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Synthesis and proton conductive properties of novel sulfonated (sulfone-triazoles) copolymers

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Abstract: A new bisphenol containing 1,2,3-triazole ring (BPT) was synthetized using the click reaction and copolymerized with diammonium salt of 4,4'-difluorodiphenylsulfone-3,3'-disulfonic acid (DFPSS) and 4,4'-difluorodiphenylsulfone (DFPS) to prepare new copper free sulfonated sulfone-(1,2,3-triazole) copolymers (SSTP) for use as a proton exchange membrane fuel cells. Four copolymers with different ion exchange capacity (IEC) in the range of 1 to 1.6 meqH^+/g were obtained by varying the molar ratio of the 3 monomers. The structure of SSTP was confirmed by NMR. They are soluble in polar aprotic solvents such as NMP, DMF and DMSO and show good thermal properties. Membranes from three of these SSTPs were prepared using the solution casting method and characterized in order to determine their water uptake (WU) and their ionic conductivity at 80°C.

Key words: Proton exchange membrane fuel cells, sulfonated polytriazoles, click reaction

INTRODUCTION

Since two decades the development of renewable energies constitutes a major challenge to replace fossil fuel and save our planet by reducing carbon emission. In this connection, fuel cells appear as an interesting technology to produce a clean energy. For car application, the most appropriate type of fuel cells is the Polymer Electrolyte Membrane Fuel Cell (PEMFC) which offers specific advantages such as a low operating temperature, a high energy capacity, stability and a long-term operation…[1,2,3]. However, efforts must be still carried out to improve the performances of these devices. Particularly, the conductivity at high temperatures and low relative humidity of polymer membranes need to be improved. In addition to the required mechanical and thermal properties, these membranes must have a competitive price.

To date the best performance was obtained with a Nafion® membrane manufactured from a perfluorosulfonic acid polymer which displays excellent chemical stability, mechanical strength, thermal stability, and good proton conductivity [4,5]. However, this polymer suffers from disadvantages such as high cost manufacturing [6] and limited operating temperature below 100 °C. In order to propose an alternative membrane, many research works [3] were concerned with the sulfonated heterocyclic polymers. To this end, sulfonated polyphenylquinoxalines [7,8], sulfonated polyimides [9-13], sulfonated polybenzimidazoles [14-19], sulfonated polyoxadiazole [20,21], and sulfonated polytriazoles [22-25] were considered in PEMFC systems. For the latter ones, it was reported that the presence of 1,2,4 or 1,2,3-triazole units in the main chain increases the chemical stability, the mechanical and thermal properties of the resulting membranes as well as the proton conductivity especially in low relative humidity. The 1,2,3-triazole ring containing polymers were obtained through copper mediated alkyne azide cycloaddition (CuAAC) polymerization. Instead, triazole can directly be provided by bis-functionalized monomers. This strategy has to the very best of knowledge not been explored so far, hence the motivation for this work. One important

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issue is that copper is removed much more efficiently from triazole-containing monomers than from polytriazoles made by CuAAC polyaddition [26]. Indeed, the hopping mechanism of proton transportation from triazole to sulfonic sites [23] could be affected by the presence of residual amount of copper which could reduce the proton conductivity.

In this work, a new bisphenol triazole monomer (BPT) was prepared in good yield and then polymerized with both 4,4'-difluorodiphenylsulfone (DFPS) and 4,4'-difluorodiphenylsulfone-3,3'-disulfonic acid diammonium salt (DFPSS) to lead to a new sulfonated polytriazoles used as PEMFC.

The obtained polymers are characterized by techniques such as ^{1}H and ^{13}C NMR, viscosimetry, thermomechanical analysis (TMA) and thermal gravimetric analysis (TGA). The proton conductivity and swelling ratio (or water uptake WU) of the obtained membranes having various ion exchange capacities (IEC) are investigated.

EXPERIMENTAL

1. Materials

All solvents were carefully dried and freshly distilled according to common laboratory techniques. 3-hydroxyphenylacetylene (≥ 95%), 3-aminophenol (98%), HCl (37%), sodium nitrite (≥ 99%), sodium azide (99,5%), $Cu(PPh_3)_3Br$, 4,4'-difluorodiphenylsulfone (DFPS) (99%), sulfuric acid : oleum (20% free SO_3), ammonium hydroxide (≥ 99,9%) and potassium carbonate anhydrous (≥ 99,9%) were purchased form Sigma-Aldrich and used as received.

