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High proton conducting fluorinated sulfonated poly(arylene ether sulfone)s copolymers with side chain grafting

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Abstract

A series of new copolymers HPPQSH-XX PS were synthesized from there preformed sulfonated ionomers HPPQSH-XX in order to get high proton conductivity along with excellent other properties. They were prepared by direct copolymerization of bisphenol HPP with two bishalides QBF and SDCDPS. Again the copolymers were post-sulfonated using 1,3-propanesultone in presence of NaH and were analysed by spectroscopic techniques. The random copolymers HPPQSH-XX with different statistical distribution of $-SO_3H$ moiety showed very small ionic clusters (5–10 nm) whereas the grafted copolymers showed larger ionic domains (60–100 nm) on their TEM images. All ionomer membranes showed good mechanical properties, high oxidative and dimensional stability with low water uptake and swelling ratios. IECs (weight and volume based) were also calculated to explain a better correlation with water uptake and proton conductivity (14-125 mS/cm at 80 ºC and 15-142 mS/cm at 90 ºC under fully hydrated condition) of the membranes.

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Introduction

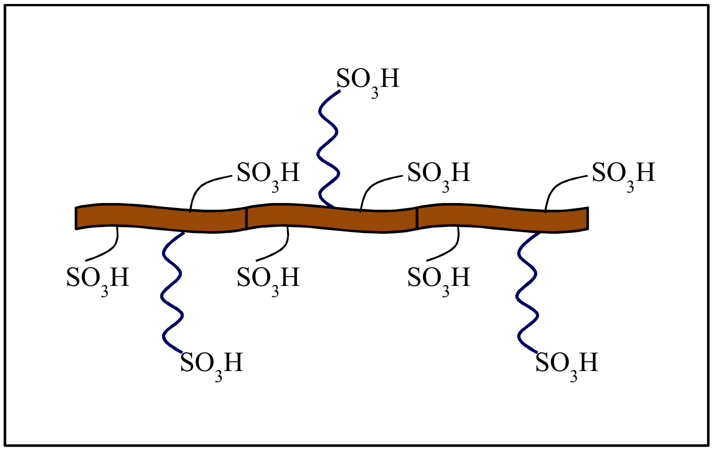
In recent years a highly demanding research field is to find alternative eco-friendly energy resources. Proton exchange membrane fuel cells (PEMFCs) have been considered one of the most widely used alternative power generator for automotive, stationary and portable application with zero emission of pollutants. A proton exchange membrane (PEM) is considered as a unique ion-selective transport channel that serves to transfer protons from anode to cathode as well as providing a barrier for fuel gas, oxidant and electrons in high performance proton exchange membrane fuel cells (PEMFCs).[1,2] Thus, structure and design of proton transport membrane have been considered as a critical and important issue in fuel cell application. The most studied and commercially available PEM materials are perfluorinated sulfonic acid ionomers such as DuPont's Nafion® due to their high mechanical and chemical properties along with high proton conductivity value, but some serious limitation such as high gas permeability, low operational temperature (< 80 °C), high cost along with environmental inadaptability prevent their widespread use in fuel cell application.[3] Such drawbacks have led to the challenge to find aromatic sulfonated polymers as alternative PEM materials.

Several classes of advanced aromatic hydrocarbon based sulfonated polymers were synthesized to develop a suitable PEM materials such as poly(arylene ether)s,[4,5] poly(arylene ether ketone)s,[6-8] poly(aryl ether ether ketone ketone)s,[9-11] poly(arylene ether sulfone)s,[12-19] poly(arylene sulfide sulfone)s,[20,21] polyimides,[22,23] and polytriazoles.[24-26] Depending upon their structural features, each class of polymers exhibited a unique set of properties in fuel technology. However, as a class of high-performance engineering thermoplastic materials, poly(arylene ether)s have some excellent properties like high glass transition temperature, high thermal and chemical stability along with good mechanical properties. In order to get some superior PEM properties, functionalisation of polymer is essential by modifying the chemical structure of the polymer.

