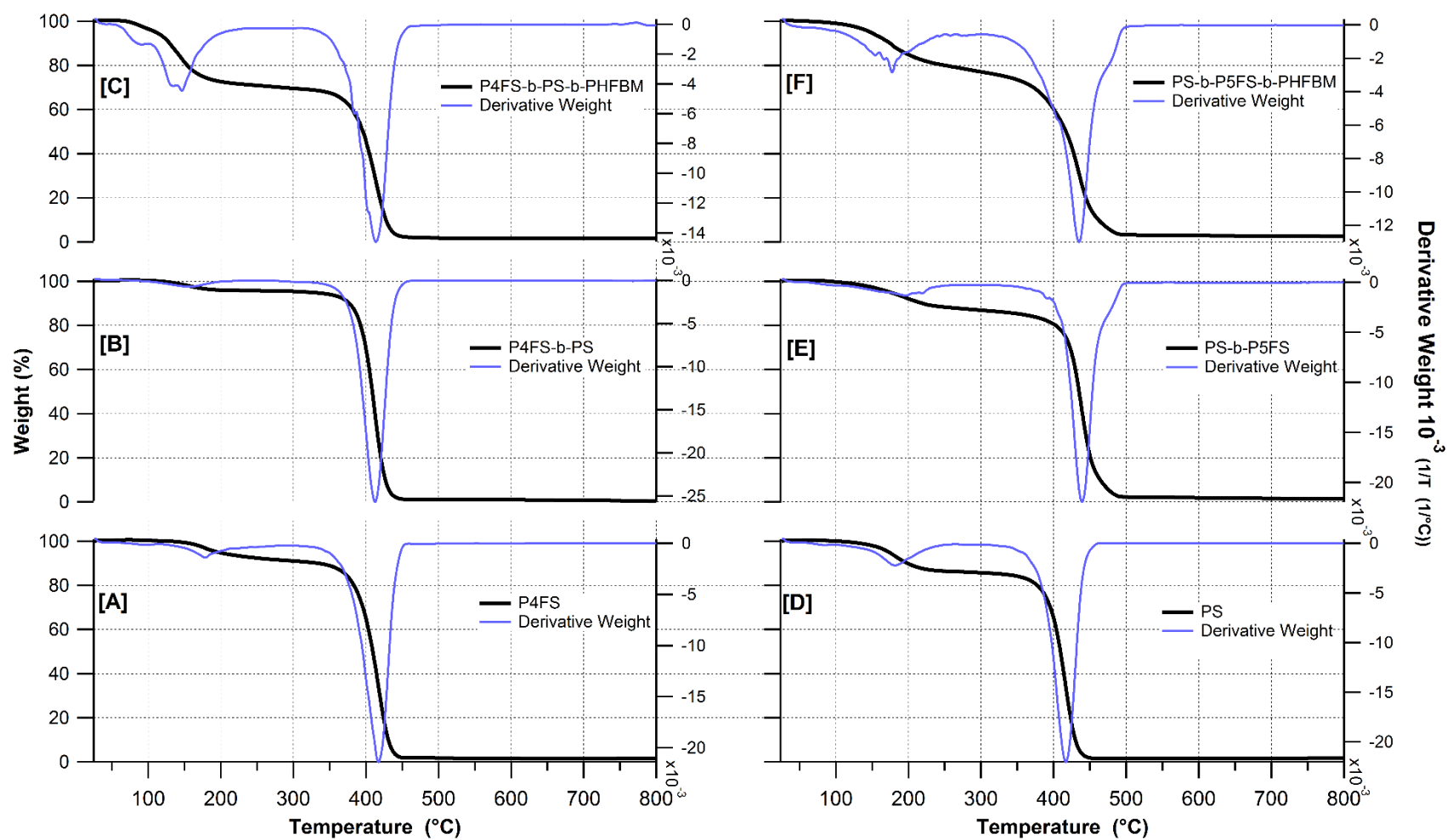
\* Absent

#### 6.4.1.5. Thermogravimetric Analysis (TGA)

The thermal degradation behavior for the fluoroblock copolymers were determined by thermogravimetric analysis over a temperature range of 25-800°C under a N<sub>2</sub> atmosphere. Figure 6.4[A] shows the thermal degradation of P4FS. This polymer presented two different degradation temperatures. The first degradation was at 177.96°C with a weight loss percent of 7.35% and the second at 417.59°C. P4PS-b-PS (Figure 6.4[B]) exhibited the degradation temperatures previously mentioned, however the thermal stability of this polymer was adversely affected when HFBM was incorporated to the polymeric chain.

Part of the fluorocarbon polymer group (ester group) suffered thermal degradation below 200°C and the remaining polymer chain was degraded in the range from 350 to 470°C. In this weight loss step, the remaining of polymeric chain of HFBM and all the P4FS-b-PS chain were overlapped (Figure 6.4[C]).

Figure 6.4 [D] exhibits PS initiated with esterified Zonyl®. This polymer presented two different degradation temperatures. The first degradation was at 181.79°C with a weight loss percent of 13.84% and the second at 416.69°C. PS-b-P5FS (Figure 6.4 [E]) exhibited changes with respect to PS, the two degradation temperatures previously mentioned were improved 13°C and 22°C respectively. The incorporation of HFBM to PS-b-P5FS also affected adversely the thermal stability, therefore the degradation temperature at lower temperature decreased 17°C and the remaining polymer chain was degraded in the range from 350 to 500°C. In this weight loss step, the remaining of polymeric chain of HFBM and all the PS-b-P5FS chain also were overlapped (Figure 6.4 [F]). Table 6.2 summarized the degradation temperatures for the polymers.



**Figure 6.4.** TGA for P4FS [A], P4FS-b-PS [B], P4FS-b-PS-b-PHFbM [C], PS [D], PS-b-P5FS [E] and PS-b-P5FS-b-PHFbM [F].

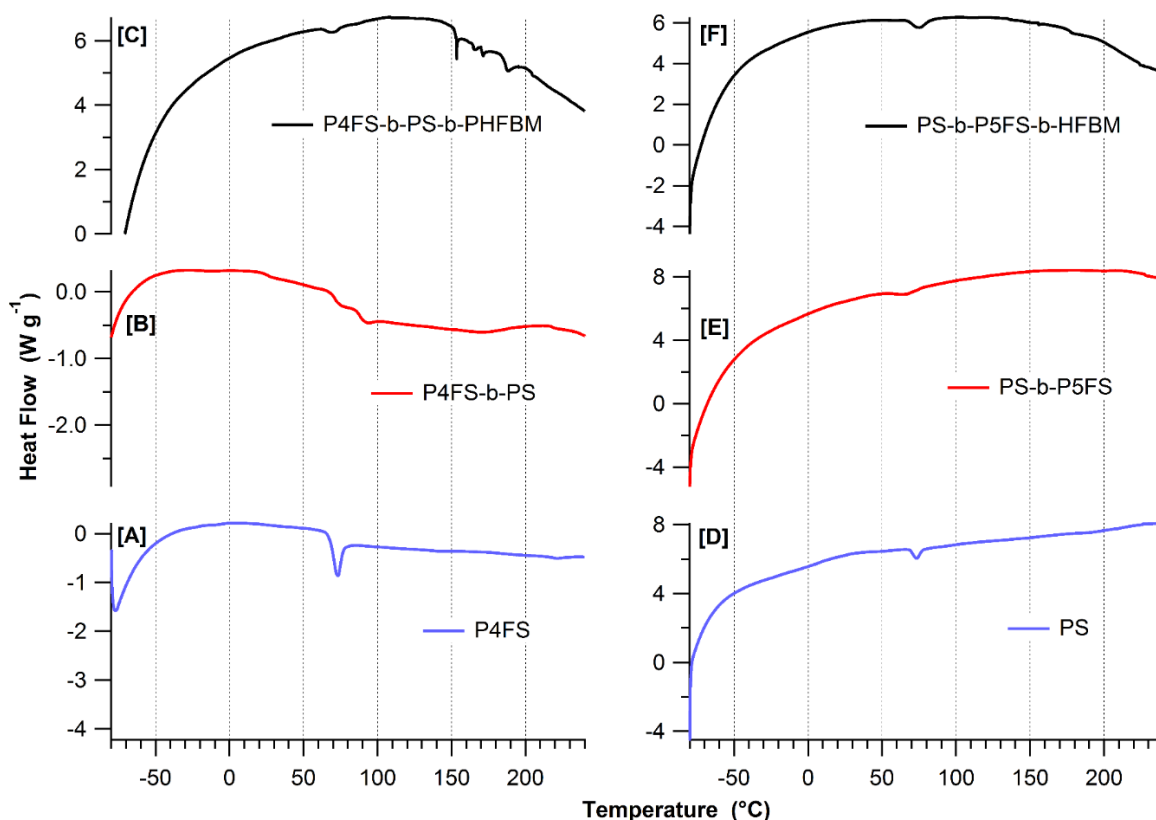
**Table 6.2.** Polymer Degradation temperatures

| <b>Membrane</b>   | <b>1<sup>st</sup><br/>Degradation<br/>(°C)</b> | <b>Weight<br/>[%]</b> | <b>2<sup>nd</sup><br/>Degradation<br/>(°C)</b> | <b>Weight<br/>[%]</b> | <b>3<sup>rd</sup><br/>Degradation<br/>(°C)</b> | <b>weight<br/>[%]</b> | <b>Residue<br/>[%]</b> |
|-------------------|------------------------------------------------|-----------------------|------------------------------------------------|-----------------------|------------------------------------------------|-----------------------|------------------------|
| P4FS              | 177.96                                         | 7.3524                | *                                              | *                     | 417.59                                         | 91.4322               | 1.2154                 |
| P4FS-b-PS         | 157.1                                          | 4.5656                | *                                              | *                     | 420.33                                         | 95.1475               | 0.2869                 |
| P4FS-b-PS-b-PHFBM | 91.93                                          | 4.0954                | 144.38                                         | 24.2846               | 413.82                                         | 70.2655               | 1.3545                 |
| PS                | 181.79                                         | 13.89                 | *                                              | *                     | 416.69                                         | 84.81                 | 1.28                   |
| PS-b-P5FS         | 194.91                                         | 12.6483               | *                                              | *                     | 439.06                                         | 85.8453               | 1.5064                 |
| PS-b-P5FS-b-PHFBM | 178.32                                         | 20.1236               | *                                              | *                     | 434.83                                         | 78.4624               | 1.414                  |

\* Absent

#### 6.4.1.6. Differential Scanning Calorimetry (DSC)

Figure 6.5 presents the DSC comparison between all the polymers synthesized. The glass transition temperature of polystyrene have been investigated and different values for this transition were found in a range from 90 to 100°C. P4FS (Figure 6.5[A]) presented the glass transition temperature shifted towards lower temperatures than polystyrene at 69°C. P4FS-b-PS (Figure 6.5[B]) showed two glass transition temperatures; the first correspond to P4FS and the second correspond to PS at 70°C and 90°C respectively. Figure 6.5 [C] show the DSC curve for P4FS-b-PS-b-PHFBM; the incorporation of HFBM to P4FS-b-PS show a new transition at 65°C, however the transitions previously mentioned disappears and the polymer at 144°C started its degradation.



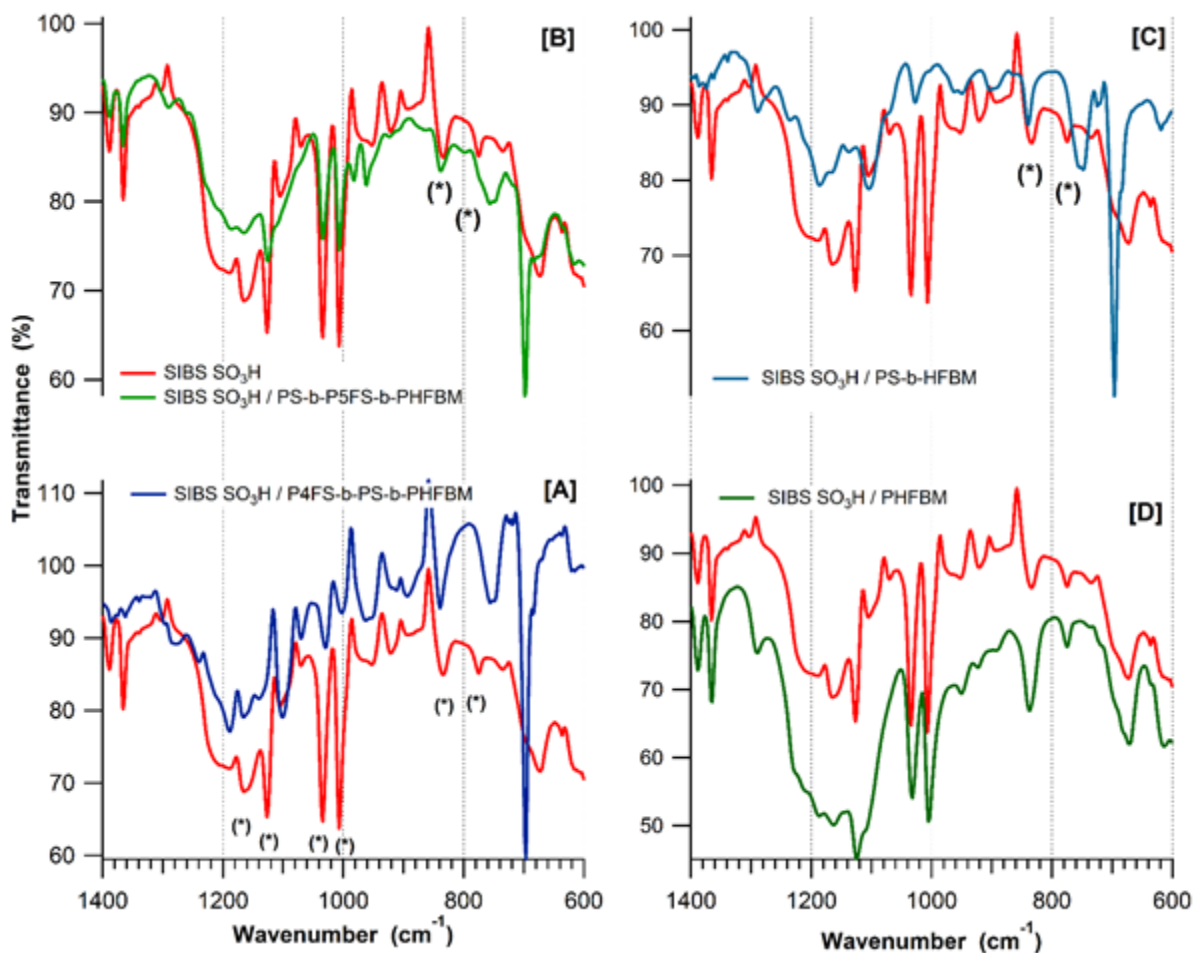
**Figure 6.5.** DSC for P4FS [A], P4FS-b-PS [B], P4FS-b-PS-b-PHFBM [C], PS [D], PS-b-P5FS [E] and PS-b-P5FS-b-PHFBM [F].

