Synthesis and Characterization of Sulfonated Poly(ether imide) with Higher Thermal Stability and Effect on CO₂, N₂, and O₂ Permeabilities

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An experimental design in different reaction conditions was applied to modify poly(ether imide), PEI, by sulfonation using acetyl sulfate. Higher temperatures and reaction times led to higher ion exchange capacity. The thermal analysis showed that our sulfonation approach accomplished preparing sulfonated PEI maintaining the thermal stability of its parent material even for the film with highest degree of sulfonation, and assessed the effect of this change on CO₂, O₂ and N₂ permeabilities. The permeability results pointed out that our sulfonation approach is an effective way to produce high performance engineered polymers for fuel cell electrolyte membranes and for CO₂ separation from air. These results also suggest that the use of milder reactive medium at higher temperatures and for longer reaction times seems to be a more promising approach to achieve thermal stability than use more aggressive sulfonation agents.

Keywords: sulfonated poly(ether imide), polymer thermal stability, gas permeation, CO₂ separation

1. Introduction

Poly(ether imide), PEI, is a thermoplastic polymer that has ether (–O–) and isopropylidene (–C(CH₃)₂–) groups, which not only ensure high rigidity, thermal stability, chemical resistance, and mechanical strength, but also are more easily processed during film synthesis1-7. Because of its excellent properties-price-processability balance1, it has gained importance in a wide variety of applications ranging from membranes1,2,4,8, sensors8,10, and as a parent material for synthesis of composites8,9,11, ion exchange films (dialysis, electrodialysis, or full cells)5,11,12, polymer blends2,6, and modified polymers1,3,7.

A promising approach to improve PEI properties is change its chemical structure by the introduction of sulfonic side groups in its backbone13,14. This sulfonated aromatic polymer shows good ion diffusivities for use as ion exchange membrane, which is a key component in solid polymer electrolyte for dialysis, electrodialysis, or fuel cell applications8,11. Some targets to be achieved in the development of new polymer electrolyte membrane (PEM) for fuel cell applications include8,15: high conductivity above 120 °C; good thermal, mechanical, and chemical stability; acceptable durability. In addition, the membrane would restrict the permeability of gases (such as O₂, N₂, CO₂, and CO) and water and fuel vapor in the system to maximize coulombic efficiency in fuel cells16,17. Sulfonated PEI (SPEI) meets most of these targets. Despite of proton conductivity data in SPEI films have already been studied in a previous work8, gas permeability data are still little studied in the literature.

Furthermore, following Scholes et al.18 and Baker and Lokhandwala19, gas permeability data are also mandatory information for sensors and gas permeation membrane applications. The gas permeation through dense polymeric films is described by the solution-diffusion mechanism, i.e. this is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Improving permeability and selectivity are not the only properties that are important. Materials need to be thermally and chemically robust, resistant to plasticization and with acceptable durability to ensure continual performance over long periods, and be cost effective to manufacture as standard membrane modules. More recently, poly(imide)s and poly(ether imide)s based membranes have shown some of the best permeability and selectivity properties for natural gas (CO₂/CH₄) and air (O₂/ N₂) separations1,6,8,18. The coupling of thermal, chemical, and plasticization resistance, as well as considerable mechanical strength, makes them attractive materials for gas separation membranes18. In addition, the polarity of the substituent groups affects chain-to-chain interactions

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which subsequently influences chain rigidity and packing efficiency. Sulfonic side groups have polar characteristics that enhance the effect of electrostatic crosslinking on the packing density of polymer chains resulting in an decrease in CO\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} permeabilities at the same time that increase the CO\textsubscript{2}/air ideal selectivities\textsuperscript{2}. Some typical values for sulfonated glassy polymers were found in the range 2 to 5.2 for CO\textsubscript{2}/O\textsubscript{2} and 25 to 35 for CO\textsubscript{2}/N\textsubscript{2}\textsuperscript{21,22}. Further, it often makes the membranes more resistant to plasticization\textsuperscript{6,19,22,23}, what impart not only efficiency in fuel cells\textsuperscript{15,16}, but also selectivity for CO\textsubscript{2} separations by gas permeation\textsuperscript{6,19,23}.