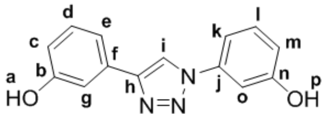
2. Analytical Methods

TGA of the polymers were performed using a TA instruments apparatus (TGA Q50 V6.7 Build 203). Scans were run from 20 to 500°C at heating rate of 10°C min^{-1} in an inert atmosphere. The glass transition temperatures (Tg) were obtained by TMA (TMA Q400 V7.4 Build 93). Scans were run from 20 to 400°C at heating rate of 10°C min^{-1} in an inert atmosphere. The values were reported from a second scan after heating and rapid cooling. The proton and carbone13 NMR spectra were recorded at ambient temperature on a 200 and 400 MHz Bruker AM spectrometers, using DMSO-d_6 as solvent. Inherent viscosity (η_{inh}) was determined from 0,5 g.dl^{-1} polymer solution in NMP at 30°C using an Ubbelohde viscometer.

3. Monomer synthesis

Preparation of Bisphenoltriazole (BPT) (Scheme 1)

3-hydroxyphenylacetylene (1,27g; 22,12mmol), meta-azidophenol (1,46g; 22,4mmol), $Cu(PPh_3)_3$ Br (502 mg; 5% mol) and 15,5 mL of toluene were placed in a three necked flask equipped with a magnetic stirrer . After stirring the solution under nitrogen for 4 h at 50°C, the reaction mixture was cooled down then filtered and washed several times with toluene.The pure product was obtained through recrystallization with acetonitrile (68%).

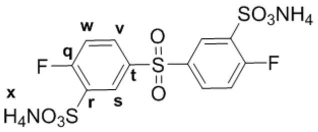


BPT

^{1}H NMR (DMSO, δ ppm) :10.05 (s, 1H, H_p) ; 9.59 (s, 1H, H_a) ; 9.17 (s, 1H, H_i) ; 7.36 (m, 6H, $H_{k,e,o,g,d,l}$) ; 6.79 (m, 1H, H_c) ; 6.76 (m, 1H, H_m).
^{13}C NMR (DMSO, δ ppm) : 158.39 C_n ; 157.72 C_b ; 147.22 C_h ; 137.56 C_j ; 131.38 C_f ; 130.67 C_l ; 129.91 C_d ; 119.36 C_e ; 116.18 C_i ; 115.52 C_g ; 115.16 C_c ; 112.02 C_m ; 110.28 C_k; 106.86 C_o.

Preparation of 4,4'-difluorodiphenylsulfone-3,3'-disulfonic acid diammonium salt (DFPSS)

DFPSS was prepared according to the method reported by Ueda [27] and Mc Grath [28-29]. 4,4'-difluorodiphenylsulfone 44.25 g (0.1741 mol) was introduced into a 250 ml reactor equipped with a mechanical stirrer, a reflux condenser, a nitrogen gas inlet, and cooled in an ice bath. 60mL of oleum (65% SO_3) was then added dropwise. The resulting solution was stirred at 90°C for 6 h. At the end of the reaction the mixture was cooled to room temperature then poured slowly into 300 mL of ice water and neutralized with an ammonium hydroxide solution. The precipitate of DFPSS formed in the solution was filtered and dried. The monomer was purified by recrystallization in ethanol to yield compounds in excess of 75%.



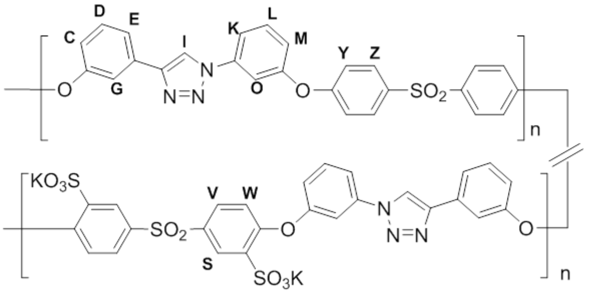
DFPSS

^{1}H NMR (DMSO, δ ppm) : 8.16 (m, 2H, H_s) ;
8.01 (m, 2H, H_v) ; 7.46 (t, 2H, H_w) ; 7.11(s, 8H, H_x).
^{13}C NMR (DMSO, δ ppm) : 163.14 C_r ; 159.70 C_t ; 136.23 C_q ; 131.07 C_v ; 128.19 C_w ; 118.44 C_s.
^{19}F NMR (DMSO, δ ppm) : - 102,51

4. Sulfonated STP polymer synthesis

The Sulfonated STP polymer were synthesized according to Scheme 2 through polycondensation of BPT, DFPS and DFPSS. Table 1 reports the amounts used for each monomer to obtain the polymers with the desired ion exchange capacities (IEC).