Generally, two ways of functionalisation technique were considered to functionalized poly(arylene ether)s. The first one is the direct polymerization or copolymerization by polycondensation between the functionalized monomers and the sulfonated monomers whereas the second one is the post-sulfonation technique, where the preformed polymer with no sulfonic acid group (-SO_3H) was sulfonated by using different modifier or by applying sulfonated functionalized reagents. However, in direct polymerization method, the sulfonic acid groups are usually located in polymer backbone and those polymers generally showed acceptable conductivities only at high ion exchange capacities which finally results an extensive water uptake above a critical degree of sulfonation or a critical temperature (percolation threshold) along with a dramatic loss of mechanical properties. Thus post-sulfonation technique was considered to overcome such limitations by modifying the polymers. However, to enhance the mechanical integrity along with distinct separation of hydrophilic moiety from hydrophobic segment in polymer matrix, side chain sulfonation method has attracted much attention. Besides, in post-sulfonation choosing of right monomer and control of grafting percentage was curial to prepare the desired product.

Perhaps for the first time, Jannasch et al. reported a post-sulfonation method where the polysulfone (PSU) was sulfonated by lithiation followed by the reaction of the lithiated sites with 2-sulfobenzoic acid cyclic anhydride (SBACA).[27] Later on the same group also reported a grafting method where the polysulfone (PSU) was initially reacted with butyllithium to form organolithium compound which on further react with 4-fluorobenzoyl chloride followed by functionalized sulfonated monomers to introduced the sulfonic acid group in polymer side chain.[28] Watanabe and co-workers reported the synthesis of fluorenylbiphenyl group containing poly(arylene ether)s followed by post-sulfonation using chlorosulfonic acid to improve the hydrolytic stability by incorporating the sulfonic acid group in side chain and keeping the polymer main chain in hydrophobic environment.[29] For the first time Lin et al. developed a novel main-chain-type and side-chain-type sulfonated poly(ether ether ketone) membranes within a single polymer backbone by reacting the sulphonic acid groups of pristine SPEEKs with 2-aminoethanesulphonic acid to improve the nano-phase separated morphology of the material.[30] Guiver et al. synthesized aromatic poly(arylene ether sulfone) copolymers by considering new fluorinated bis-phenol monomer followed by the incorporation of sulfonic acid group by choosing suitable sulfonated phenolic monomer. These grafted sulfonated copolymers showed excellent thermal and chemical stability. In addition, Guiver and co-workers also synthesized rigid aromatic comb-shaped poly(arylene ether sulfone) copolymers wherein the sulfonic acid sites are on linear or branched pendent chains. They reported that such polymers with the sulfonated groups attached to pendant side groups are very stable under heat, hydrolysis and oxidation.[31,32] Recently, Guiver et al. reported a novel class of fully aromatic comb-shaped polymers with highly sulfonated aromatic graft chains that can self-assemble into nanoscale organized structures and displayed high proton conductivity over a wide range of humidity along with better stability.[33] So, in order to get better PEM materials with desired set of properties still more work is required.

In the present work, a series of high molecular weight fluorinated sulfonated poly(arylene ether sulfone) copolymers (architecturally shown in Figure 1) were prepared by applying a combination of direct polymerization or copolymerization method followed by post-sulfonation technique. At first HPPQS-XX copolymers with varying degree of sulfonation are prepared using direct polycondensation of 4,4′-bis(4′-fluoro-3′-trifluoromethyl benzyl)biphenyl (QBF) and 3,3′-disodiumsulfonyl-4,4′-dichlorodiphenylsulfone (SDCDPS) with 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP) to incorporate the sulfonic acid group into polymer backbone. Finally HPPQS-XX PS copolymers are synthesized from preformed HPPQS-XX copolymers by applying post-sulfonation technique using 1,3-propanesultone in presence of sodium hydride as a base. In order to get high mechanical strength, good phase separated morphology and high proton conductivity with low swelling, a sulfonated aliphatic side chain was introduced with proper tuning of hydrophobic and hydrophilic moiety in the polymer matrix. Thus the present work demonstrates the feasibility and success of this synthetic methodology along with detailed investigation of the morphology and selected PEM properties such as proton conductivity, water uptake, mechanical strength and swelling ratio, thermal, and chemical stability.