On the other hand, sulfonation of an aromatic polymer can be very complex because of its reversibility, and can lead to polymer degradation and to losses in thermal and mechanical stability\textsuperscript{2,4}. Furthermore, partial desulfonation is observed at temperature range between 200-400 °C\textsuperscript{11,24}.

From the analysis of the literature, one can see that, by controlling the reactivity of the sulfonation medium, the PEI sulfonation process has potential to lead to new materials with optimized physicochemical properties for applications previously highlighted. Exemplifying the importance of this control, it is also worth mentioning that PEI samples with a high extent of sulfonation become soluble in methanol and isopropanol\textsuperscript{5}, becoming useless as methanol fuel cell membranes, while low degrees of sulfonation might lead to lower proton conductivity\textsuperscript{3}. In this sense, it is important to access the effect of reaction conditions on the desired material properties.

Pinto et al.\textsuperscript{4} have propose a method that prepared lightly sulfonated PEI (SPEI) using acetyl sulfate, that seem to be a promising approach to achieve a desired sulfonation control. They analyzed the degree of sulfonation for the SPEI films obtained at different reaction conditions by Fourier transform infrared (FTIR) spectroscopy, ion-exchange capacity (IEC), and water sorption. Using a stoichiometric ratio PEI/Acetyl Sulfate at 1:2 or 1:4 and temperatures ranging at 40-60 °C for 30 min, the authors\textsuperscript{4} have obtained films with IEC range 0.08-1.32 meq H\textsuperscript{+}/g polymer showing good mechanical properties. All SPEI films were swelled by water, however those prepared with stoichiometric ratio PEI/Acetyl Sulfate at 1:4 showed lower water sorption and IEC\textsuperscript{45}, showing that an increase in the stoichiometric ratio of sulfonation agent may not be the better option to enhance degree of sulfonation.

Following Pinto et al.\textsuperscript{4} procedure, Loredo et al.\textsuperscript{5} obtained SPEI films also using stoichiometric ratio PEI/Acetyl Sulfate at 1:2 and monitoring the reaction temperature at 60 °C for 30 or 60 min. These authors investigated the influence of the degree of sulfonation (by changing reaction time) not only on IEC, thermal stability, and glass transition, but also on proton conductivity, obtaining IEC in the range 0.08-0.77 meq H\textsuperscript{+}/g polymer\textsuperscript{4}. Loredo et al.\textsuperscript{5} pointed the importance of optimizing synthesis conditions in order to achieve higher degree of sulfonation.

Analyzing those previous results, both used ratio PEI/Acetyl Sulfate at 1:2 or higher\textsuperscript{4,5}. However, Lakshmi et al.\textsuperscript{1} observed that sulfonated PEI samples having less than one –SO\textsubscript{2}H content/repeat unit showed better thermal stability. In this context, an objective of the investigation of our present work was to study the effect of the reaction parameters, such as temperature (40-60 °C) and sulfonation time of poly(ether imide) (30-90 min), following Pinto et al.\textsuperscript{4} sulfonation approach with stoichiometric ratio PEI/Acetyl Sulfate at 1:1, and to study the thermal behavior of sulfonated PEI, aiming at enhancing thermal stability. Furthermore, we organized a detailed review comparing the FTIR spectra for Sulfonated PEI (SPEI) with its parent material, which helped in the characterization of the SPEI films. Finally, the discussion involving our original permeability data for CO\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} in SPEI were conducted in order to correlate the role of introduced side groups with gases diffusion (hindering segmental mobility) and sorption (preferential interaction with CO\textsubscript{2}) in the polymer matrix. These gases were chosen because they are involved not only in environment gas separations, but also in methanol fuel cells. Despite of being well known as a promising material for ultrafiltration\textsuperscript{7} and dialysis process\textsuperscript{4}, SPEI is still little studied for gas permeation purposes.