The typical procedure used to prepare copolymers was as follows: BPT, DFPS, DFPSS and K_2CO_3 (2,4 eq) were added to DMSO in reactor equipped with a mechanical stirrer a reflux condenser, a nitrogen gas inlet. The solvent quantity was used to have 30 wt. % in each case. The reaction mixture was heated at 160 °C under a nitrogen atmosphere for 24h. The mixture was then cooled to room temperature before precipitation of the polymer in an excess of distilled water. The obtained water was washed repeatedly with water, filtered and dried in vacuum at 90°C during 24h.



^{1}H NMR (DMSO, δ ppm): 9.43 (s, 2H, H_I) ; 8.32 (m, 2H, H_S) ; 7.95 (s, 4H, $H_{V,W}$) ; 7.74(m, 8H, $H_{Y,Z}$), 7.19 (m, 8H, $H_{C\text{-}E,G,K\text{-}M,O}$)

5. Film casting and membrane acidification

Polymer (1.0g) was dissolved at 80°C in 10mL of NMP. The solution was stirred overnight, filtered through a 45µm filter, and casted onto a clean glass substrate. The solvent was evaporate at 50°C overnight under nitrogen flux, then at 80°C for 1h, 120°C for 1h, 150°C for 1h and 180°C for 2h.

After cooling back to room temperature, membrane was lifted off the glass plates by immersion in water. Then it was then acidified in a 2M H_2SO_4 solution for 24h. The acidified membrane was washed thoroughly with deionized water to drain out excess acid. All membranes were obtained following this procedure.

6. Membrane characterization

- The dried membranes were immersed in deionized water at room temperature for 24h, then removed and blotted with filter paper to remove any excess surface water and immediately weighed (W_{wet}). The membranes were then dried at 120°C for 24h to determine their dry weights (W_{dry}). The water uptake (WU ;%) was calculated using Eq (1).

$$WU(\%) = \frac{W_{wet}-W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

- The IEC (in meqH^+/g) were calculated using Eq (2).

$$IEC = 1\,000 \,.\, \frac{X.n_{SO_3H}}{X.M_a+Y.M_b} \qquad (2)$$

n_{SO_3H} : number of sulfonic acid functions in the hydrophilic repeat unit

- The hydration number λ, defined as the number of water molecules per ionic group was calculated using Eq (3).

$$\lambda = \frac{\text{WU}}{18 \times \text{IEC}} \qquad (3)$$

The proton conductivity of the membrane was determined with an electrochemical impedance analyzer. Measurements were made on FUMATECH MK3 conductivity cell equipped with a potentiostat / Galvanostat / ZRA 600TM Reference of Gamry Instruments. Measurements were carried out in the plan with samples having 1.5 cm by 4 cm.

The proton conductivity was calculated according to Eq (4).

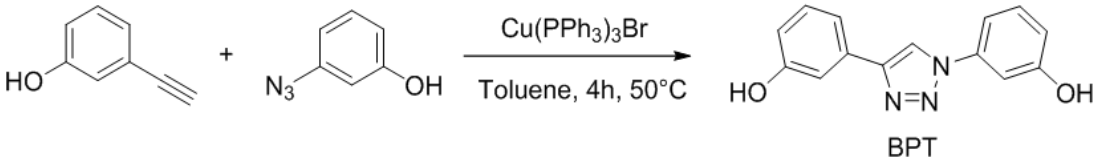
$$\sigma = \frac{L}{R\,.\,A} \qquad (4)$$

where: σ is the proton conductivity (in S cm^{-1}), L is the distance between the electrodes (cm), A is the membrane section area (in cm^2), and R is the impedance of the membrane (in ohms).

RESULTS AND DISCUSSION

Bisphenoltriazole (BPT) synthesis

The synthesis of the new BTP monomer is shown in scheme 1. The copper mediated reaction involved 3-hydroxyphenylacetylene and meta-azidophenol which was prepared from meta-aminophenol as reported in literature [30]. The reaction was completed after 4 hours at 50°C in toluene and under nitrogen. A good yield (68%) of pure product was obtained after recrystallization in acetonitrile. Characterization of newly prepared BPT monomer was carried out by ^{1}H and ^{13}C NMR spectroscopy. As shown in Figure 1, the chemical structure of this monomer was confirmed by the ^{1}H spectrum.