Scheme 1. Representations of rigid polyaromatic sulfonated backbone with linear pendent side chain containing sulfonic acid groups.

Experimental section

Materials

3,3′-Disodiumsulfonyl-4,4′-dichlorodiphenylsulfone (SDCDPS) was purchased from Chemos GmbH and was used as received. The perfluoroalkylated monomer, 4,4′-bis(4′-fluoro-3′-trifluoromethyl benzyl) biphenyl (QBF) was prepared[34] and the bisphenol monomer, 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP) was prepared according to the procedure reported in the literature.[35] 1,3-Propanesultone was purchased from Sigma-Aldrich and was used as received. *N*-methyl-*2*-pyrrolidone (NMP) (E. Merck) was vacuum-distilled prior to use. Toluene (Merck) was refluxed over Na metal to remove water and was freshly distilled before use. All other chemicals were reagent grade and were used as received.

Synthesis of homopolymer (HPPQ) and copolymers (HPPQS-XX)

The homopolymer and the copolymers were prepared by the polycondensation reaction varying the mole percentage of the bishalide (QBF and SDCDPS) and bisphenol (HPP) monomers. XX gives the mole percentage of SDCDPS in the bishalide mixture. As example the preparation of HPPQS-30 (HPP:QBF:SDCDPS = 1:0.7:0.3) is described as follows: A dried 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a Dean-Stark trap fitted with condenser and a nitrogen inlet ware charged with 0.5079 g (1.60 mmol) of HPP, 0.5360 g (1.12 mmol) of QBF, 0.2358 g (0.48 mmol) of SDCDPS, and 0.4866 g (3.52 mmol) of K_2CO_3. Then 10 mL NMP and 8 mL toluene were added into the reaction mixture under nitrogen atmosphere. The reaction mixture was heated to reflux at 160 °C in an oil bath for 3–4 h to remove the in situ generated water azeotropically with toluene. After removal of toluene, the reaction temperature was increased to 180 °C for another 16 h till the reaction solution became highly viscous. After cooling to room temperature and dilution with DMAc, the polymer solution was poured into isopropanol with vigorous starring. The precipitated polymer was washed thoroughly with distilled water several times, filtered and dried under vacuum at 100 °C for at least 24 h. The yield was 99%.

Preparation of grafted copolymers (HPPQS-XX PS) using post-sulfonation technique

All preformed sulfonated copolymers (including non-sulfonated homopolymer) were post-sulfonated by using 1,3-propanesultone. The preparation of HPPQS-30 PS is described as follows: 1.1582 g (1.54 mmol) of HPPQS-30 and 0.0815 g (3.39 mmol) of NaH were placed in a dried 50 mL nitrogen-flushed three-necked round-bottomed flask equipped with a magnetic stirrer. Then 9 mL NMP were added under inert atmosphere and stirred for 1 hr at room temperature. After complete dissolution of the starting materials, 0.27 mL (3.39 mmol) 1,3-propanesultone was added and the reaction mixture was stirred for another 12 hr. The resulting viscous solution was precipitated in isopropanol with vigorous starring. The post-sulfonated polymer was washed several times in distilled water to remove any impurities, filtered and finally dried under vacuum at 100 °C for 24h. The yield was 1.135 g (98% based on the initial weight of the HPPQS-30 taken).