2. Experimental

2.1. Materials and synthesis of sulfonated poly(ether imide) (SPEI)

0.03 kg PEI (ULTHEM) mass (± 10\textsuperscript{−7} kg) was solubilized in 10\textsuperscript{−4} m\textsuperscript{3} of N-methyl-2-pyrrolidone (NMP, VETEC Brazil, 99%) at 60 °C under constant stirring for 24 h. Subsequently, the sulfonation agent, acetyl sulfate, was prepared following Pinto et al.\textsuperscript{4} procedure. The temperature was monitored at (40 or 60)°C after adding all the sulfonating agent and the reaction times were 30 or 90 min. The stoichiometric ratio PEI monomer/acetyl sulfate was 1:1, with an equimolar ratio of sulfuric acid (VETEC Brazil, >95%)/acetic anhydride (VETEC Brazil, 97%). The sulfonation reaction was conducted in a dry nitrogen atmosphere. The sulfonated polymer was so precipitated and repeatedly washed with ethanol (VETEC, 98%) until mixture reached pH 5. The polymer was dried under vacuum at 40 °C.

2.2. Characterization techniques

The ion-exchange capacity (IEC) of SPEI was determined by the method of Fisher and Kunin\textsuperscript{2}, i.e. 1 g of SPEI was washed in 50 mL of NaOH 1 mol·L\textsuperscript{−1} for 1 day. Then, aliquots (25 mL) of the solution were titrated using HCl 1 mol·L\textsuperscript{−1} and phenolphthalein as indicator. Three sulfonation reaction was conducted at midpoint conditions (50 °C and 60 min). The estimated standard uncertainty was 0.16 meq H\textsuperscript{+}/g of polymer.

Thermogravimetry/derivative thermogravimetry curves were obtained by a TGA/DSC 1 Mettler-Toledo. The samples were loaded in Al\textsubscript{2}O\textsubscript{3} pans and measured in the temperature range of 30 °C to 950 °C with a heating rate of 10 °C/min under dynamic N\textsubscript{2} (50 ml/min). DSC experiments were conducted using a DSC Q2000 (TA Instruments) with RCS cooling system. Baseline was calibrated with sapphire [43x34] and indium (NIST SRM #2232). The experiments were made under N\textsubscript{2} dynamic atmosphere (50 mL/min). Primarily, the sample, sealed in
an aluminum pan, was heated from 150 to 250 °C with a rate of 10 °C/min to remove any previous thermal history. After 10 min at 250 °C, the sample was cooled to 150 °C and remained at this temperature for 10 min. The sample was heated again to 250 °C at the same heating rate. The glass transition temperature of the materials was obtained from the second heating curve. All thermal analysis were performed in duplicate.

Fourier transform infrared (FTIR) spectra were obtained on a Perkin Elmer Spectrum GX analyzer (16 scans and 4 cm⁻¹ resolution) using the ATR technique (total reflectance attenuated using zinc selenide crystal).

The film morphology was done using Scanning Electron Microscopy (SEM - electron microscope Quanta FEI Company). To reduce the distortions, the cross sections of the samples were obtained by fracturing the frozen membrane in liquid nitrogen. As pretreatment, the samples were glued to a backing coated with a thin layer of gold by “sputtering”.

2.3. Film preparation and permeations measurements

The dense films were prepared by casting on a glass plate a polymer/chloroform (VETEC Brazil as reagent grade) solution (30 wt%); the solvent evaporation was controlled by enclosing it in a container with dry N₂ stream saturated in chloroform for 24 h at room temperature. After the film formation, drying was completed at room temperature and it was conditioned under vacuum at 40 °C. The film thicknesses were measured using a digital micrometer.