Scheme 1: Synthesis of Bisphenoltriazole (BPT)

Sulfonated STP polymer synthesis

A series of sulfonated STP polymers were successfully synthesized by polycondensation of BPT, with DFPS and DFPSS (see Scheme 2). The polymerization reaction was carried out in DMSO for 24 hrs at 160°C and using K_2CO_3 as base. In Table 1 are reported the different ratios of the three monomers used to obtain polymers with IEC ranging from1 to 1.6 meqH^+/g.

Polymer solubility

The polymers were found fairly soluble in polar aprotic solvents such as *N*-methylpyrrolidone (NMP), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) but not soluble in usual organic solvent such as THF, chloroform, dichloromethane, ethyl acetate, and acetonitrile (see Table 1).

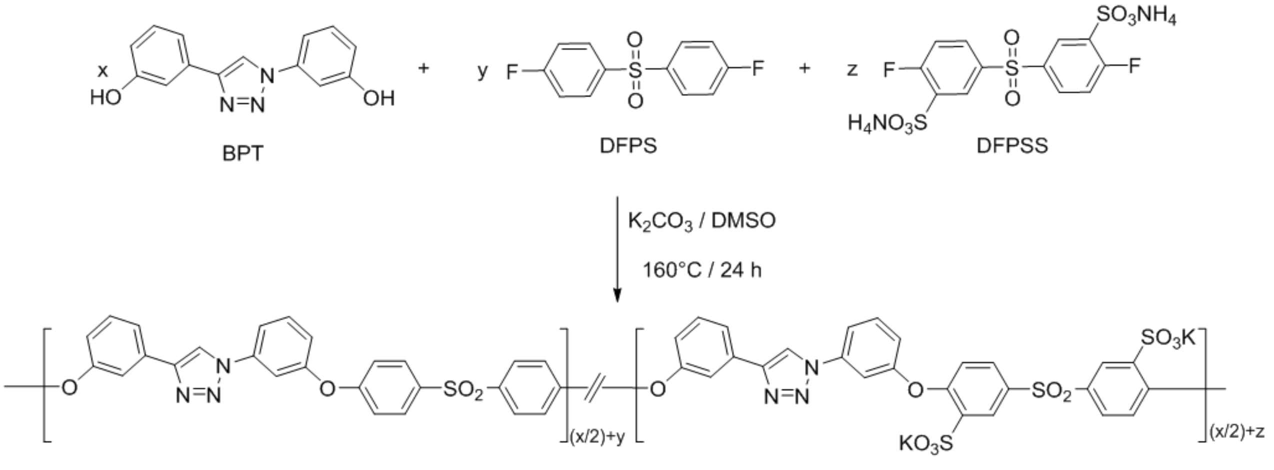
Characterization of Sulfonated STP polymers

The chemical structures of synthesized polymers were confirmed by ^1H NMR spectroscopy as shown in Figure 1. Formation of the polymer chain resulted in the appearance of broad peaks in the aromatic proton region. For instance, Figure 1 exhibits the typical chemical shift changes for the sulfonated polytriazole which was obtained from the polycondensation of BPT, DFPS and DFPSS monomers (Scheme 2). The characteristic peak corresponding to the proton H_I of 1,2,3-triazole ring of BPT monomer initially situated at 9.17 ppm (H_i) was shifted to 9.43 ppm and appears as an overlapping of three peaks due to the different neighboring groups on each side of the BPT monomer unit (two diphenylsulfone units or one diphenylsulfone and one sulfonated diphenylsulfone units or two sulfonated diphenylsulfone units). On the other hand, the peak at 8.32 ppm corresponding to the proton H_S confirmed the incorporation of the sulfonated diphenylsulfone units in the polymer chain. It worth to note also the complete disappearance of the peaks assigned to protons $H_{c,m,a,p}$, and H_s which indicates that a high conversion was reached.

The viscosity values shown in table 1 were obtained in NMP at 30°C with Ubbelohde viscometer. These values are in the range of 1.33 and 2 dL/g and thus indicate high molecular weights.

Thermal properties

The thermal properties of sulfonated STP polymers were investigated by thermo-mechanical analysis (TMA) and thermo-gravimetric analysis (TGA).