Figure 6.5 [D] show the DSC for PS. This polymer presented a thermal transition at 73°C. PS-b-P5FS (Figure 6.5 [E]) presented the same transition shifted towards lower temperatures at 67°C, however the incorporation of HFBM to PS-b-P5FS shifted the transition at 78°C.

## 6.4.2. Polymer blend characterization

### 6.4.2.1. FT-IR spectroscopy

Figure 6.6 [A] presents the FT-IR spectrum of SIBS SO<sub>3</sub>H and SIBS SO<sub>3</sub>H / P4FS-b-PS-PHFBM membranes. SIBS SO<sub>3</sub>H membrane exhibited four distinctive bands at 1151, 1124, 1034, 1007 cm<sup>-1</sup> associated to the sulfonic group.<sup>14</sup> The bands at 1034 and 1151 cm<sup>-1</sup> were caused by the symmetric and asymmetric stretching vibration of the sulfonated group attributed to the S=O bond. Other important band correspond to the para-substitution of the sulfonic group at 830 cm<sup>-1</sup> on the aromatic ring in poly(styrene). This figure shows the FTIR for SIBS SO<sub>3</sub>H / P4FS-b-PS-PHFBM membrane. The addition of the fluoroblock copolymer to SIBS SO<sub>3</sub>H membrane shifts the asymmetric stretching vibration of the S=O group towards higher wavenumber, however the para-substitution shifted to lower wavenumber. These results suggest that the fluoroblock copolymer are interacting with the sulfonic group and the aromatic ring, therefore a change of energy is required to produce the bands at those specific wavenumbers. Figure 6.6 [B] and 6.6 [C] shows the FT-IR spectrum of SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM and SIBS SO<sub>3</sub>H / PS-b-PHFBM membranes. The incorporation of both polymer to SIBS SO<sub>3</sub>H membrane also shifted the asymmetric stretching vibration of the S=O group and the para-substitution band, suggesting an interaction between the sulfonic group, aromatic ring with the fluoroblock copolymer; however SIBS SO<sub>3</sub>H / PHFBM presented no shifts in the bands associated to the sulfonic group and the aromatic ring. Other experiments are presented ahead to understand the impact of the incorporation of the fluoroblock copolymer in SIBS SO<sub>3</sub>H membranes.

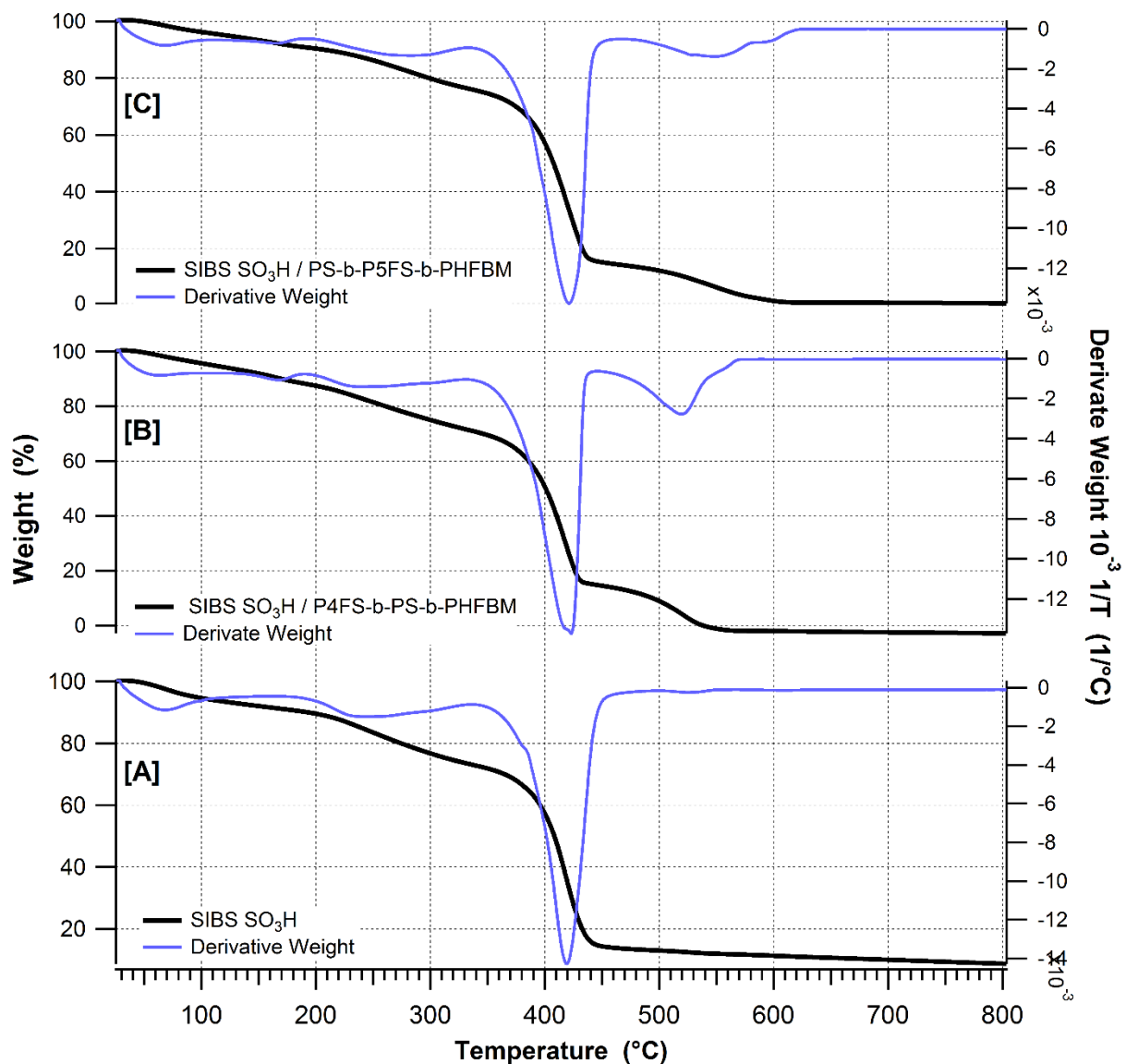


**Figure 6.6.** FTIR spectra for SIBS-SO<sub>3</sub> / P4FS-b-PS-b-PHFBM [A], SIBS-SO<sub>3</sub> / PS-b-P5FS-b-PHFBM [B], SIBS-SO<sub>3</sub> / PS-b-PHFBM [C] and SIBS-SO<sub>3</sub> / PHFBM [D].

#### 6.4.2.2. Thermogravimetric Analysis (TGA)

Figure 6.7 [A] shows the TGA curve for SIBS SO<sub>3</sub>. The TGA curve for this membrane exhibited three degradation temperatures, the first one at 50 – 100°C corresponds to water absorbed inside the membrane, the second degradation region at 245°C represents the sulfonic group, and third degradation at 419°C represent polymer backbones.<sup>13</sup> Figure 6.7 [B] shows the TGA curve for SIBS SO<sub>3</sub> / P4FS-b-PS-PHFBM membrane. This membrane presents two regions in the TGA that remained unchanged, however two additional weight loss are observed at 171°C and 520°C respectively. P4FS-b-PS-PHFBM presents a high weight loss around 160°C, therefore the incorporation of this polymer into sulfonated SIBS membrane induce a weight loss at lower

temperature than the sulfonic group. Ionic interactions with the sulfonic group suggest a new weight loss at higher temperatures in sulfonated SIBS membranes.<sup>13</sup>



**Figure 6.7.** TGA spectra for SIBS-SO<sub>3</sub> [A], SIBS-SO<sub>3</sub> / PS-b-P5FS-b-PHFBM [B] and SIBS-SO<sub>3</sub> / P4FS-b-PS-b-PHFBM [C].

The new degradation at higher temperatures could be attributed to the interaction between the sulfonic group and P4FS-b-PS-PHFBM. Figure 6.7 [C] shows the TGA curve for SIBS SO<sub>3</sub> / PS-b-P5FS-PHFBM membrane. The incorporation of this polymer to sulfonated SIBS produced two

additional weight losses at 170°C and 549°C, respectively. Ionic interactions between the sulfonic group and the fluoroblock copolymer suggest the weight loss at higher temperatures. PS-b-P5FS-PHFBM possess a higher weight loss around 170°C, therefore the new degradation at lower temperatures in SIBS SO<sub>3</sub> / PS-b-P5FS-PHFBM membrane could be attributed to the degradation of the fluoroblock copolymer. Table 6.3 summarized the degradation temperatures for the polymeric blend membranes.

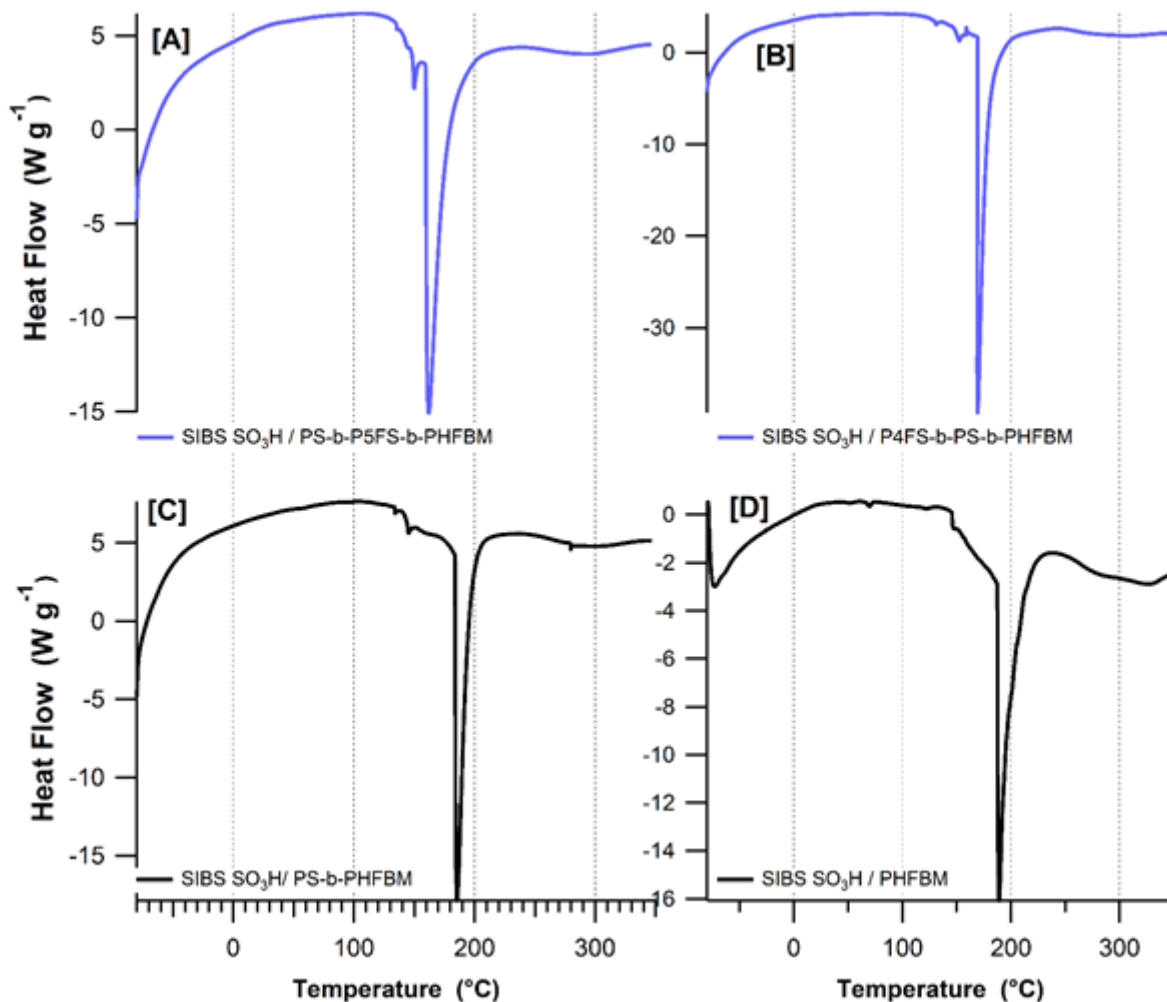
**Table 6.3.** Degradation temperatures for the polymeric blend membranes

| Membrane                                 | 1 <sup>st</sup><br>Degradation<br>(°C) | 2 <sup>nd</sup><br>Degradation<br>(°C) | 3 <sup>rd</sup><br>Degradation<br>(°C) | 4 <sup>th</sup><br>Degradation<br>(°C) |
|------------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| SIBS-SO <sub>3</sub>                     | Absent                                 | 245                                    | 419                                    | Absent                                 |
| SIBS-SO <sub>3</sub> / P4FS-b-PS-b-PHFBM | 171                                    | 241                                    | 423                                    | 520                                    |
| SIBS-SO <sub>3</sub> / PS-b-P5FS-b-PHFBM | 170                                    | 250                                    | 421                                    | 549                                    |

#### 6.4.2.3. Differential Scanning Calorimetry (DSC)

The incorporation of the fluoroblock copolymer to the SIBS SO<sub>3</sub>H membrane produced unique DSC curves for each of the polymer studied. Sulfonated membranes exhibit two endothermic transitions, one was attributed to the ionic domains, while the peak at higher temperature was ascribed to the crystalline regions.<sup>15</sup> SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM (Figure 6.8 [A]) presented a difference in both the energy and temperature required to produce the endothermic transitions. These changes in temperature, are related to the energy needed to overcome the crystalline bonding forces and changes in the molecular conformation of the chains in the polymer.<sup>16</sup> DSC results for sulfonated membranes showed that changes in the energy and temperature required to produce the endothermic transition for the ionic group and crystalline regions are associated to a new configuration for the ionic domain and the polymeric backbone.<sup>17</sup> SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PHFBM (Figure 6.8 [B]) also presented changes in the temperature and energy required to produce the endothermic transitions. This membrane required more energy to produce the

endothermic transition for the crystalline region than SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM, however the energy required to produce the ionic transitions decreased. SIBS SO<sub>3</sub> / PS-b-PHFBM (Figure 6.8 [C]) exhibited differences in both energy and temperature required to produce the endothermic transitions. SIBS SO<sub>3</sub> / PHFBM (Figure 6.8 [D]) showed the highest reduction in the energy required to produce the crystalline transition, while the transition for the ionic domain disappeared. These results are related to the changes induced by the incorporation of the polymer on the molecular conformation of the polymeric chains and sulfonic group in the membrane showed in the FTIR and TGA experiments. Table 6.4 summarizes the endothermic transition temperatures and their corresponding energies for the membranes studied.