Permeabilities and ideal selectivities were measured using a pressure increase apparatus presented elsewhere at (24.7 ± 1.5) °C and difference of 3 bar through the membrane. The ideal selectivity (or permselectivity), α_AB, of membranes was calculated as

\[ \alpha_{AB} = \frac{P_A}{P_B} \]

where \( P_A \) and \( P_B \) are pure component permeabilities of gases A and B.

3. Results and Discussion

The experimental design results for the synthesis of SPEI are presented in Table 1.

From Table 1, it can be confirmed insertion of sulfonic groups by the increase of IEC, when compared to the precursor PEI. No significant sulfonation was observed at lowest temperature and time conditions (SPEI-1). The SPEI-5 has the highest IEC value. From experimental design results, it was observed that an increase in reaction time and reaction temperature resulted in an increase in the extent of sulfonation. Similar results were observed elsewhere. The analysis indicates that this reaction is favored at high temperatures, but equilibrium was not achieved up to 90 min, even at highest analyzed temperature (60 °C). Comparing IEC results of Table 1 and those presented by Shen et al., one can observe that increasing the mole ratio Acetyl Sulfate/PEI monomer is also possible to produce more sulfonated materials. However, it can lead to partial degradation of the polymer. Comparing our IEC results with those of Loredo et al., it is possible to conclude that, even using a lower mole ratio Acetyl Sulfate/PEI monomer (a milder reaction medium), it is possible to achieve higher degrees of sulfonation with longer reaction times, showing the importance of better understand the kinetic of this reaction. On the other hand, once the IEC range obtained in both works comparable, it is expected that the proton conductivity of our SPEI are similar to those reported by Loredo et al.

SPEI-5 was used in following analyses (denoted by SPEI). FTIR film spectra to PEI and SPEI are presented in Figure 1. This spectral range contains all characteristic bands of PEI. In the infrared spectra of PEI, there are absorption bands on stage and off stage associated with the vibration of the two carbonyl groups of imide functional group. The asymmetric and symmetric stretching vibrations of C=O groups were observed in the region of 1776 cm⁻¹ and 1715 cm⁻¹. Other absorption bands related to carbonyl, transverse and out of plane vibration of C–N in phthalimide rings, were present in the range of 1350-1360 cm⁻¹, 1070-1100 cm⁻¹ and 737-745 cm⁻¹, as shown in Figure 1. Vibrations at 1268, 1233, 1072, and 1014 cm⁻¹ are due to ary ether bonds (C–O stretching of aromatic ether).

In sulfonated samples, absorption bands due to asymmetric vibration (stretching O=S=O) can be observed at 1233 cm⁻¹. The region of aromatic groups and the S–O bond in 1010-1024 cm⁻¹ presents a broadening of the peak in the SPEI spectra. Further, the shoulder at 950 cm⁻¹ is also noticeable.

### Table 1. IEC of PEI and SPEI’s at different reaction conditions.

| Sample | Temperature (°C) | Time (min) | IEC (meq H+/g of polymer) |
|--------|-----------------|------------|--------------------------|
| PEI    | -               | -          | 0.08                     |
| SPEI-1 | 40              | 30         | 0.09                     |
| SPEI-2 | 40              | 90         | 0.35                     |
| SPEI-3 | 50              | 60         | 0.31                     |
| SPEI-4 | 60              | 30         | 0.62                     |
| SPEI-5 | 60              | 90         | 0.92                     |