Scheme 2: Synthesis of the sulfonated STP polymers

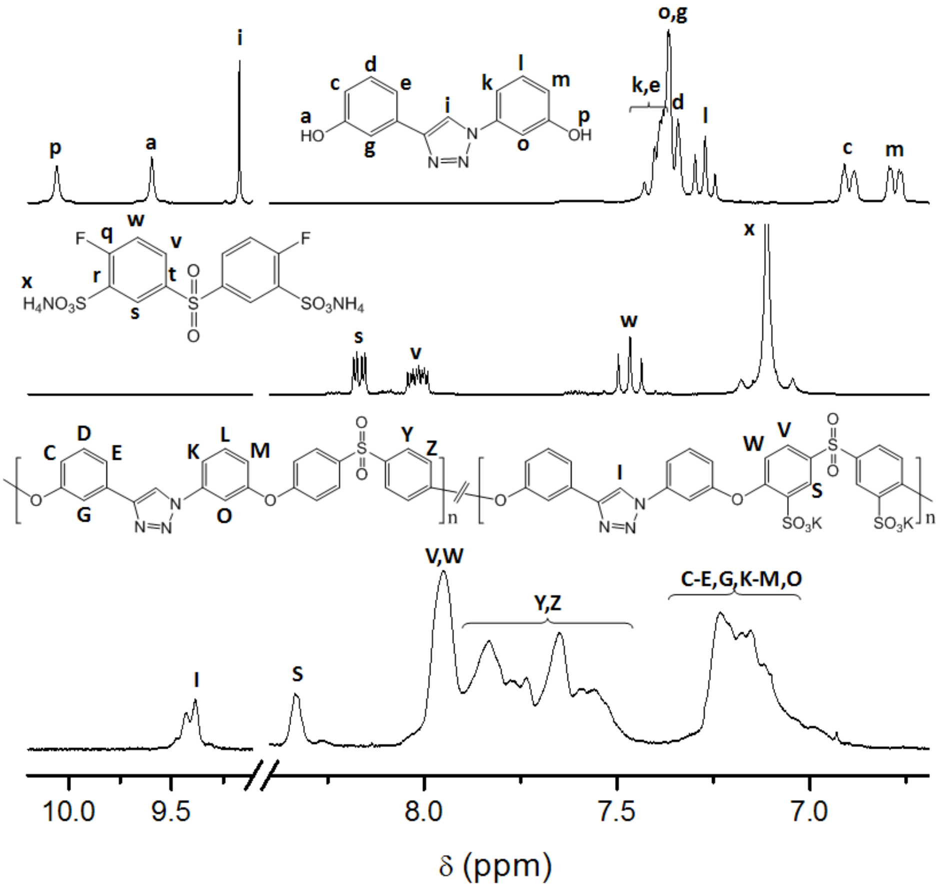


Figure 1: From top to bottom H^1 NMR spectra of BPT monomer , DFPSS monomer and one sulfonated STP polymer

Table I: Solubility, physical and thermal properties of sulfonated STP polymers

	Calc. IEC[(a)] (meqH$^+$/g)	BPT (mmol.10^3)	DFPS (mmol.10^3)	DFPSS (mmol.10^3)	Yield (%)	η[(b)] (dL/g)	Tg[(c)] (°C)	$T_{d5\%}$[(d)] (°C)	Solubility[(e)]		
									NMP	DMF	DMSO
Polym 1	1	2.63	1.96	0.669	58	2.09	165	249	~	~	~
Polym 2	1.2	2.85	1.96	0.883	61	1.33	254	286	+	~	~
Polym 3	1.4	3.11	1.96	1.15	63	1.61	259	352	++	+	+
Polym 4	1.6	3.44	1.96	1.47	58	1.46	-	386	++	+	+

(a) IEC calculated from feed monomer ratio
(b) 0,5 g/dL in NMP, 30°C with Ubbelohde viscometer
(c) obtained by TMA
(d) Temperature at 5% weight loss in TGA at 10°C/min heating rate under helium
(e) (+) soluble at 1mg/mL ; (++) soluble at 10 mg/mL ; (~) soluble at 1mg /mL with heat.