**Figure 6.8.** DSC for SIBS SO<sub>3</sub> H / PS-b-P5FS-b-PHFBM [A], SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PHFBM [B] SIBS SO<sub>3</sub>H/ PS-b-PHFBM [C] and SIBS SO<sub>3</sub> H / PHFBM [D].

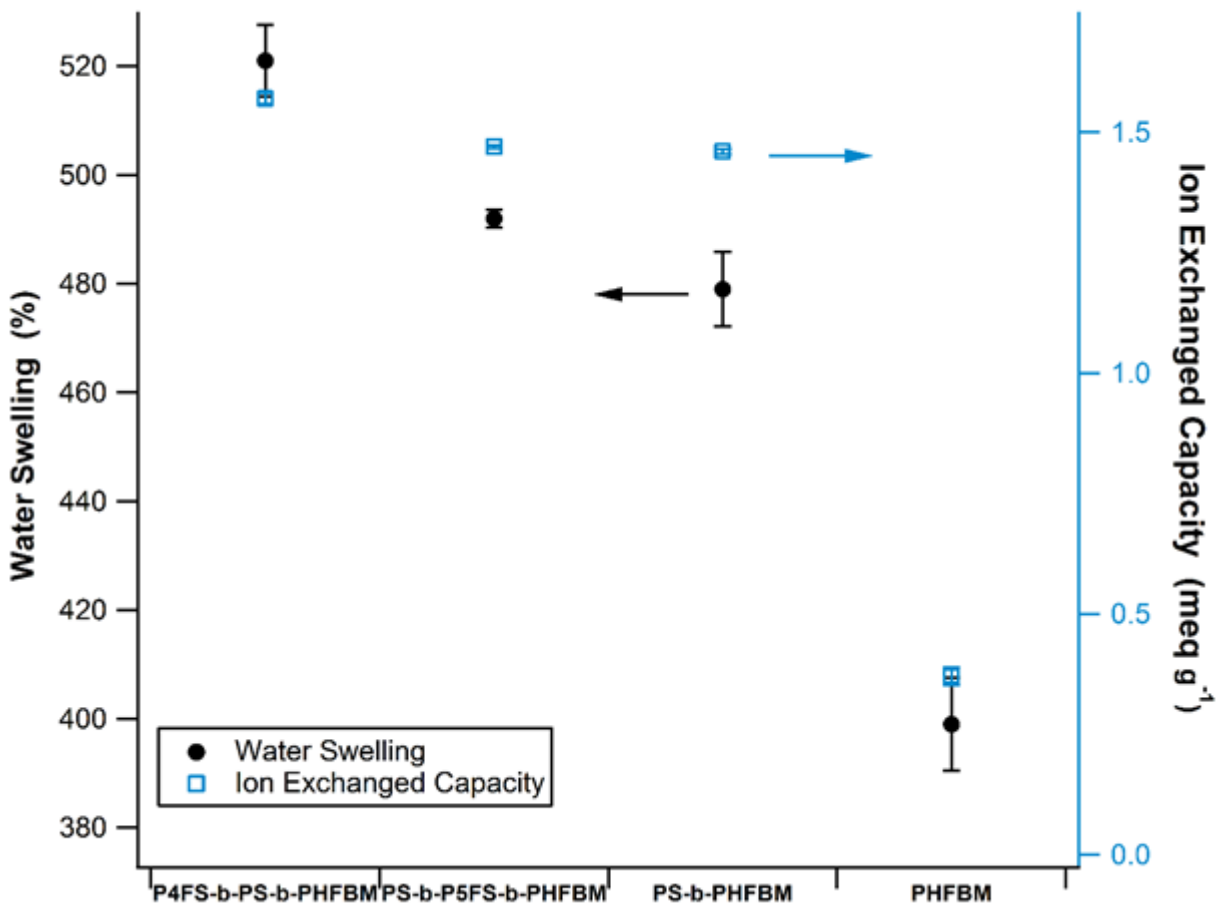
**Table 6.4.** Endothermic transition temperatures for polymeric blend membranes

| Membrane                                   | First Transition |                                    | Second Transition |                                    |
|--------------------------------------------|------------------|------------------------------------|-------------------|------------------------------------|
|                                            | T (°C)           | $\Delta H$<br>(J g <sup>-1</sup> ) | T (°C)            | $\Delta H$<br>(J g <sup>-1</sup> ) |
| SIBS SO <sub>3</sub> H                     | 140              | 1.58                               | 177               | 304.9                              |
| SIBS SO <sub>3</sub> H / P4FS-b-PS-b-PHFBM | 152              | 3.89                               | 168               | 263.3                              |
| SIBS SO <sub>3</sub> H / PS-b-P5FS-b-PHFBM | 150              | 5.09                               | 162               | 251.7                              |
| SIBS SO <sub>3</sub> H / PS-b-PHFBM        | 143              | 2.47                               | 185               | 199.45                             |
| SIBS SO <sub>3</sub> H / PHFBM             | *                | *                                  | 188.94            | 102.9                              |

\* Absent

#### 6.4.2.4. Ion Exchange Capacity (IEC) and Water uptake

Figure 6.9 presents IEC and water swelling for the polymer membranes studied. The incorporation of the polymer into the membrane produced different but unique IEC and water uptake for each of the polymer studied. SIBS SO<sub>3</sub> / PHFBM membrane exhibited the lowest IEC for all the membrane studied. IEC and water uptake seems to be sensitive to the fluoropolymer type. The IEC of P4FS-b-PS-b-PHFBM, PS-b-P5FS-PHFBM and PS-b-PHFBM was 1.57, 1.47 and 1.46 meq g<sup>-1</sup> respectively, however the IEC of PHFBM was 0.37 meq g<sup>-1</sup>. The water absorbed by SIBS SO<sub>3</sub>H exhibited the same behavior, therefore the lowest percent of water uptake corresponds to SIBS SO<sub>3</sub> / PHFBM membrane. These results suggest a new morphology induce by the fluoropolymer. The IEC and water absorbed by SIBS SO<sub>3</sub>H membranes are related to the polymer structure of the ionomer domains, and the morphology of the membrane.<sup>7,13</sup> Table 6.5 presents the IEC and water swelling for the polymer membranes studied.



**Figure 6.9.** Water uptake and Ion Exchanged Capacity for SIBS SO<sub>3</sub>H/P4FS-b-PS-b-PHFBM, SIBS SO<sub>3</sub> H/PS-b-P5FS-b-PHFBM, SIBS SO<sub>3</sub>H/ PS-b-PHFBM and SIBS SO<sub>3</sub> H / PHFBM.

**Table 6.5.** Ion Exchanged Capacity (IEC), water uptake for sulfonated SIBS/Fluoropolymer membranes

| Membrana                                   | IEC<br>(meq g <sup>-1</sup> ) | Water uptake<br>(%) |
|--------------------------------------------|-------------------------------|---------------------|
| SIBS SO <sub>3</sub> H                     | 1.84                          | 608.14              |
| SIBS SO <sub>3</sub> H / P4FS-b-PS-b-PHFBM | 1.57                          | 521                 |
| SIBS SO <sub>3</sub> H / PS-b-P5FS-b-PHFBM | 1.47                          | 492                 |
| SIBS SO <sub>3</sub> H / PS-b-PHFBM        | 1.46                          | 479                 |
| SIBS SO <sub>3</sub> H / PHFBM             | 0.371                         | 399                 |

#### 6.4.2.5. Small angle X-ray Scattering (SAXS)

SAXS profiles for the polymeric membranes are shown in Figure 6.10. SIBS SO<sub>3</sub>H exhibited a first-order reflection at  $Q = 0.141 \text{ nm}^{-1}$ , however, sulfonated SIBS exhibits a nonperiodic morphology at higher ion content (above 1 mequiv g<sup>-1</sup>) at lower  $Q$  vectors.<sup>7</sup> The incorporation of the fluoroblock copolymer to the SIBS SO<sub>3</sub>H membrane produced unique SAXS profile for each of the polymer studied. The first order reflection for SIBS SO<sub>3</sub>H shifted towards lower scattering vector at  $Q = 0.128 \text{ nm}^{-1}$  with the addition of both P4FS-b-PS-b-PHFBM and PS-b-P5FS-b-PHFBM and  $Q = 0.134 \text{ nm}^{-1}$  with the addition PS-b-PHFBM, however PHFBM obtained a first-order scattering vector similar than SIBS SO<sub>3</sub>H at  $Q = 0.141 \text{ nm}^{-1}$ .

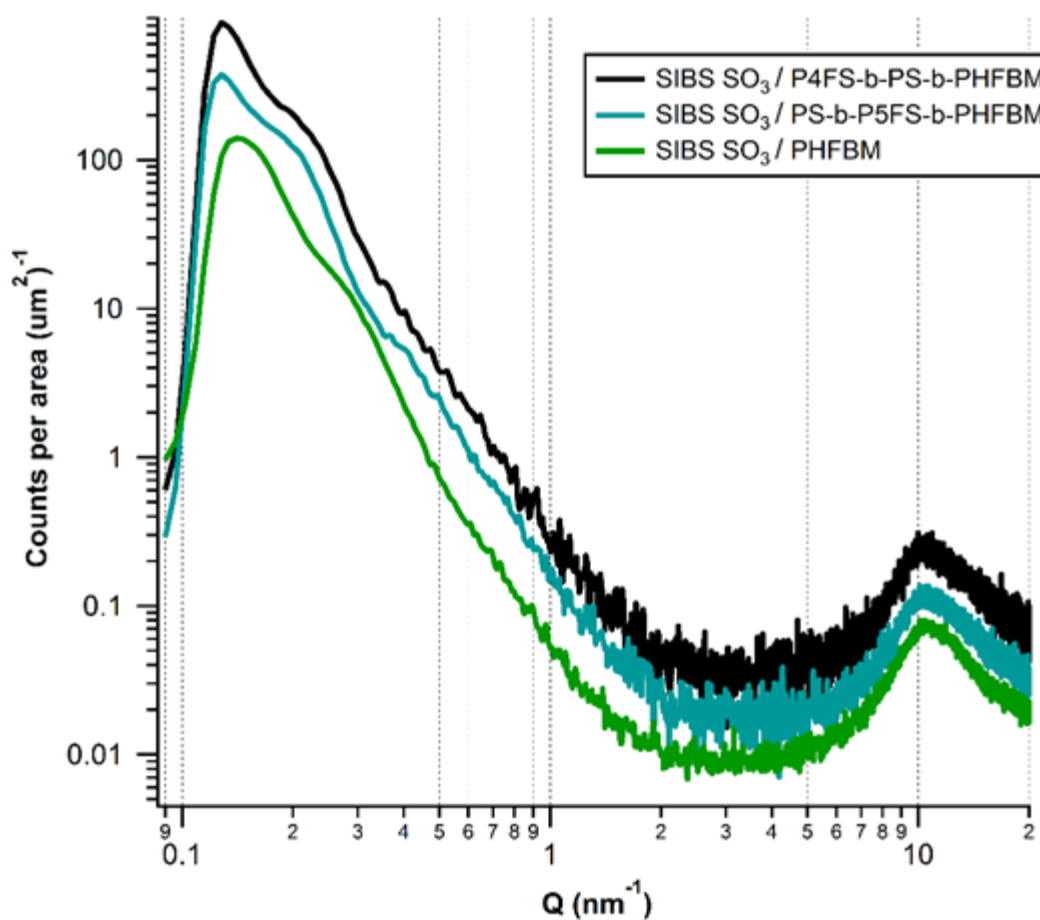
The incorporation of P4FS-b-PS-b-PHFBM, PS-b-P5FS-b-PHFBM, PS-b-PHFBM and PHFBM induced a morphological change in SIBS SO<sub>3</sub>H membranes; one additional peak appear at  $Q = 0.185, 0.179, 0.205$  and  $0.262 \text{ nm}^{-1}$ , respectively. Combining Bragg's law with the scattering vector ( $Q$ ) obtained from the SAXS plot, the interstitial was determined from the maximum in the first-order reflection and the additional peak. The Bragg distance for the first order reflection, increases with the incorporation of the polymer from 44.56 to 49.08 nm for P4FS-b-PS-b-PHFBM and PS-b-P5FS-b-PHFBM. The incorporation of the fluoropolymer to SIBS SO<sub>3</sub>H, results in large clusters and different polymeric domains which impacts in the polymer blend morphology. The incorporation of PHFBM presented the lowest Bragg distance for the additional cluster induced by the fluoropolymer on the membranes ( $d = 23.98 \text{ nm}$ ). This results agree with the previously presented DSC results, where a new configuration was obtained depending on the fluoro block copolymer selected.