![Figure 1. PEI (dashed line) and SPEI (solid line) FTIR spectra.](image-url)
attributed to the S–O stretching. Moreover, near 3500 cm\(^{-1}\) the characteristic broadband related to the presence of hydroxyl of sulfonic groups, –SO\(_2\)–OH, appears. The spectra have shown that there are three typical absorbances for the sulfonic group (S=O) at 1670, 1149 and 779 cm\(^{-1}\). The shoulder between 1650-1690 cm\(^{-1}\) could be due to intermolecular hydrogen bond between hydrogen from the sulfonic (–SO\(_2\)H) and carbonyl (C=O) groups. Pinto et al. state that a large band at 1684 cm\(^{-1}\) could be explained as due to intermolecular hydrogen bond between these groups. All together, these differences between spectra suggest that the sulfonic groups were successfully introduced into PEI. The absorption at 1175-1149 cm\(^{-1}\) is attributed to the S=O symmetric stretching vibration as double peaks and the absorption at 779-746 cm\(^{-1}\) represents the S–O bond of sulfonic group as a single peak. The spectra are typical, although many of the oxy absorbances from the 4,4′-diphenylether units occur within a crowded and highly overlapped region of the spectrum, mainly between 1350 and 950 cm\(^{-1}\), where the S–O stretching may occur.

Thermogravimetry/derivative thermogravimetry (TG/DTG) curves are shown in Figure 2 for a film sample of PEI and for a film sample of SPEI in nitrogen atmosphere. The analysis with each film were performed in duplicate. There were no significant variations between duplicates.

TGA curves of PEI and SPEI exhibited two stages of degradation. The first stage between 100-250 °C, is believed to be associated with loss (~5 wt%) of residual solvent. The second, around 530 °C, was related to the main chain decomposition. It was expected an intermediary stage at temperature range between 200-400 °C attributed to partial desulfonation, not observed in Figure 2. TGA studies with Nafion, other sulfonated polymer, confirm that occur desulfonation in this temperature range. It suggests that the sulfonating method applied in this work promoted not only PEI sulfonation, but also greater thermal stability for the –SO\(_2\)H groups. Lakshmi et al. observed that sulfonated PEI samples having less than one –SO\(_2\)H content/repeat unit did not show the three distinct mass losses.

In the DSC curves for PEI and SPEI, a displacement of the base line around 217.5 °C was observed, attributed to the glass transition temperature (T\(_g\)). For PEI, this transition is usually observed around 217 °C. So, in our study sulfonation led to no significant change in T\(_g\).

The thermal analysis (TGA and DSC) of the polymers showed that even changing molecular structure, insertion of sulfonic group had little effect on the thermal properties of the polymer. These results suggest that, if more sulfonated films are required, the use of milder reactive medium at higher temperatures and for longer reaction times seems to be a more promising approach to achieve thermal stability than use more aggressive sulfonation agent, as sulfuric acid or chlorosulfonic acid, or use higher stoichiometric ratio PEI/Acetyl Sulfate.

Superficial and cross-section MEV results have not shown porous or defects in the membranes. CO\(_2\), N\(_2\), and O\(_2\) permeabilities and CO\(_2\) ideal selectivities are shown in Table 2.

As can be seen from Table 2, the sulfonated poly(ether imide) had lower permeabilities, enhancing the applicability of this material for fuel cell purposes. Moreover, its CO\(_2\)/O\(_2\) and CO\(_2\)/N\(_2\) selectivities are higher as expected to taylormade materials focused on CO\(_2\) separation. The present results can be explained by the electrostatic crosslinking effects on the packing density of polymer chains, which might lead to less free-volume and lower diffusivities. On the other hand, the selectivity of CO\(_2\) relative to O\(_2\) and N\(_2\) increased 38% and 35%, respectively. CO\(_2\) has shorter kinetic diameter (3.30 Å) than O\(_2\) and N\(_2\) (3.46 and 3.64, respectively), therefore its diffusivity is less disturbed by slight reductions in free-volume. Further, molecular interactions between sulfonic groups and CO\(_2\) may favor its sorption.