Film casting and acidification

The membrane was prepared by dissolution of the dried salt form of sulfonated copolymers (HPPQS-XX and HPPQS-XX PS) in DMAc (10% w/v) and spreading the vicious solution onto a flat Petri dish followed by sequential heating at 80 ºC (24 h), 100 ºC, 120 ºC, 140 ºC each for half an hour and at 160 °C for 15 minutes in an oven under nitrogen and finally under vacuum (2 mbar) at 120 ºC for 24 h. The membranes were removed from the Petri dishes at room temperature and for each case brownish (white only for HPPQS-PS), flexible and transparent membranes were obtained with thicknesses in the range of 40-50 µm. The as-cast membranes were converted to acid form by immersing in 1.5 M sulfuric acid for 24 h. Finally, the acidified membranes were immersed (24 h) and washed thoroughly with deionized water to drain out excess acid, and dried under vacuum at 100 °C for 24 h.

Measurements and characterization

FTIR spectra of the copolymers were recorded from a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature and humid free atmosphere. ^{1}H (500.13 MHz), ^{13}C (125.76 MHz) and ^{19}F (470.59 MHz) NMR spectra of the polymers were recorded on an Avance III 500 NMR spectrometer (Bruker, Germany) at 60°C (^{13}C, ^{19}F) and 90°C (^{1}H), respectively. The monomer was measured at 30°C. DMSO-d_6 was used as solvent and internal reference (δ (^{1}H) = 2.50 ppm; δ (^{13}C) = 39.6 ppm). The ^{19}F NMR spectra were referenced on external C_6F_6. The signal assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C correlated spectra. To ensure full ^{1}H relaxation a pulse delay of 60 s was applied for the ^{1}H NMR measurements. The molecular weight of polymers was measured by size-exclusion chromatography (SEC) with sample concentration was 1 mg/mL. A mixture of DMAc with 3 g/L LiCl were used to dissolve the sample and as eluent at a flow rate of 1 mL/min. The apparatus consists of a Gynkotek HPLC pump, a Agilent Autosampler 1200, linear columns [All GRAM, Polymer Standards Service (PSS)] consisting of a pre-column 10 µm/8mm×50mm, a column 10 Å/8mm × 300mm and two columns 3000 Å/8mm × 300mm. A refractive index (RI) detector (Knauer) was used as a detector. For calibration, linear PMMA with molecular weight between 500 and 1,000,000 Da were used. DSC measurements were made on NETZSCH DSC 200PC instrument at a heating rate of 10 °C /min under nitrogen. The middle point of the step transition in the second heating run was taken to determine glass transition temperatures (T_g). Thermogravimetric analysis (TGA) was conducted under N_2 atmosphere by using NETZSCH TG 209 F1 Instruments at a heating rate of 10 °C/min. The mechanical properties of both salt and acid form of the dry membrane (10mm × 25mm) were measured at room temperature using TINIUS OLSEN H5KS, at a strain rate of 5% of the sample length per minute. The ion exchange capacity (IEC_W) was represented as the molar equivalents of ion conductor per mass of dry membrane, or milliequivalents of ion per gram (meq/g or mmol/g) of polymer (EW=1000/IEC_W) sample and calculated from the relationship $IEC_W = (1000/ MW_{repeat\ unit)} \times DS \times 2$; where, DS is the degree of sulfonation (mol% fraction of the sulfonic acid monomer for the non post-sulfonated polymers but for post-sulfonated polymers it means the sum of the mol% fraction of the sulfonic acid monomer and of the mol% of sulfonated HPP comonomer). The IEC_W values of the acid form membranes were also determined by acid-base titration method according to the literature.[14,18] A volume based IEC (IEC_V) was also calculated by multiplying the density of the membranes with IEC_W which was derived from copolymer structure. The dry based IEC_V was obtained based on the dry membrane density whereas the wet based IEC_V was calculated by considering the water uptake of the membranes. The water uptake, swelling ratio and oxidative stability of the membranes were determined according to the reported protocol.[14,19,36] Atomic force microscope (AFM) analysis was considered using AFM 5500 (Agilent technology) to get some better understanding on surface morphology after side chain grafting.Transmission electron microscopy (TEM) was undertaken of ultra-microtome membranes using a TEM instrument (FEI-TECNAI G2 20 S- TWIN) at an operating voltage of 80 kV. First, the acid form of the membranes were stained with Pb^{2+} ions by ion exchange of protons of $–SO_3H$ groups in 0.5M $Pb(CH_3COO)_2 \cdot 3H_2O$ aqueous solution overnight, washed thoroughly with deionised water and dried at room temperature for 24 h. Then, the stained samples were ultra-microtomed under cryogenic condition with a thickness of 100 nm and were embedded in carbon-coated copper grids for TEM analysis. The proton conductivity (in plane) of the polymer membranes were determined by measuring the resistance (R) value using AC impedance spectroscopy (HIOKI 3532-50 LCR Hi-TESTER) over a frequency range of 100 Hz–2 MHz using homemade two probe conductivity cell.[19,36]