Another important parameter is the radius of gyration ( $R_g$ ). This parameter was obtained using the Guinier equation, which provides the relation between  $R_g$ , the intensity in a SAXS profile and the scattering vector ( $Q$ ).  $R_g$  was estimated using the slope of the linear relationship between  $\ln(I(Q))$  and  $Q^2$ .<sup>18</sup> For polymers, this parameter represents the dimension of a polymer chain and can be used to evaluate changes with the variables studied. The incorporation of each fluoropolymer into the SIBS SO<sub>3</sub>H membrane produced unique  $R_g$ 's. SIBS SO<sub>3</sub>H/P4FS-b-PS-b-PHFBM obtained the highest  $R_g = 17.22 \text{ nm}$  for the membranes studied while SIBS SO<sub>3</sub>H/PHFBM

was the lowest:  $R_g = 14.09$  nm. Table 6.6 shows the values for the Bragg's distance and the  $R_g$  results for all the membranes studied.

**Table 6.6.** Scattering vector, Bragg distance and radius of gyration for the polymeric blend membranes.

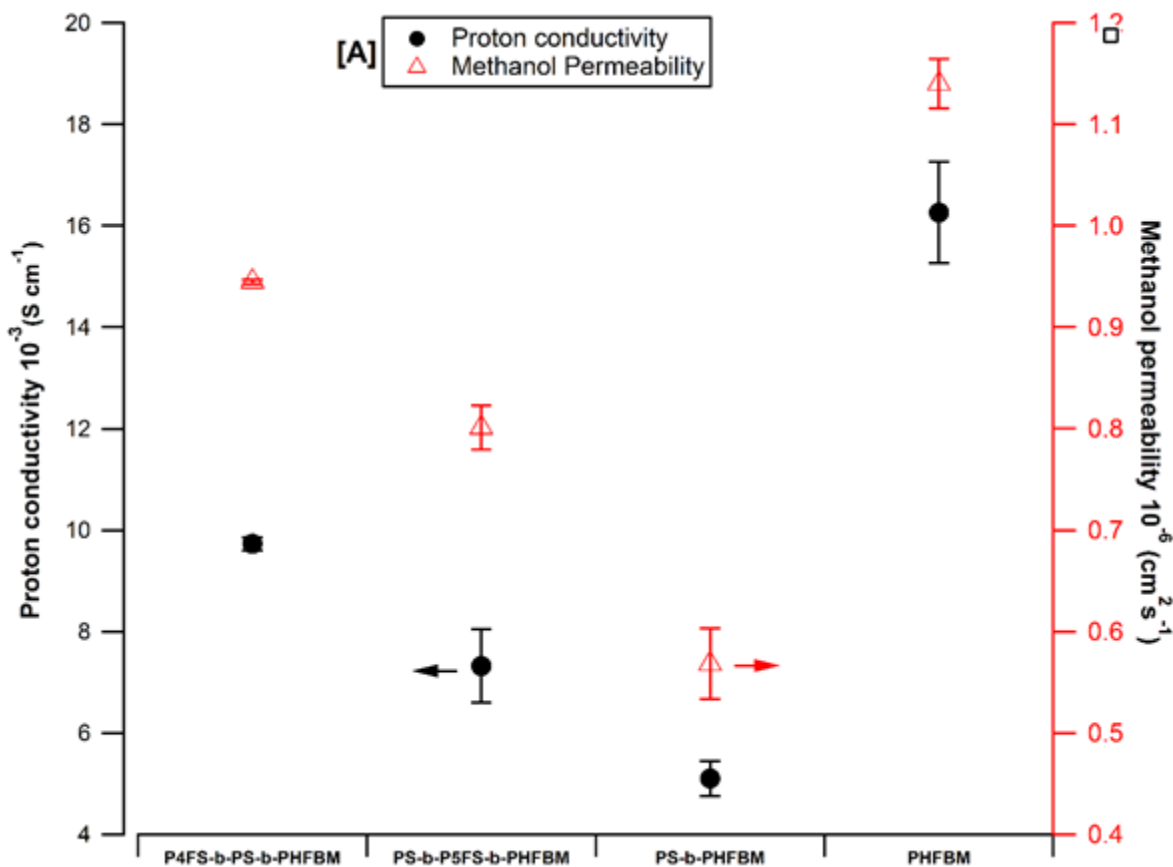
| Membrane                                       | $Q_{1\text{Bragg}}$<br>( $\text{nm}^{-1}$ ) | $d_{1\text{Bragg}}$<br>(nm) | $Q_{2\text{Bragg}}$<br>( $\text{nm}^{-1}$ ) | $d_{2\text{Bragg}}$<br>(nm) | Radius of<br>gyration<br>(nm) |
|------------------------------------------------|---------------------------------------------|-----------------------------|---------------------------------------------|-----------------------------|-------------------------------|
| SIBS $\text{SO}_3\text{H}$ / P4FS-b-PS-b-PHFBM | 0.128                                       | 49.08                       | 0.185                                       | 33.96                       | 17.22                         |
| SIBS $\text{SO}_3\text{H}$ / PS-b-P5FS-b-PHFBM | 0.128                                       | 49.08                       | 0.179                                       | 35.10                       | 15.55                         |
| SIBS $\text{SO}_3\text{H}$ / PS-b-PHFBM        | 0.134                                       | 45.89                       | 0.205                                       | 30.65                       | 14.66                         |
| SIBS $\text{SO}_3\text{H}$ / PHFBM             | 0.141                                       | 44.56                       | 0.262                                       | 23.98                       | 14.09                         |



**Figure 6.10.** SAXS log-log profile for SIBS  $\text{SO}_3\text{H}$ /P4FS-b-PS-b-PHFBM, SIBS  $\text{SO}_3\text{H}$ /PS-b-P5FS-b-PHFBM and SIBS  $\text{SO}_3\text{H}$  / PHFBM.

#### 6.4.2.6. *Methanol Permeability and Proton Conductivity*

Methanol permeability and proton conductivity for SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-PHFBM and SIBS SO<sub>3</sub>H / PHFBM membranes are presented in Figure 6.11. SIBS SO<sub>3</sub>H / PHFBM shows the higher proton conductivity for the all the membranes studied. This membrane presented one order of magnitude higher proton conductivity than the other membranes at the same SIBS SO<sub>3</sub>H content and similar fluoropolymer content. SIBS SO<sub>3</sub>H / PS-b-PHFBM exhibited the lowest proton conductivity. Other studies have related the proton conductivity in sulfonated membranes with the IEC and the water content in the membrane. However, the IEC's and water swelling (Figure 6.9) shows that the highest proton conductivity membrane has the lowest IEC and water swelling, while the lowest proton conductivity membrane has similar IEC and water swelling to the other membranes. These results suggest that the difference in the chemical composition among the fluoropolymers leads to differences in morphology and therefore proton conductivity. This is addressed in more detail in the subsequent section in relation to the fluoropolymer content, the polymer morphology and transport properties. The methanol permeability of these membranes showed a similar behavior. The transport of methanol also depends on the chemical composition and the polymeric blend morphology. This results suggest that the protons and methanol have similar transport mechanism for these polymeric blends membranes. SIBS SO<sub>3</sub>H / PHFBM and SIBS SO<sub>3</sub>H / PS-b-PHFBM show the highest and the lowest methanol permeability for the all the membranes studied respectively. These results agree with the previously presented DSC, FTIR, TGA and IEC results, where the variation of the methanol permeability and proton conductivity is linked to the new sulfonic group and polymer conformation producing a unique morphology depending on the fluoropolymer used. Table 6.7 summarized the values for methanol permeability and proton conductivity for all the membranes studied.



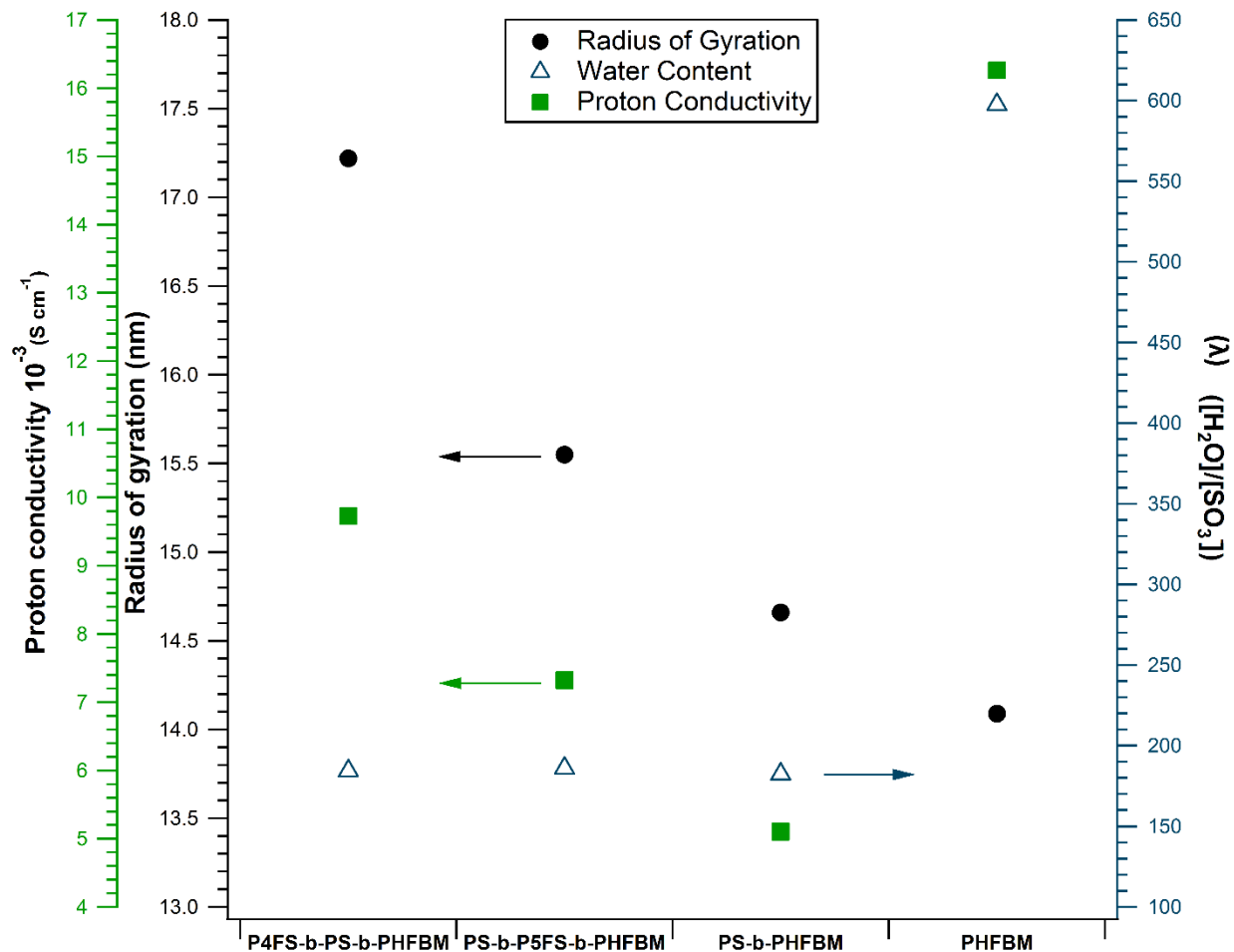
**Figure 6.11.** Comparison between methanol permeability and proton conductivity for SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-PHFBM and SIBS SO<sub>3</sub>H / PHFBM.

**Table 6.7.** Methanol permeability and proton conductivity for polymeric blend membranes

| Membrana                                   | Methanol Permeability (cm <sup>2</sup> s <sup>-1</sup> ) | Proton conductivity $\sigma$ (S cm <sup>-1</sup> ) |
|--------------------------------------------|----------------------------------------------------------|----------------------------------------------------|
| SIBS SO <sub>3</sub> H / P4FS-b-PS-b-PHFBM | 9.45e-07                                                 | 0.0097                                             |
| SIBS SO <sub>3</sub> H / PS-b-P5FS-b-PHFBM | 8.01e-07                                                 | 0.0073                                             |
| SIBS SO <sub>3</sub> H / PS-b-PHFBM        | 5.68e-07                                                 | 0.0051                                             |
| SIBS SO <sub>3</sub> H / PHFBM             | 1.14e-06                                                 | 0.0162                                             |