Additionally, ideal selectivities of O\(_2\) relative to N\(_2\) in both samples are promising (around 11), once recent

![Figure 2. TG (a) and DTG (b) curves of PEI (gray line) and SPEI (black line).](image)

### Table 2. Permeabilities measured with pure gases and CO\(_2\) ideal selectivity at (24.7 ± 1.5)°C and 3 bar through the membrane.

| Polymer | Permeability (Barrer) | Ideal selectivity |
|---------|-----------------------|------------------|
|         | O\(_2\) | N\(_2\) | CO\(_2\) | \(P_{CO2,m}/P_{O2,m}\) | \(P_{CO2,m}/P_{N2,m}\) | \(P_{O2,m}/P_{N2,m}\) |
| PEI     | 0.76   | 0.064 | 2.63 | 3.5 | 41.1 | 11.9 |
|         | 0.054\(^b\) | 1.01\(^b\) |   |   |   |   |
|         | 0.38\(^b\) | 0.052\(^b\) | 1.56\(^b\) | 4.1\(^b\) | 30\(^b\) | 7.3\(^b\) |
| SPEI    | 0.46   | 0.043 | 2.22 | 4.83 | 55.5 | 10.7 |

\(^a\) #1 barrer = 10\(^{-10}\) cm\(^3\) (STP)/cm\(^2\) s cmHg. \(^b\) Properties measured at 10 bar feed pressure, 35 °C. \(^c\) Properties measured at 3 bar feed pressure, 30 °C.
literature has pointed that values higher than 9 are considered attractive\textsuperscript{10}. These results agree with the premise that sulfonation is a promising process for development of more efficient membranes.

4. Conclusion

An experimental design varying temperature and reaction time for synthesis of SPEI pointed out an increase in IEC at higher reaction conditions, and set a synthesis conditions that produced stable sulfonated PEI at temperatures above 400 °C, i.e. undesired partial desulfonation at temperature range between 200-400 °C was not observed for our SPEI samples. Analysis of FTIR spectra, besides a detailed review comparing the FTIR spectra of Sulfonated PEI (SPEI) with its parent material, confirmed that sulfonic groups were successfully introduced into PEI and hydrogen bonds arise among SPEI chains. The highest achieved IEC was higher than those obtained by Loredo et al.\textsuperscript{5} even using a lower sulfonation agent stoichiometric ratio, showing the importance of using longer reaction times in milder reaction conditions.

Sulfonation imparted a reduction around 16%, 40%, and 33% in CO\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} permeability, respectively, enhancing the performance of this material in fuel cell applications, and also an increase of 38% and 35% in selectivity of CO\textsubscript{2} relative to O\textsubscript{2} and N\textsubscript{2}, respectively, enhancing the performance of this material in CO\textsubscript{2} separation applications. By controlled sulfonation, both CO\textsubscript{2} sorption and diffusion changes led to better selectivity results. The permeability results pointed out that our sulfonation approach is an effective way to produce high performance engineered polymers for fuel cell electrolyte membranes and for CO\textsubscript{2} separation from air.