Results and discussion

Syntheses and Characterization of HPPQSH-XX and HPPQSH-XX PS copolymers Sulfonated as well as fluorinated poly(arylene ether sulfone)s copolymers (HPPQSH-XX, XX = mole percentage of SDCDPS monomer) were synthesized by one pot K_2CO_3 mediated random polycondensation reaction of a bisphenol (HPP) using different proportion of a bisfluoro monomer (QBF) and a disulfonated dichloro monomer (SDCDPS) in NMP (as solvent) and in toluene (as co-solvent). In the synthesis, the QBF was chosen as one of the bishalide monomers in order to incorporate the $-CF_3$ groups in the final polymers. Similarly, SDCDPS allowed controlling the backbone sulfonation of the copolymers. The 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP) was chosen as bisphenol monomer in the synthesis of the copolymers that not only provide a rigid polymer backbone but further post-sulfonation was achieved through the reactive nitrogen center of the lactam ring by incorporating the pendent aliphatic side chain with SO_3H group. Initially the reaction temperature was kept at 140-150 ºC and the in situ generated water was effectively removed through a Dean-Stark trap by forming azeotropic mixture with toluene. Then the reaction temperature was raised to 180 ºC and was allowed to reflux for another 16 h for effective nucleophilic substitution reaction. Finally, the viscous mixture was precipitated in isopropanol after diluted with DMAc. The polymers obtained were washed with distilled water for the removal of salt impurities and were dried at 100 ºC in vacuo for at least 24 h. The membranes in the salt forms were cast from their DMAc solution and converted to acid form by sulfuric acid treatment.

A variety of PEMs have been prepared either by direct copolymerization method with one or two pendant sulfoalkyl groups as a side-chain[37-39] or by chemically grafting the pendants onto polymers.[40-45] In this regard, direct copolymerization technique is the more efficient method to control the degree of sulfonation in polymers rather than the chemical grafting method. Except a few, preparation of most of the sulfonated monomers with high content of sulfonic groups requires extreme rigorous conditions, stringent moisture free environment and exasperating efforts. Thus it is very much difficult to synthesize those sulfonated monomer in purified form. The chemical grafting method is the only way to avoid the synthesis of sulfonated monomers and offers an easier route to introduce the sulfonic moiety as a pendant side-chain. Gieselman and Reynolds introduced a sulfopropyl group to the amide nitrogen of aramid poly(p-phenyleneterephthalamide) (PPTA) through a nucleophilic ring-opening reaction with 1,3-propanesultone using NaH as a base.[46] By applying this method, Gao et al. synthesized a series of cardo poly(arylene ether sulfone)s with different length containing pendant sulfoalkyl groups as a side chain which are attached with the nitrogen centre of the lactam ring.[41] It has been seen that, for primary and secondary amides N-alkylation is more favoured than O-alkylation (except when the counterion is Ag^+) if the reaction was carried out at room temperature using a strong base, but the reverse phenomenon was observed at elevated temperature probably due to the higher reactivity of O-centre. So in order to get desired N-sulfopropylated product we treated preformed sulfonated polymers (HPPQS-XX) with 1,3-propanesultone using a strong base like NaH at room temperature for 12 h (Scheme 2). Finally, the viscous reaction mixture was precipitated in isopropanol, washed with distilled water, filtered and dried under vacuum at 100 °C for at least 24h. Repeatedly (2-3 times) the post sulfonation technique was considered either by adding greater amount of NaH or 1,3-propanesultone or by adding both to get 100% post-sulfonation, but unfortunately complete post-sulfonation (maximum 83% side chain sulfonation) did not occur in any case as it was analysed from NMR spectra. GPC results showed (Table 1) the formation of high molecular weights copolymers (before and after post-sulfonation) with relatively narrow dispersities (Đ). However, the values as presented in Table 1 are not a true representation of the molar mass of the polymers. These polymers (polyelectrolytes) interact partly with the column and the separation was not according hydrodynamic volume (size) as was observed from the GPC. Thus, the molecular weight and polydispersity values of the copolymers did not show any direct relationship with copolymer composition.