#### 6.4.2.7. *Correlation between proton conductivity, water content, and radius of gyration*

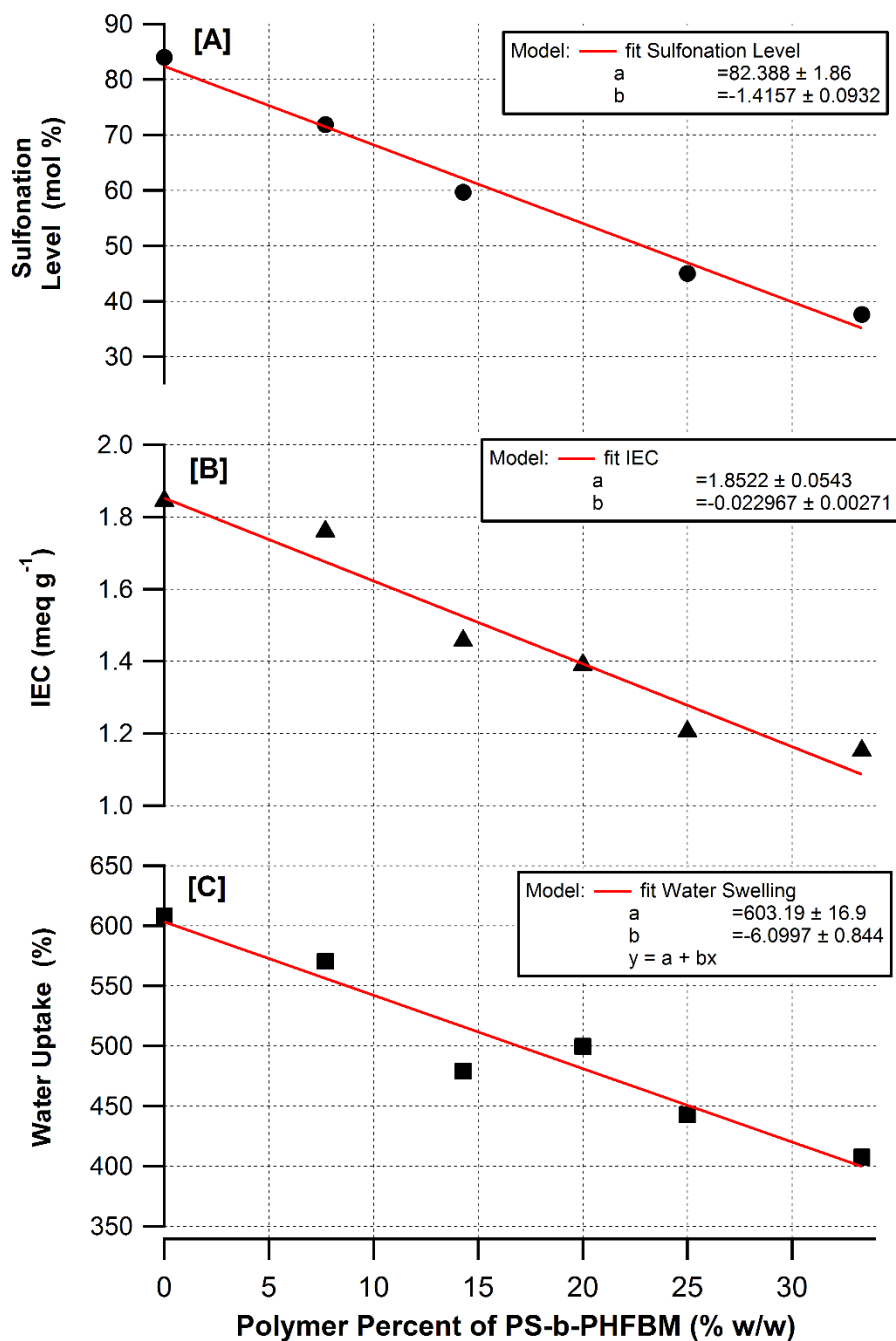
The transport of protons used the hydrated sulfonic groups in the polymeric membrane; the predominant mechanism consists in a series of Eigen-Zundel-Eigen or Zundel-Zundel transformations that depend on the sulfonic group,<sup>47</sup> the water content,<sup>48</sup> and the morphology.<sup>49</sup> Water content represents the moles of water per moles of ionic domain, which is an important parameter for the transport of protons. The water content ( $\lambda$ ) was calculated using Eq. 5.1. Figure 6.12 shows the correlation between the radius of gyration, proton conductivity and water content as a function of the fluoropolymer nature. The results show that  $\lambda$  increases with the incorporation of PHFBM, however, the other fluoropolymer membranes presented similar values but 69% lower than PHFBM. Upon incorporation of PHFBM the proton conductivity is the highest for all the membranes studied, perhaps the different ionic domains induced by the incorporation of PHFBM, are interconnected by the large amount of water content and the reduction of the radius of gyration.



**Figure 6.12.** Correlation between proton conductivity, radius of gyration and water content for SIBS SO<sub>3</sub>H / P4FS-b-PS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-P5FS-b-PHFBM, SIBS SO<sub>3</sub>H / PS-b-PHFBM and SIBS SO<sub>3</sub>H / PHFBM.

#### 6.4.2.8. Effect of the fluoropolymer content on Morphology-Transport Property Relationships.

Figure 6.13 shows the sulfonation percent [A], IEC [B] and water swelling [C] as a function of a fluoroblock copolymer content (%w/w) in sulfonated SIBS membrane.



**Figure 6.13.** Sulfonation percent [A], IEC [B] and water swelling [C] as a function of fluoroblock copolymer percent in SIBS membranes

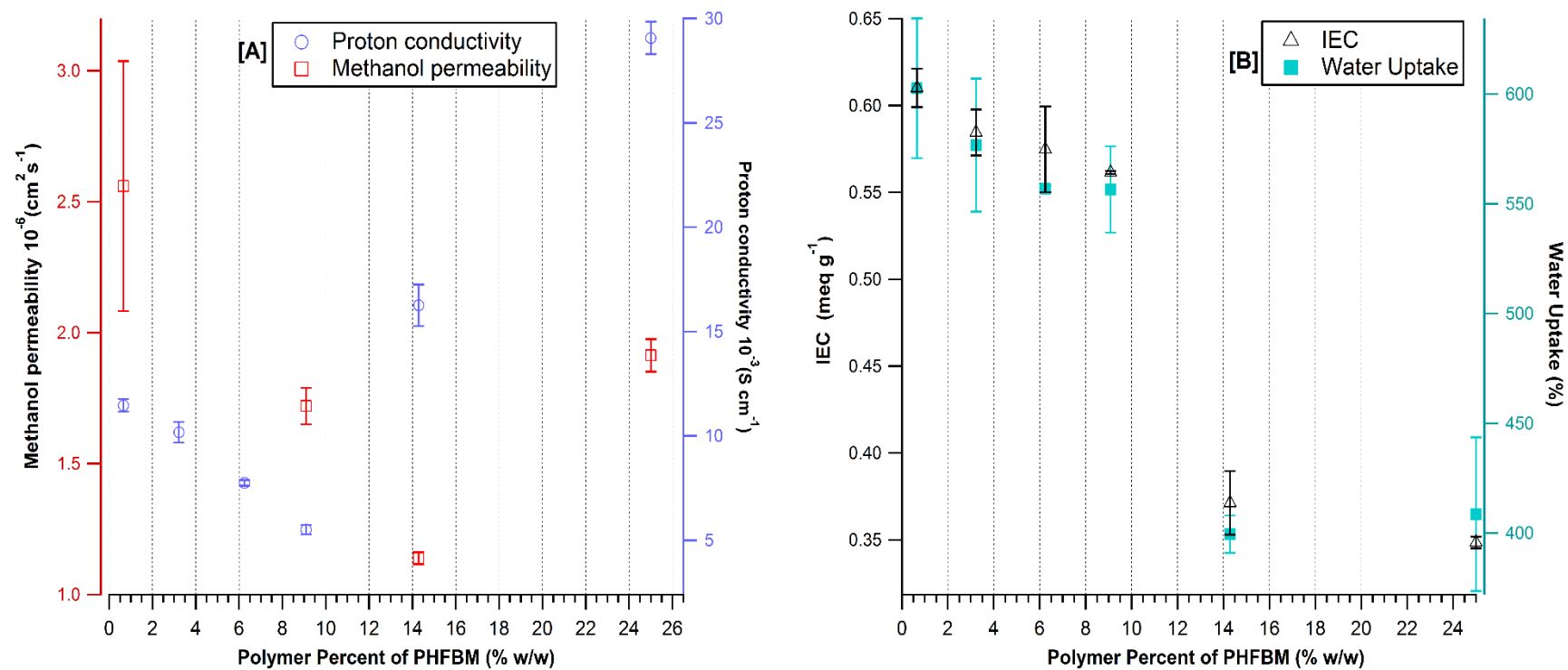
These experiments were evaluated using PS-b-HFBM. Figure 6.13 [A] and 6.13 [B] show that the sulfonation level and the IEC are inversely proportional to the fluoroblock copolymer percent.

The water swelling also reduced its value linearly as the fluoropolymer percent increased (Figure 6.13 [C]).

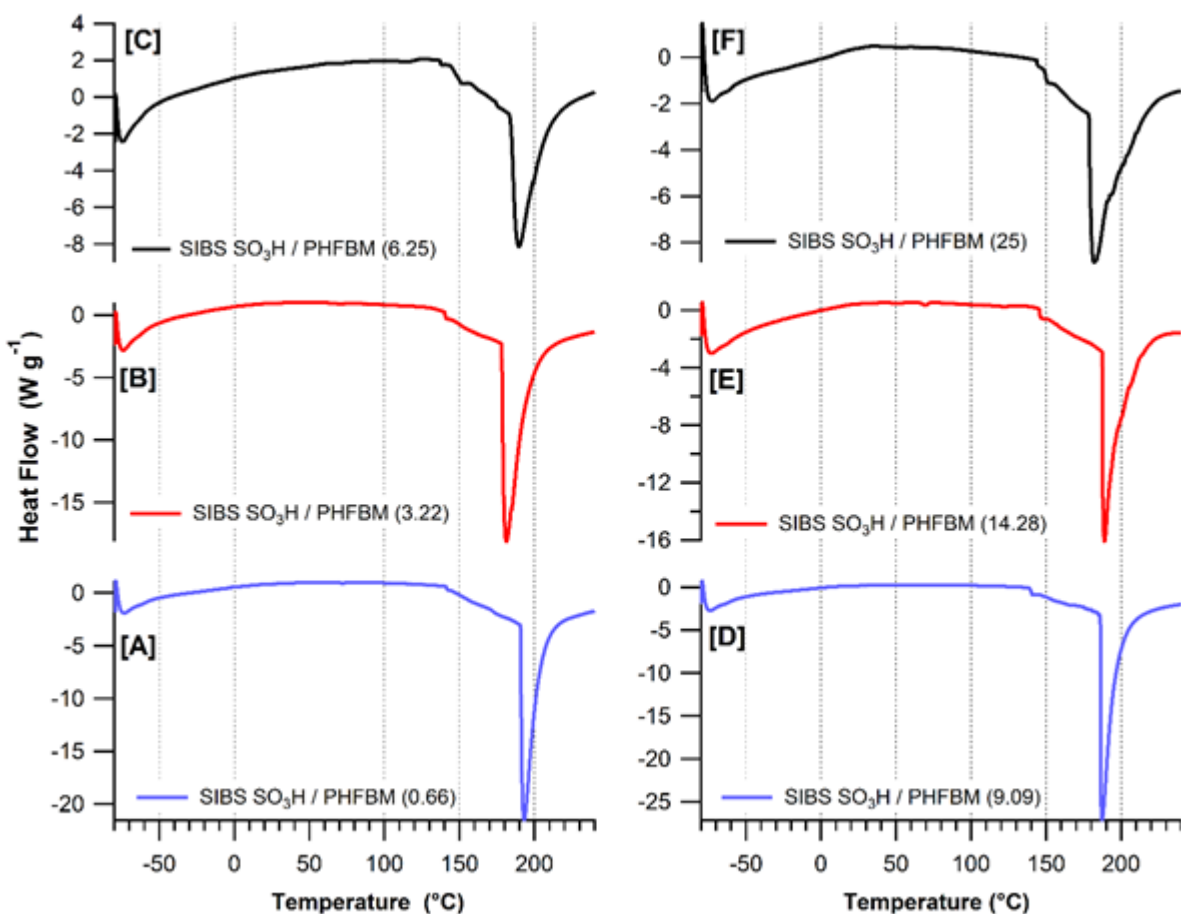
Interestingly, when PHFBM was used for the same experiment, there is a discontinuity in the trend of the IEC and water swelling as a function of a fluoroblock copolymer content. The IEC and water swelling decreased linearly; however, as the polymer percent increased above 9 %w/w HFBBM/SIBS SO<sub>3</sub>H the linearly between IEC and the fluoropolymer percent is disrupted (shown in Figure 6.14[A] and 6.14[B]). The proton conductivity and methanol permeability exhibited the same behavior; however above 9 %w/w PHFBM/SIBS SO<sub>3</sub>H the proton conductivity and methanol permeability increased linearly as a function of the polymer percent. These results suggest that the difference in the fluoropolymer percent leads to differences in the interaction between PHFBM and SIBS SO<sub>3</sub>H, the morphology and therefore, proton conductivity and methanol permeability.

The physical-chemical interaction with the sulfonic group plays an important role in the transport properties, however the morphology (related to the mass-transfer limitation) and the chemical groups impacts greater the transport properties of these polymeric blend membranes.

To understand the relationship between the morphology and transport properties SAXS profiles and DSC curves were obtained. The incorporation of different fluoropolymer percent to the SIBS SO<sub>3</sub>H membrane produced unique DSC curves for each of the percent studied (Figure 6.15 [A]-[F]). All the membranes presented difference in both the energy and temperature required to produce the endothermic transitions. These changes are related to a different molecular conformation depending of PHFBM percent into SIBS SO<sub>3</sub>H membrane.

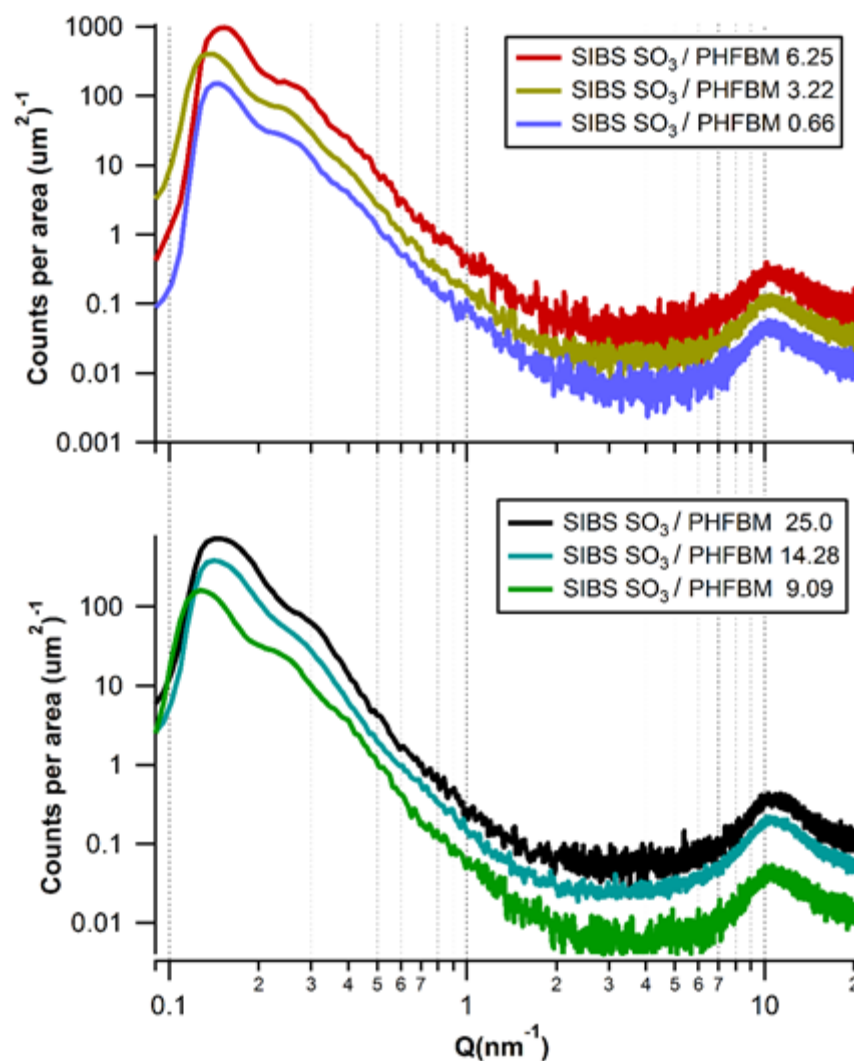


**Figure 6.14.** Comparison between methanol permeability and proton conductivity [A], and IEC and water swelling [B] as a function of the polymer percent of HFBM.