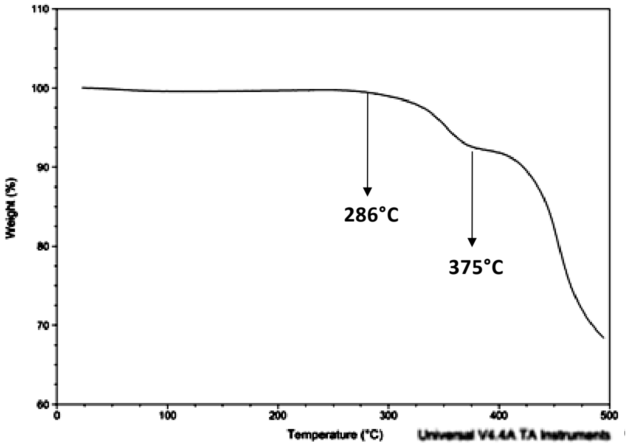


Figure 2: TGA Curve of polymer 2

The glass temperature of the polymers was determined from TMA analysis and found between 165 and 259°C. These high Tg values especially for the polymers 2 and 3 are probably due to the rigid backbones and the interactions between sulfonic groups and triazoles rings.

The thermal stability of the polymers used in PEMF application is one important property. In order to study the thermal behavior of the obtained sulfonated polymers several runs were conducted by TGA from 25 to 500°C at 10°C/min heating rate under helium. The temperatures corresponding to 5% weight loss are reported in Table 1; they are in the 249-386 °C range. The TGA curves exhibit two distinct degradation steps. The first one is attributed to the labile sulfonic groups and the second weight loss found at around 380°C corresponds to the decomposition of the triazole rings [25]. For example in the TGA curve of the polymer 2 shown in figure 2 one can easily notice the first weight loss which started at around 286°C while the second one is set near 375°C. Moreover the increase of the temperature at 5% weight loss with the IEC observed in table 1 could be related to the increase of hydrogen bond interactions between sulfonic groups and triazole rings.

Characterization of membranes

The water uptake (WU), the hydration number (λ) and proton conductivity (σ) of sulfonated STP based membranes are summarized in Table 2. All values were measured at 85°C and 98% of relative humidity (RH). Nafion 117 membrane was also characterized in the same conditions for the sake of comparison . Because of the too much water swelling of membrane based on the polymer 4, their properties were not determined.

From the results shown in Table 2, one can notice that the increase of WU of membranes is related to the increase of IEC polymers. The membrane swelling caused by WU can generate side effects such as the loss of mechanical properties and then a low dimensional stability. In our case the WU as well as λ values remain acceptable especially for polymer 2. It worth noting that this λ value is similar to this of Nafion measured in the same conditions. For the sulfonated polytriazoles Chang [23] explained this fact by the acid-base interactions between sulfonic acid groups and triazole rings which act as physical crosslinking that reduces membrane swelling and therefore the λ values.

The proton conductivities in the range of 0.017 and 0.030 $S.cm^{-1}$ at 80°C of respectively polymers 2 and

Table II - Proton conductivity and water uptake of sulfonated polytriazoles membranes

	Calc. IEC ($meqH^+/g$)	WU $^{(a)}$ (%)	λ (H_2O/H^+) $^{(a)}$	σ $^{(a)}$ ($S.cm^{-1}$) at 98% RH
Polymer 1	1	14.3	8	0.003
Polymer 2	1.2	58	27	0.017
Polymer 3	1.4	107	42	0.030
Nafion-117®	0.92	35.6$^{(b)}$	25.4	0.093$^{(c)}$, 0.151$^{(d)}$

$^{(a)}$ Measured at 85°C
$^{(b)}$Measured at 30°C [23]
$^{(c)}$Measured at 90%RH and 30°C [23]
$^{(d)}$Measured at 90%RH and 80°C [23]

3 are higher than 0.01 S.cm^{-1} which is the lowest value required for membranes used in PEMFC. Compared with those obtained for the polybenzimidazoles (PBI), which are known for their very good chemical and thermal stability and having conductivity between 0.001 and 0.010 S.cm^{-1} [31] these values remain good.

CONCLUSION

A new triazole containing bisphenol monomer was synthesized from which different sulfonated aromatic and heterocyclic polymers were successfully prepared via nucleophilic substitution reaction. These polymers have a high Tg and display a good thermal stability. From solution casting method, though membranes were prepared with IEC varying between 1 and 1.6 meqH^{+}.g^{-1}. A good compromise between water uptake and conductivity at 85°C and 98% of RH was obtained with the membrane based on the polymer with the IEC of 1.2 meqH^{+}/g.

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