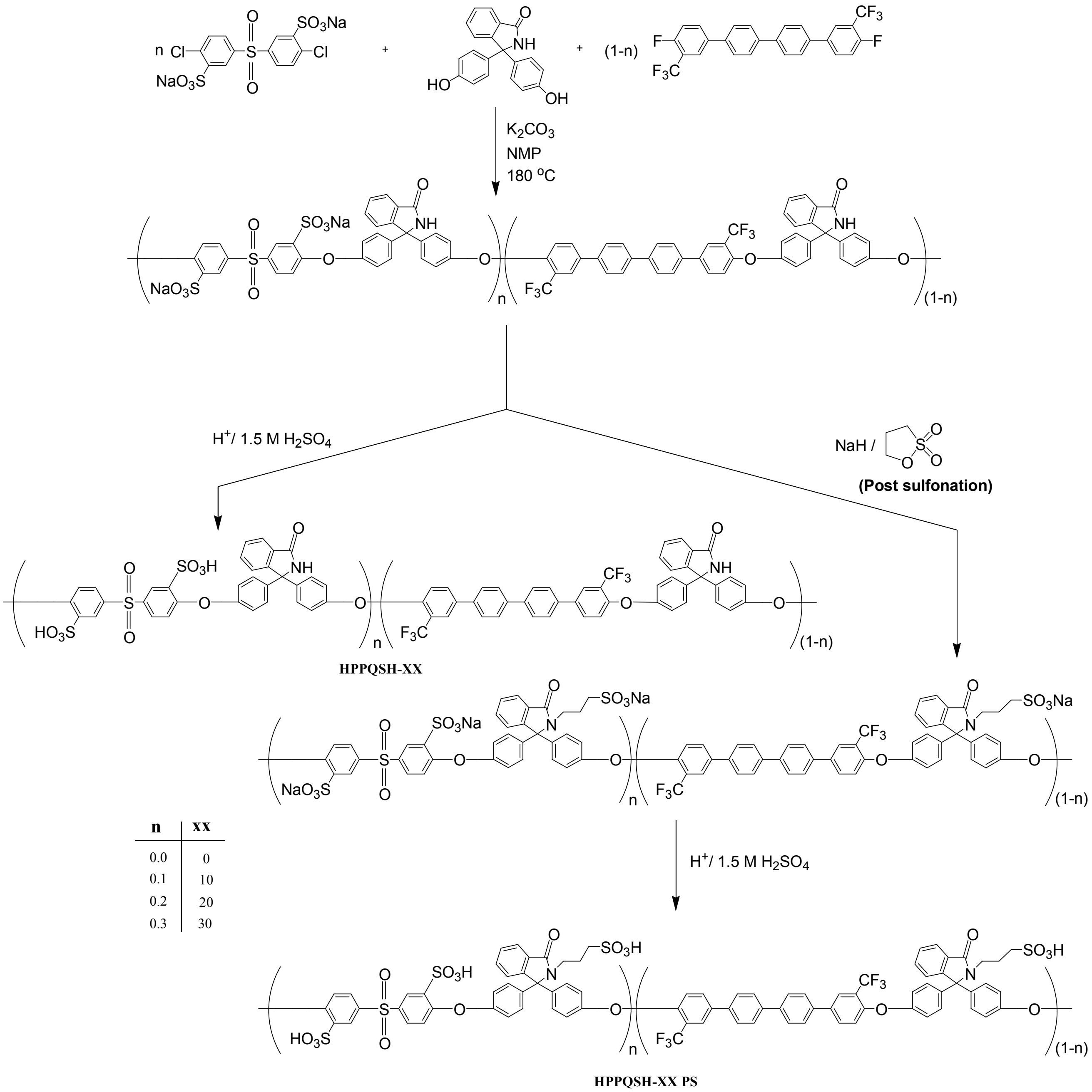
Table 1. Properties of PTAQSH-XX copolymers