**Figure 6.15.** DSC for SIBS SO<sub>3</sub> H with different polymer percent of PHFBM: 0.66 % [A], 3.22% [B], 6.25% [C], 9.09% [D], 14.28% [E], 25% [F].

The incorporation of the fluoroblock copolymer to the SIBS SO<sub>3</sub>H membrane produced unique SAXS profile for each of the fluoropolymer percent (Figure 6.16). The first order reflection for SIBS SO<sub>3</sub>H shifted depending on the percent used.



**Figure 6.16.** SAXS log-log profile for SIBS SO<sub>3</sub> H with different polymer percent of PHFBM.

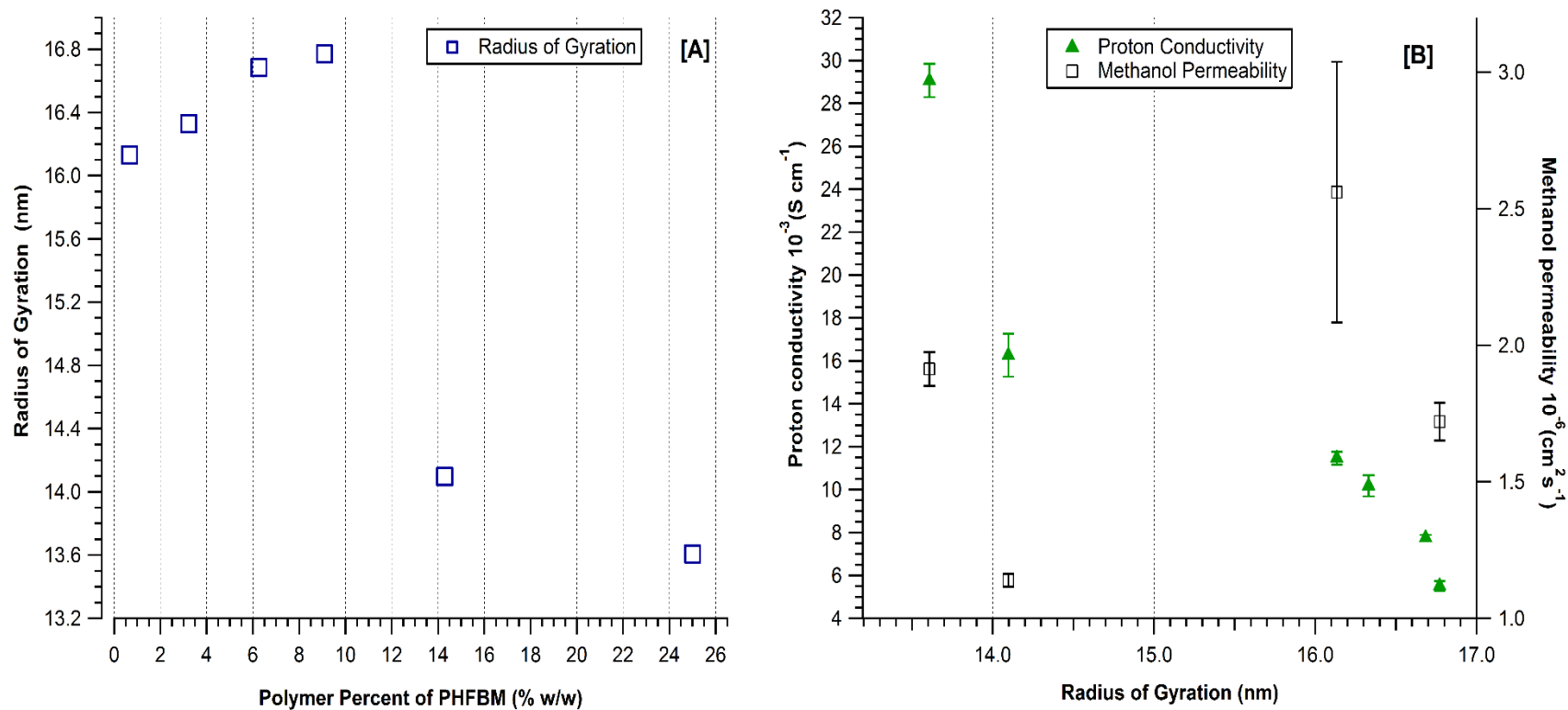
The Bragg distance for the first order reflection vary from 42 to 49 nm. This results agree with the previously presented DSC results, where a new configuration was obtained depending on fluoropolymer percent.

Figure 6.17 [A] shows the radius of gyration as a function of the polymer percent of HFBM. The results show a discontinuity in the trend of the radius of gyration as a function of a fluoroblock copolymer content. The radius of gyration increased linearly. However, as the polymer percent increased above 9 %w/w PHFBM/SIBS SO<sub>3</sub>H the linearly disrupted; therefore the radius of gyration decreased as a function of a fluoroblock copolymer content. These results suggest that

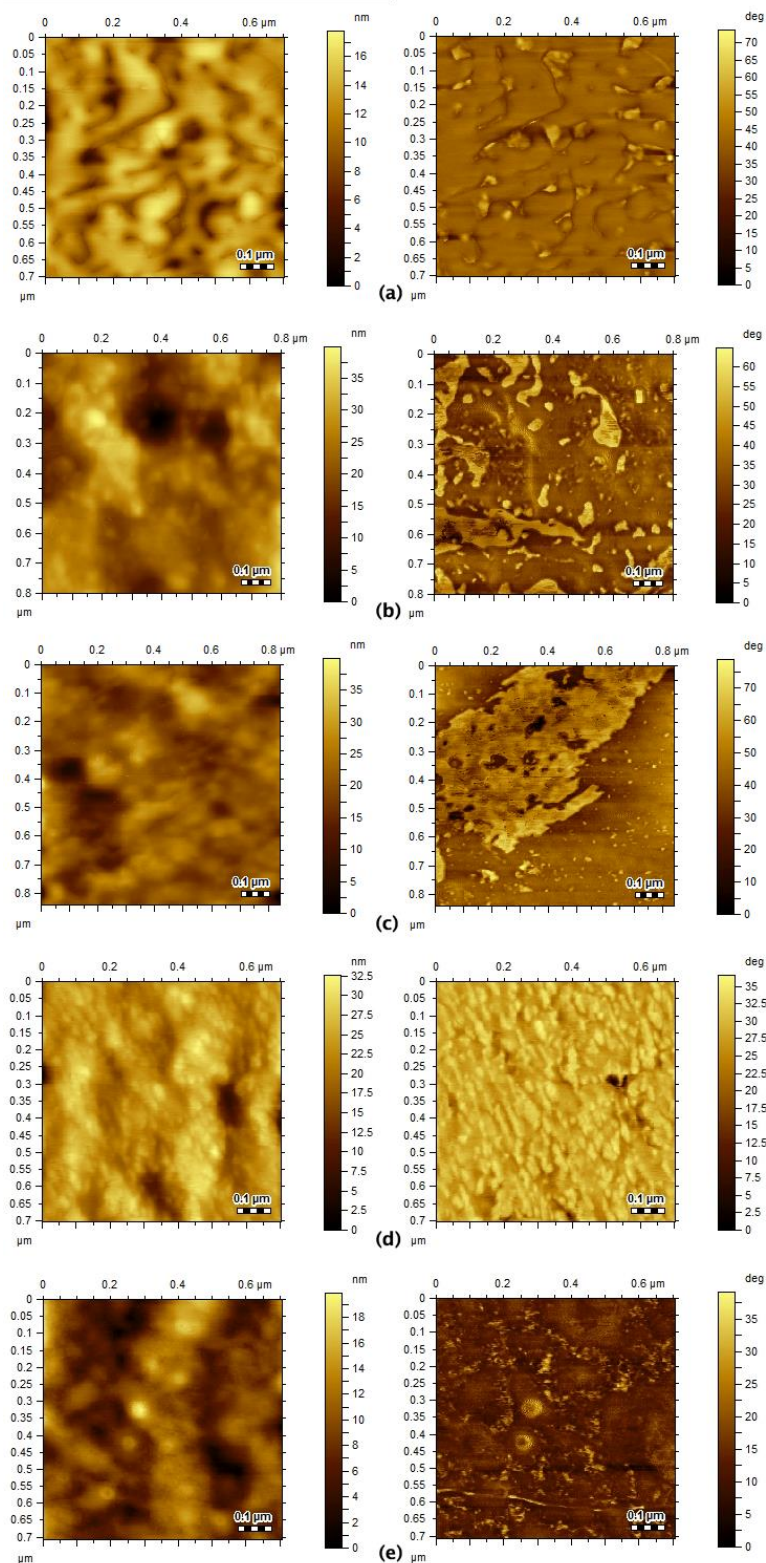
the difference in the fluoropolymer percent leads to differences in the morphology; above 9 %w/w all the polymeric chains were compacted creating a new molecular configuration. These results agree with the water swelling, IEC and the transport properties, where a new configuration for the ionic domain and polymeric matrix was obtained depending on the fluoropolymer percent.

Figure 6.17 [B] shows the relationship between the proton conductivity, methanol permeability and the radius of gyration for SIBS SO<sub>3</sub>H/ PHFBM membranes. This figure shows that at higher fluoropolymer content the radius of gyration decreased. These results suggested that by increasing the fluoropolymer amount, the polymeric chains are compacted. A different nanostructure induced by the chemical groups leads to the improvement to the proton conductivity. The methanol permeability shows a different behavior; at higher radius of gyration the methanol permeability increased. These results suggest a competitive effect in the methanol permeability depending on the chemical nature of the functional groups and the free volume obtained with different polymer compositions.

Figure 6.18 shows the topography and phase images of SIBS SO<sub>3</sub>H with the different percentage of PHFBM obtained by AC-AFM mode. The surface morphology of the different membranes was obtained by the comparison between the topography and the phase imaging. The results suggested that the surface changes as the percentage of PHFBM increased. This behavior could be related to the form as polymers are assembling in the membrane during the membrane casting. As the percentage of PHFBM increased, a higher percentage of the fluoropolymer is on the surface, therefore different clusters resulted above 9%.



**Figure 6.17.** Radius of Gyration as a function of the polymer percent of PHFBM [A]. Proton conductivity and methanol permeability as a function of radius of gyration [B].

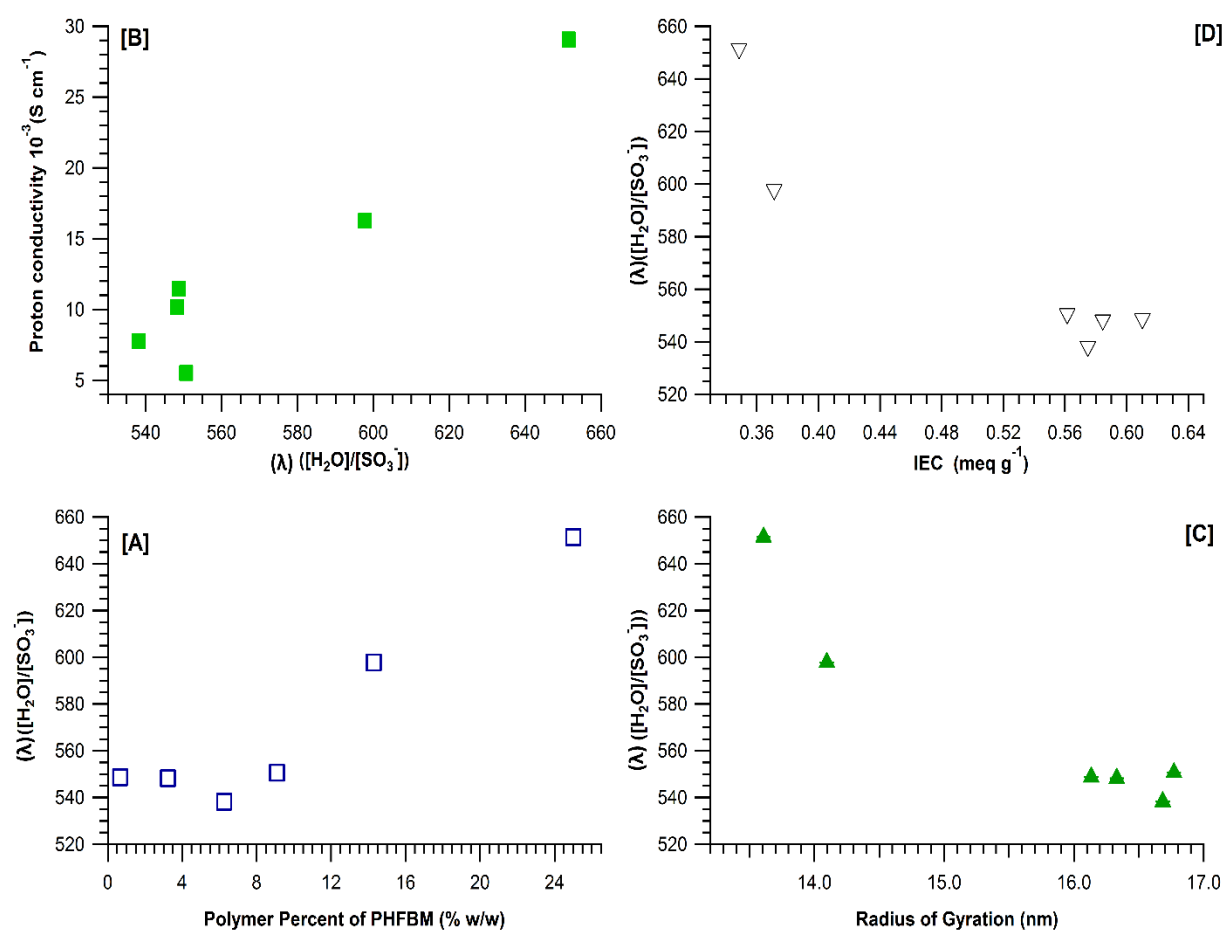


**Figure 6.18.** AFM phase images of (a) SIBS SO<sub>3</sub>H, (b) SIBS SO<sub>3</sub>H/ PHFBM (0.66%), (c) SIBS SO<sub>3</sub>H/ PHFBM (6.25%), (d) SIBS SO<sub>3</sub>H/PHFBM (14.2%), and (f) SIBS SO<sub>3</sub>H/PHFBM (25%).