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References

1. Rezac ME and Schöberl B. Transport and thermal properties of poly(ether imide)/acetylene-terminated monomer blends. \textit{Journal of Membrane Science}. 1999; 156(2):211-222. http://dx.doi.org/10.1016/S0376-7388(98)00346-9
2. Shen LQ, Xu ZK, Yang Q, Sun HL, Wang SY and Xu YY. Preparation and characterization of sulfonated polyetherimide/polyetherimide blend membranes. \textit{Journal of Applied Polymer Science}. 2004; 92(3):1709-1715. http://dx.doi.org/10.1002/app.20128
3. Lakshmi RT, Bhattacharya S and Varma JK. Effect of sulfonation on thermal properties of poly (ether imide). \textit{High Performance Polymers}. 2006; 18(2):115-126. http://dx.doi.org/10.1177/0954008306056503
4. Pinto BP, Santa Maria LC and Sena ME. Sulfonated poly(ether imide): a versatile route to prepare functionalized polymers by homogenous sulfonation. \textit{Materials Letters}. 2007; 61(11-12):2540-2543. http://dx.doi.org/10.1016/j.matlet.2006.09.060
5. Loredo DES, Paredes MLL and Sena ME. Synthesis and characterization of sulfonated poly(ether imide) membranes using thermo-analysis and dialysis process. \textit{Materials Letters}. 2008; 62(19):3319-3321. http://dx.doi.org/10.1016/j.matlet.2008.02.040
6. Xiao Y, Low BT, Hosseini SS, Chung TS and Paul DR. The strategies of molecular architecture and modification of polyimide-based membranes for CO\textsubscript{2} removal from natural gas - A review. \textit{Progress in Polymer Science}. 2009; 34(6):561-580. http://dx.doi.org/10.1016/j.progpolymsci.2008.12.004
7. Sen SK and Banerjee S. Spiro-biindane containing fluorinated poly(ether imide): Synthesis, characterization and gas separation properties. \textit{Journal of Membrane Science}. 2010; 365(1-2):329-340. http://dx.doi.org/10.1016/j.memsci.2010.09.038
8. Romero AI, Parentis ML, Habert CH and Gonzo EE, Synthesis of polyetherimide/silica hybrid membranes by the sol-gel process: influence of the reaction conditions on the membrane properties. \textit{Journal of Materials Science}. 2011; 46(24):4701-4709. http://dx.doi.org/10.1007/s10853-011-5380-4
9. Cakar F, Moroglu MR, Cankurtaran H and Karaman F. Conducting poly(ether imide)-graphite composite for some solvent vapors sensing application. \textit{Sensors and Actuators B - Chemical}. 2010; 145(1):126-132. http://dx.doi.org/10.1016/j.snb.2009.11.045
10. Erhard DP, Lovera D, Von Salis-Soglio C, Giesa R, Altstadt V and Schmidt HW. Recent Advances in the Improvement of Polymer Electret Films. In: \textit{Complex macromolecular systems II - Advances in Polymer Science Series}, vol. 228. Heidelberg: Springer; 2010. p. 155-207. http://dx.doi.org/10.1007/12_2009_45
11. Heo Y, Yun S, Im H and Kim J. Low methanol permeable sulfonated poly(ether imide)/sulfonated multiwalled carbon nanotube membrane for direct methanol fuel cell. \textit{Journal of Applied Polymer Science}. 2012; 126(S2):E467-E477. http://dx.doi.org/10.1002/app.36881
12. Mistri EA, Mohanty AK, Banerjee S, Kombor H and Voit B. Naphthalene dianhydride based semifluorinated sulfonated copoly(ether imide): Synthesis, characterization and proton exchange properties. \textit{Journal of Membrane Science}. 2013; 441:168-177. http://dx.doi.org/10.1016/j.memsci.2013.03.015
13. Piroux F, Espuche E, Mercier R, Pinéri M and Gebel G. Gas transport mechanism in sulfonated polyimides - Consequences on gas selectivity. \textit{Journal of Membrane Science}. 2002; 209(1):241-253. http://dx.doi.org/10.1016/S0376-7388(02)00350-2
14. Yave W, Car A, Funari SS, Nunes SP and Peinemann KV. CO\textsubscript{2}-philic polymer membrane with extremely high separation performance. \textit{Macromolecules}. 2010; 43(1):326-333. http://dx.doi.org/10.1021/ma901950u
15. Chandan A, Hattenberger M, El-kharouf A, Du S, Dhir A, Self V et al. High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC) - A review. \textit{Journal of Power Sources}. 2013; 231:264-278. http://dx.doi.org/10.1016/j.jpowsour.2012.11.126
16. Smitha B, Sridhar S and Khan AA. Solid polymer electrolyte membranes for fuel cell applications - a review. *Journal of Membrane Science*. 2005; 259(1-2):10-26. http://dx.doi.org/10.1016/j.memsci.2005.01.035