Figure 6.19 shows the relationship between the proton conductivity, water content, IEC, radius of gyration, and polymer percent of PHFBM. Figure 6.19 [A] shows that the water content is directly proportional to the fluoroblock copolymer percent. Interestingly, below 9 %w/w the water content remains constant. When the concentration increases above 9 %w/w the water content increases linearly as a function of the polymer percent of PHFBM. The proton conductivity as a function of the water content (Figure 6.19 [B]) possess the same behavior previously mentioned: the proton conductivity increases linearly with the water content.

Figure 6.19 [C] shows the relationship between the radius of gyration and the water content for SIBS SO<sub>3</sub>H/ PHFBM membranes. This figure shows that the water content remains slightly constant from 16 to 17 nm of the radius of gyration. Once the radius of gyration decreased, the water content increased linearly. The water content and IEC were correlated in Figure 6.19 [D]. This figure shows that the water content remains constant from 0.56 to 0.61 meq g<sup>-1</sup>; however, before 0.30 meq g<sup>-1</sup> the water content increases linearly when the IEC decreases.

These results suggested that by increasing the fluoropolymer amount, there are ionic clusters that are interconnected by the large amount of water per ionic group. Additionally, the polymeric chains are compacted, and the distance between these ionic clusters decreases. Therefore a different nanostructure induced by the incorporation of PHFBM to SIBS SO<sub>3</sub>H leads to the improvement to the proton conductivity.



**Figure 6.19.** Water content ( $\lambda$ ) as a function of the polymer percent of PHFBM [A]. Proton conductivity as a function of the Water content ( $\lambda$ ) [B]. Water content ( $\lambda$ ) as a function of the radius of gyration [C] and IEC [D].

## 6.5. CONCLUSION

Two novel tetra fluoroblock copolymers and their homopolymers were successfully synthesized using ATRP. The transport properties of physical blends of these four fluoro block copolymers, a difluoroblock copolymer and a homofluoropolymer with SIBS  $\text{SO}_3\text{H}$  were obtained. These results suggest that the different chemical compositions among the fluoropolymers lead to different morphologies and therefore transport properties for DMFC applications (proton conductivity and methanol permeability). IEC and water swelling also seem to be sensitive to the fluoropolymer, where a new configuration for the ionic domains and the polymeric matrix was obtained depending on the fluoropolymer. PHFBM resulted in the highest proton conductivity among all the fluoropolymer studied perhaps due to the ionic synergism of the ester or the fluorinated domains with the sulfonic group. The proton conductivity and methanol permeability dependence varied with the composition of PHFBM in SIBS  $\text{SO}_3\text{H}$  membranes. The results suggested that increasing the PHFBM composition compacted the polymeric chains creating a different nanostructure that led to the improvement in the proton conductivity. In addition, the difference in the fluoropolymer composition led to differences in the interaction between PHFBM and SIBS  $\text{SO}_3\text{H}$ , the morphology and therefore the transport properties. The physical-chemical interaction with the sulfonic group plays an important role in the transport properties; however, the morphology (related to the mass-transfer limitation) and the chemical groups impacts greater the transport properties of these polymeric blend membranes.

## 6.6. REFERENCES

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## CHAPTER 7

### Concluding Remarks

Transport properties of polymer membranes for specialty separations and applications such as direct methanol fuel cell (DMFC) can be influenced by both chemistry and morphology. This investigation studied both chemistry and morphology of polymer membranes with the intention to contribute to the understanding of the connection between the nanostructure and the resulting transport properties. First, the state-of-the-art perfluorosulfonic membrane Nafion® was processed with SCF CO<sub>2</sub> to influence its morphology and then exchanged with different counter ions to change the chemical nature of the ionic domains. In addition, novel fluoroblock copolymers were synthesized with different polymerization techniques to evaluate the changes of different initiators in the thermal and electronic configurations of the resulting polymers and their relationship with transport properties. In addition, changes in the chemical nature of the blocks and their composition were also studied in sulfonated blend membranes as ionic domains interconnect and also influence transport properties.

The morphological changes to Nafion® membranes induced by the SCF processing with CO<sub>2</sub> promote the transport of protons through the membrane and inhibit the methanol permeability. The molecular interaction between CO<sub>2</sub>, the fluorocarbon backbone and the sulfonic group creates a unique rearrangement in the polymer membrane. Different equilibrium properties such as: water swelling, thermal degradations, thermal endothermic transitions, polymer crystallinity and morphology was critically studied to understand the nanostructure. The SCF CO<sub>2</sub> processing and counter ion substitution inhibited both the transport of protons and methanol through Nafion® membrane, therefore, the incorporation of counter ions influences the ionic domains uniquely for each cation studied. The chemical nature of each counter ion influences uniquely the crystallinity, the morphology, and the water swelling, which impacted the transport properties for Nafion® membranes. Although the transport properties of both protons and methanol were reduced upon the incorporation of cations, suggesting some similarities in their

transport mechanism, the magnitude of the changes were significantly different, suggesting that there are fundamental differences in their transport mechanism that can be further explored to create more selective membranes. The transport properties in Nafion® are primarily limited by the nature of the cation exchanged and not the order, suggesting that the physically-induced changes by the supercritical fluid although important, do not limit the chemically-induced changes.

The synthesis of different fluoropolymers and their homopolymers were successfully synthesized by ATRP. Two fluorinated initiators (esterified Zonyl® and esterified octafluoro 4-4'-biphenol) and 1-bromo ethyl benzene were employed. The incorporation of these initiators in the polymeric chain have a significant impact on the thermal and UV properties of poly(PS), poly(HEMA), the diblock copolymers. The transport properties of polymeric blends composed of poly(PS) synthesized with different initiators and SIBS SO<sub>3</sub>H were limited by the nature of the initiator and the interaction of the polymer with the sulfonic group. Therefore this chemical interaction influences the ionic domains uniquely, but also influences the IEC, the water swelling, and the blend morphology, which are very important in the transport of protons and methanol through the membrane.

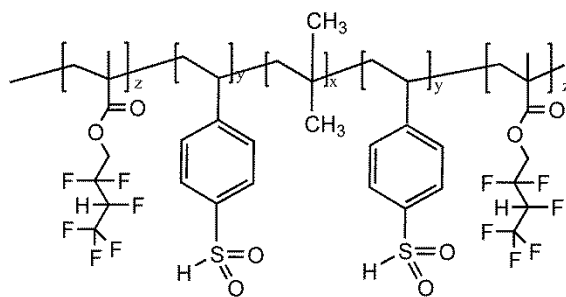
Two tetrafluoroblock copolymers, a difluoroblock copolymer and a homofluoropolymer were incorporated into an elastomeric matrix; therefore, physical blends of sulfonated poly(styrene-isobutylene-styrene) and unsulfonated fluoroblock copolymer were cast and analyzed. These results suggest that the difference in the chemical composition among the fluoropolymers leads to differences in morphology and therefore the transport properties: proton conductivity and methanol permeability. IEC and water swelling also seems to be sensitive to the fluoropolymer, where a new configuration for the ionic domain and polymeric matrix was obtained depending on the fluoropolymer. PHFBM obtained the highest value of proton conductivity among all the fluoropolymer studied. The proton conductivity and methanol permeability depends on the PHFBM percent in SIBS SO<sub>3</sub>H membranes. The results suggested that increasing the PHFBM amount, the polymeric chains are compacted; therefore a different nanostructure induced by the

homofluoropolymer leads to the improvement to the proton conductivity. In addition, the difference in the fluoropolymer percent leads to differences in the interaction between PHFBM and SIBS  $\text{SO}_3\text{H}$ , the morphology and therefore the transport properties. The physico-chemical interaction with the sulfonic group plays an important role in the transport properties, however the morphology (related to the mass-transfer limitation) and the chemical groups impacts greater the transport properties of these polymeric blend membranes.

## CHAPTER 8

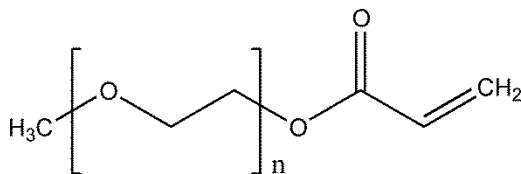
### Recommendations

Based on the previous results, the polymerization of novel block copolymers by ATRP and cationic polymerization opens a potential area for further investigation. Different block copolymers could be synthesized in order to obtain elastomeric fluoroblock membranes. Figure 8.1 shows the molecular structure for a proposed membrane. Poly(isobutylene) could be synthesized with cationic polymerization with a bifunctional initiator, then the follow block copolymers will be attached by ATRP.



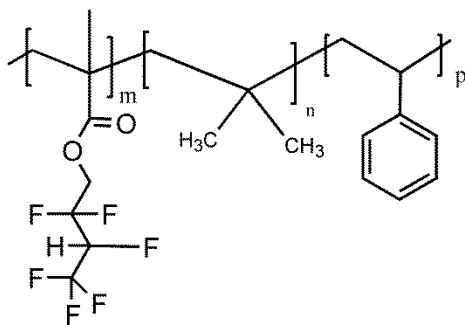
**Figure 8.1.** Proposed elastomeric fluoroblock membranes

Since transport properties are limited by the chemical group in the membrane poly(ethylene glycol) methyl ether acrylate (Figure 8.2) is another alternative to understand the impact of different chemical groups in the membrane.



**Figure 8.2.** Poly(ethylene glycol) methyl ether acrylate

Different block copolymers can be obtained combining ATRP and cationic polymerization. Figure 8.3 shows another option. The first block copolymer could be synthesized with ATRP, then PIB with cationic polymerization and finally PS could be attached with ATRP.



**Figure 8.3.** PHFBM-b-PIB-b-PS structure

Counter-ion substitution has a strong influence in the transport properties; nevertheless, the chemical coordination of the counter ion in the membrane and the amount have to be investigated.

Since the transport properties of polymeric blends are related to chemistry and morphology, a morphological characterization could be used to understand the coordination of these fluoropolymer in the membrane. Different polymers can be synthesized and used to compare the impact of different groups like ethers or amides in the transport properties of these polymeric blend membranes.

## APPENDIX A

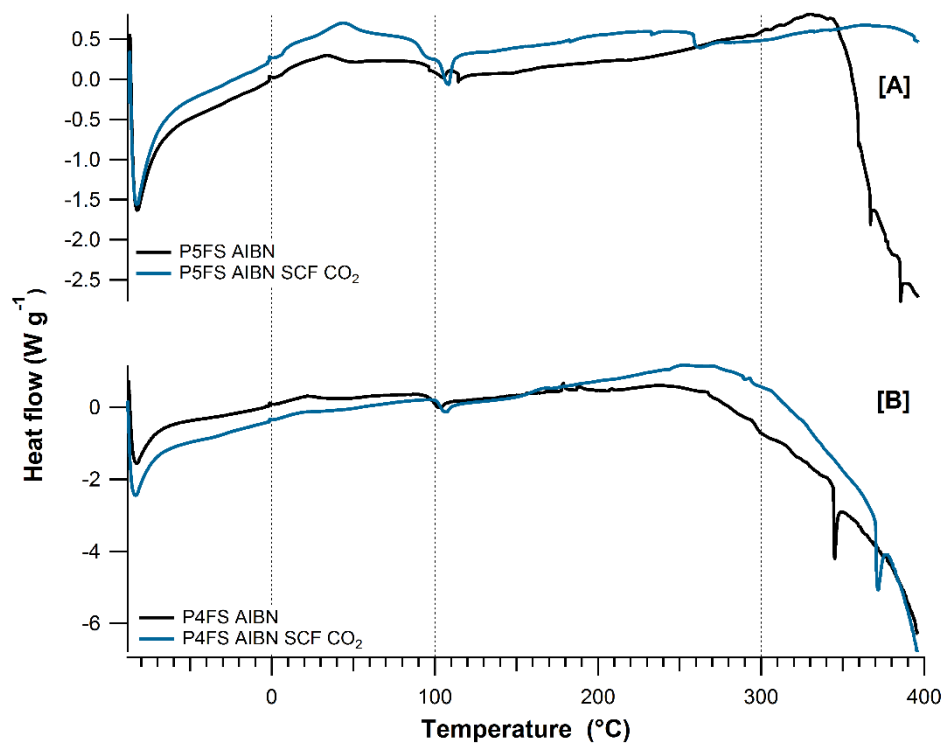
### A.1. High pressure CO<sub>2</sub> fluoropolymer synthesis

#### A.1.1. ABSTRACT

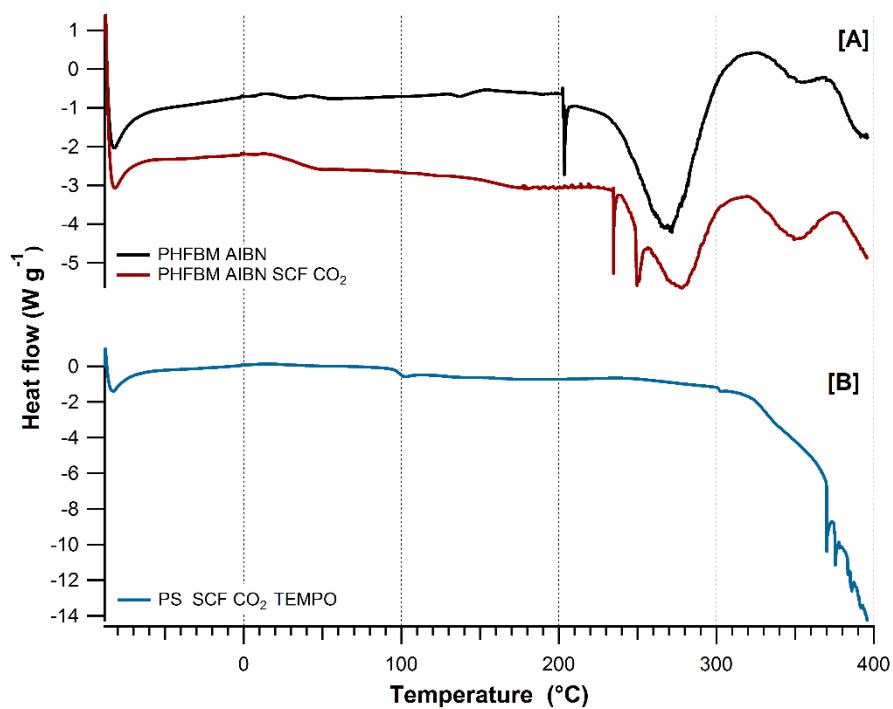
This investigation studied the synthesis of fluoropolymers in high pressure CO<sub>2</sub> and their resulting structure after the polymerization. The proposed work used different polymerization techniques: conventional free radical polymerization (FRP), high pressure CO<sub>2</sub> FRP, control radical polymerization (CRP) by stable free radical polymerization (SFRP) and high pressure CO<sub>2</sub> SFRP. The polymer proposed are poly(styrene), poly(2,3,4,5,6,pentafluorostyrene), poly(4-fluorostyrene) and poly(2,2,3,4,4,4-hexafluorobutyl- methacrylate). These monomers were selected due their high solubility in high pressure CO<sub>2</sub>. This methodology is proposed as an alternative to obtain an advanced fluorinated materials with unique morphology. All the polymers were characterized physically and thermally (e.g. TGA, DSC). Significant differences in their thermal and physical properties were observed when the polymer was synthesized using different polymerization techniques.

**Table A.1.** Molecular weight

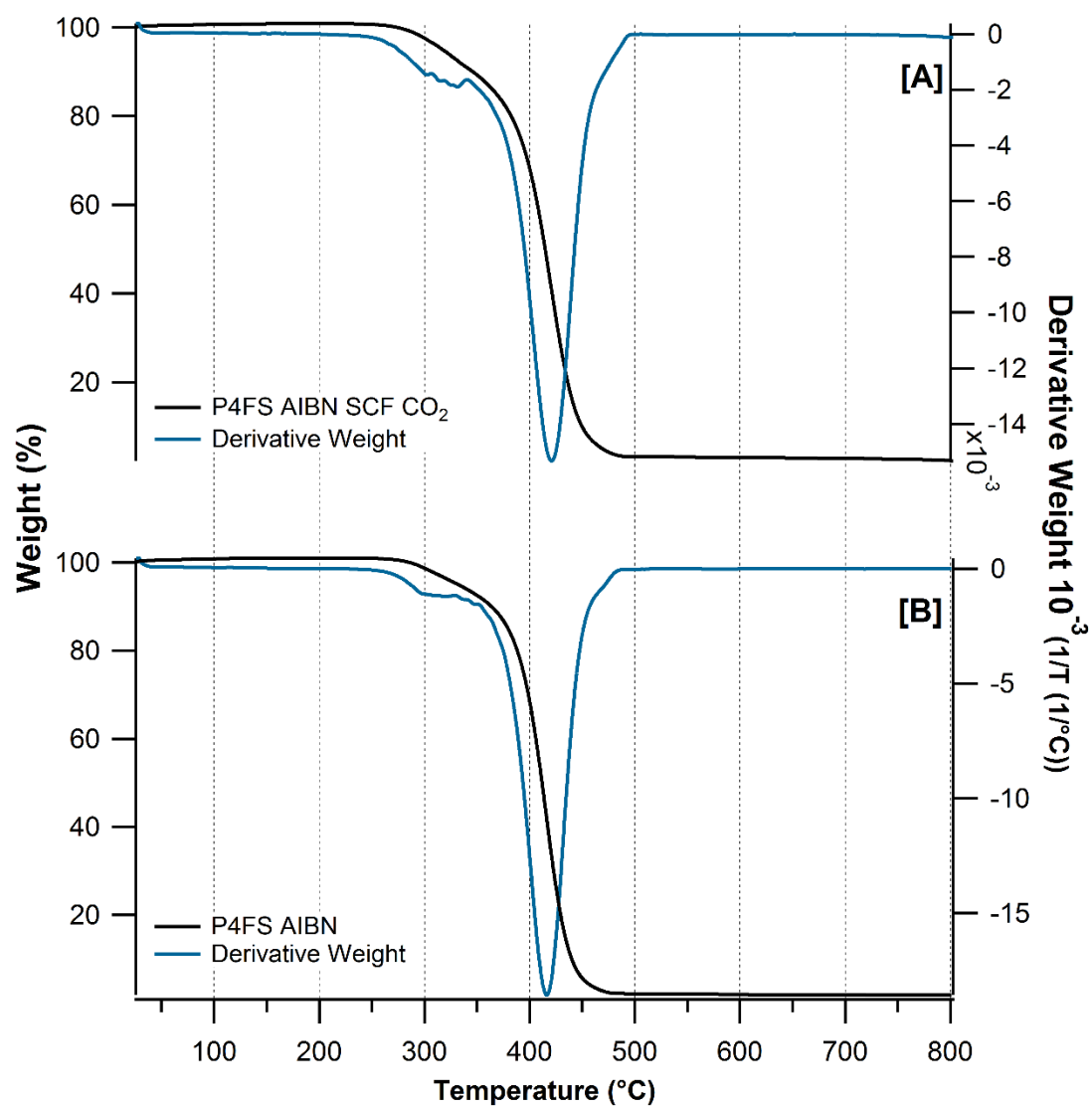
| Polymer | Polymerization technique | Mn*e-3 (g/mol) | Mw*e-3 (g/mol) | Mn/Mw |
|---------|--------------------------|----------------|----------------|-------|
| PS      | TEMPO                    | 3.52           | 5.40           | 1.54  |
|         | TEMPO SCF CO2            | 6.52           | 2.07           | 3.18  |
|         | AIBN                     | 5.71           | 1.62           | 2.83  |
|         | AIBN SCF CO2             | 6.44           | 1.07           | 1.65  |
| P5FS    | AIBN                     | 3.66           | 6.10           | 1.67  |
|         | AIBN SCF CO2             | 3.74           | 6.57           | 1.76  |
| P4FS    | AIBN                     | 9.54           | 7.99           | 8.37  |
|         | AIBN SCF CO2             | 7.31           | 9.91           | 1.36  |



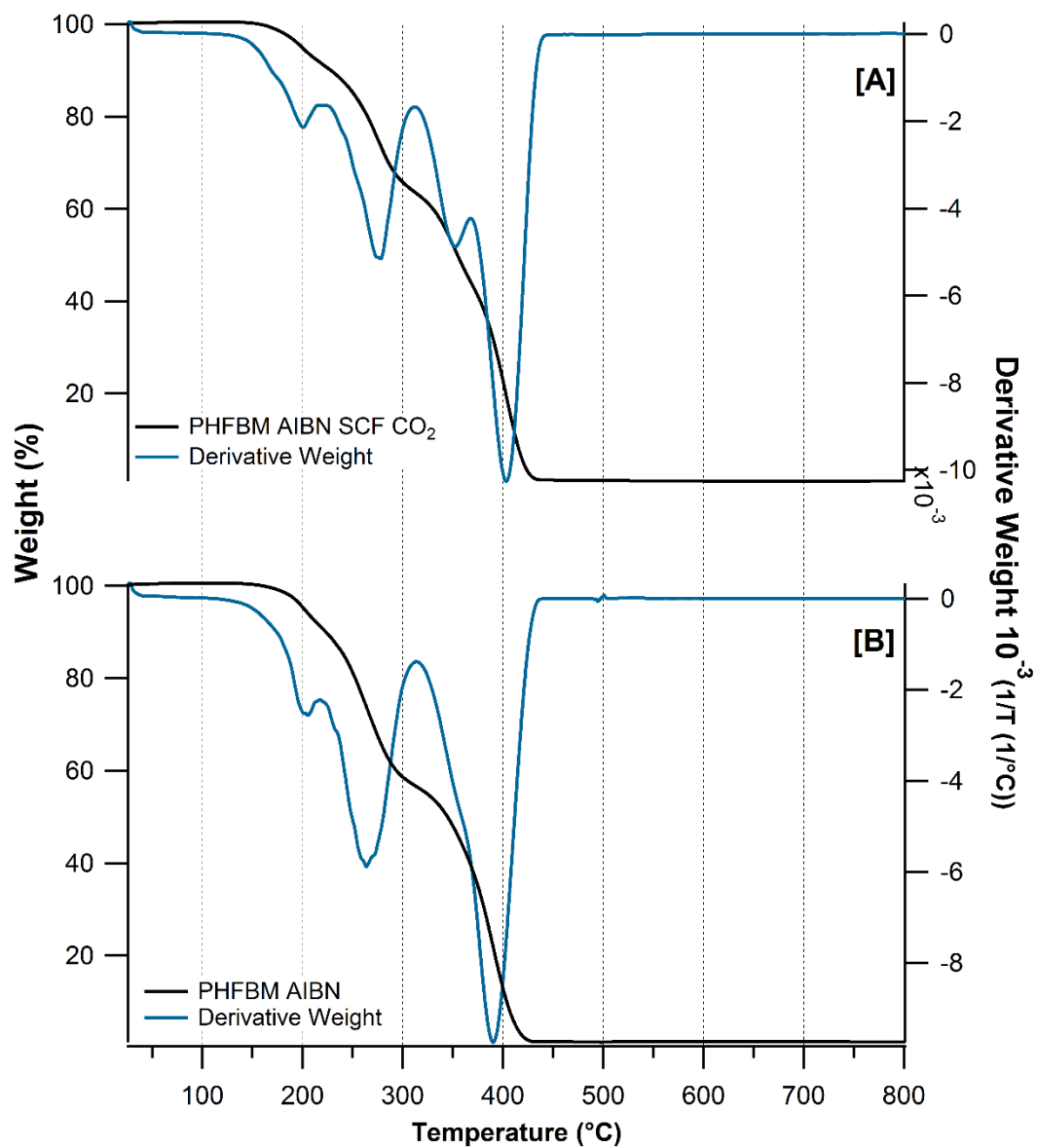
**Figure A.1.** DSC for P4FS AIBN, P4FS AIBN SCF  $\text{CO}_2$  [A] and P5FS AIBN, P5FS AIBN SCF  $\text{CO}_2$  [B].



**Figure A.2.** DSC for PHFBM AIBN, PHFBM AIBN SCF  $\text{CO}_2$  [A] and PS SCF  $\text{CO}_2$  TEMPO [B].



**Figure A.3.** TGA for P4FS AIBN SCF CO<sub>2</sub> [A] and P4FS AIBN [B].



**Figure A.4.** TGA for PHFBM AIBN SCF CO<sub>2</sub> [A] and PHFBM AIBN [B].

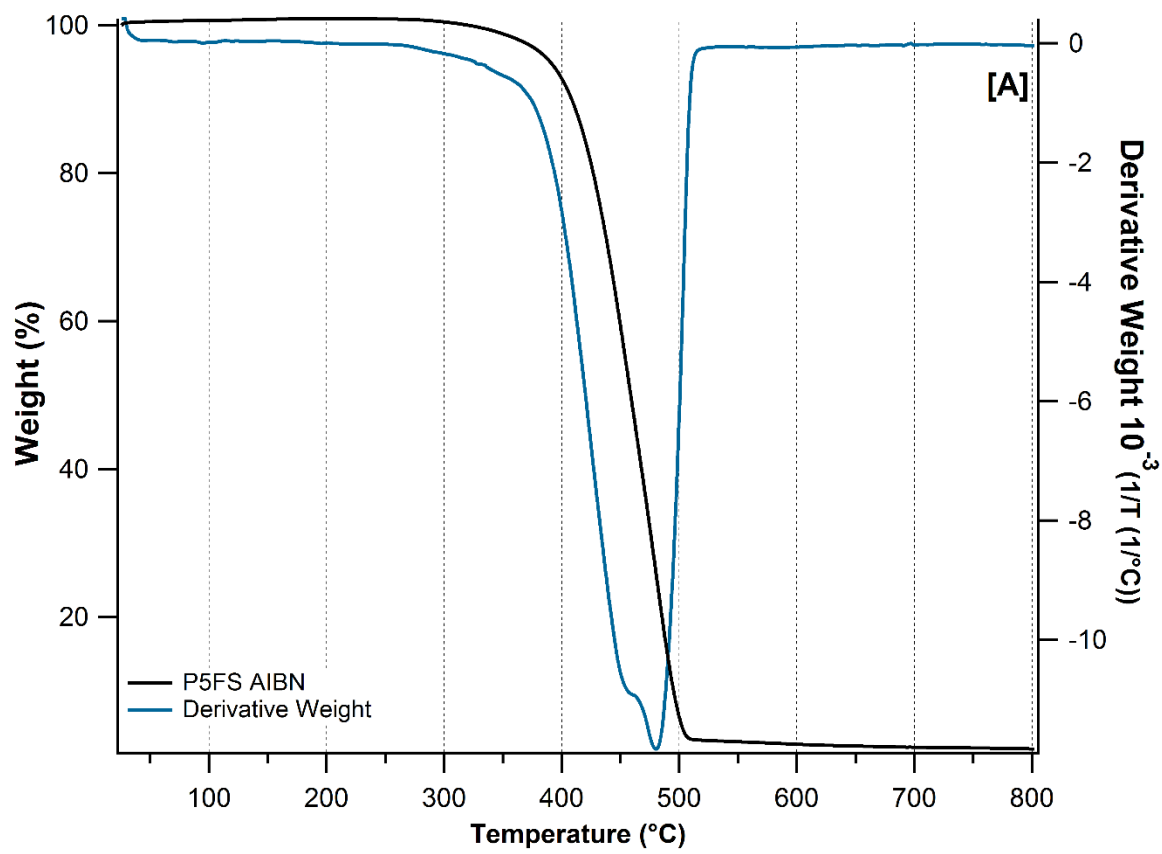


Figure A.5. TGA for P5FS AIBN [A].