17. Mistri EA, Mohanty AK and Banerjee S. Synthesis and characterization of new fluorinated poly(ether imide) copolymers with controlled degree of sulfonation for proton exchange membranes. *Journal of Membrane Science*. 2012; 411-412: 117-129. http://dx.doi.org/10.1016/j.memsci.2012.04.023

18. Scholes CA, Kentish SE and Stevens GW. Carbon dioxide separation through polymeric membrane systems for flue gas applications. *Recent Patents on Chemical Engineering*. 2008; 1(1):52-66. http://dx.doi.org/10.2174/2211334710801010052

19. Baker RW and Lokhandwala K. Natural gas processing with membranes: an overview. *Industrial & Engineering Chemistry Research*. 2008; 47(7):2109-2121. http://dx.doi.org/10.1021/ie071083w

20. Kruczek B and Matsuura T. Development and characterization of homogeneous membranes de from high molecular weight sulfonated polyphenylene oxide. *Journal of Membrane Science*. 1998; 146(2):263-275. http://dx.doi.org/10.1016/S0376-7388(98)00120-3

21. Li Y and Chung TS. Highly selective sulfonated polyethersulfone (SPES)-based membranes with transition metal counterions for hydrogen recovery and natural gas separation. *Journal of Membrane Science*. 2008; 308(1-2):128-135. http://dx.doi.org/10.1016/S0376-7388(07)00120-3

22. Lin H and Freeman BD. Materials selection guidelines for membranes that remove CO$_2$ from gas mixtures. *Journal of Molecular Structure*. 2005; 739(1-3):57-74. http://dx.doi.org/10.1016/j.molstruc.2004.07.045

23. Guhathakurta S and Min K. Post sulfonation of bisphenol A poly(arylene ethers). *Journal of Applied Polymer Science*. 2010; 115(4):2514-2522. http://dx.doi.org/10.1002/app.31240

24. Nørgaard CF, Nielsen UG and Skou EM. Preparation of Nafion 117™-SnO$_2$ composite membranes using an ion-exchange method. *Solid State Ionics*. 2012; 213:76-82. http://dx.doi.org/10.1016/j.ssi.2011.10.014

25. Martinez-Felipe A, Imrie CT and Ribes-Greus A. Spectroscopic and thermal characterization of the swelling behavior of nafion membranes in mixtures of water and methanol. *Journal of Applied Polymer Science*. 2013; 127(4):246-256. http://dx.doi.org/10.1002/app.37881

26. Samms SR, Wasmus S and Savinell R F. Thermal stability of Nafion® in simulated fuel cell environments. *Journal of The Electrochemical Society*. 1996; 143(5):1498-1504. http://dx.doi.org/10.1149/1.1836669

27. Oliveira AJB, Aguiar AP, Aguiar MRMP and Santa Maria LC. How to maintain the morphology of styrene-divinylbenzene copolymer beads during the sulfonation reaction. *Materials Letters*. 2005; 59(8-9):1089-1094. http://dx.doi.org/10.1016/j.matlet.2004.12.014

28. Coutinho FMB, Souza RR and and Gomes AS. Synthesis, characterization and evaluation of sulfonic resins as catalysts. *European Polymer Journal*. 2004; 40(7):1525-1532. http://dx.doi.org/10.1016/j.europoly.2004.02.003

29. Talakesh MM, Sadeghi M, Chenar MP and Khoosravi A. Gas separation properties of poly(ethylene glycol)/poly(tetramethylene glycol) based polyurethane membranes. *Journal of Membrane Science*. 2012; 415-416:469-477. http://dx.doi.org/10.1016/j.memsci.2012.05.033

30. Liu Z, Liu B, Li L, Zhang Y and Jiang Z. Synthesis of novel poly(aryl ether sulfone)s bearing bulky pendants for gas separation membranes. *Macromolecular Research*. 2013; 21(6):608-613. http://dx.doi.org/10.1007/s12223-013-1056-z