Polymer	**M_n**[a]	**Đ**[b]	**DS**	
			theo.[c]	NMR[d]
HPPQ	48700	2.11	0	0
HPPQSH-10	21700	1.74	0.1	0.06
HPPQSH-20	19800	1.60	0.2	0.17
HPPQSH-30	22800	1.74	0.3	0.24
HPPQSH-PS	58200	2.14	1.0	0.73
HPPQSH-10 PS	24000	1.59	1.1	0.88
HPPQSH-20 PS	19500	1.58	1.2	1.00
HPPQSH-30 PS	23800	1.79	1.3	1.06

[a] M_n, number average molecular weight. [b] Đ, dispersity.

[c] Degree of sulfonation is theoretically calculated from the monomer feed ratio. For PS samples the value represents complete alkylation.

[d] Calculated from ^1H NMR signal intensities.



n	xx
0.0	0
0.1	10
0.2	20
0.3	30

Scheme 2. Synthesis of HPPQSH-XX and HPPQSH-XX PS copolymers.

The chemical structure of all copolymers (HPPQS-XX and HPPQS-XX PS) was confirmed by ATR-FTIR, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy. The ATR-FTIR spectrum of homopolymer HPPQ and its post-sulfonated form HPPQS-PS is shown in Figure S1a. The characteristic symmetric stretching band at 1051 cm^{-1} clearly indicated the presence of aromatic ether linkages in the polymers. In post-sulfonated polymer (HPPQS PS) an additional absorption band appeared at 1039 cm^{-1} corresponding to the stretching vibration of aliphatic sulfonic acid group. Besides, the strong absorption band at 1700 cm^{-1} was shifted to 1676 cm^{-1} (corresponding to the stretching vibration of secondary amide carbonyl and tertiary amide carbonyl respectively) indicating the formation of tertiary nitrogen centre after post-sulfonation. The FTIR spectra of copolymers are shown in Figure S1b. The characteristic symmetric stretching band at 1051 cm^{-1} and asymmetric stretching bands at 1333 and 1483 cm^{-1} were attributed to the aromatic ether linkages in the polymers. In addition, both homopolymer and copolymers exhibited aromatic C=C stretching band at 1584 cm^{-1} and C–F stretching band at 1240–1127 cm^{-1}. All the copolymers (before and after grafting) showed symmetric and asymmetric stretching band of the aromatic sodium sulfonate at 1027 cm^{-1} and 1095 cm^{-1}. These two absorption bands increased gradually with increase of SDCDPS content. Additionally, in post-sulfonated copolymers two characteristic stretching bands appeared at 1039 cm^{-1} and 1676 cm^{-1} corresponding to the aliphatic sulfonic acid group and tertiary amide carbonyl, respectively. The peaks associated with aromatic sulfonic acid group were shifted towards higher frequency with simultaneous increase of DS which indicated the possibility of hydrogen bonding with bound water. This phenomenon becomes more significant in post sulfonated copolymers due to the incorporation of additional SO_3H group as side chain grafting.

Figure 1a depicts the ^{1}H NMR spectrum of HPPQ. The analysis of this spectrum and of the corresponding ^{13}C NMR spectrum (Figure S2) is straightforward and confirms the expected structure. The signal assignment for the post-sulfonated polymer HPPQSH PS is more challenging because the alkylation of the NH group is not complete and results in a terpolymer structure. The ^{1}H NMR spectrum (Figure 1b) is characterized by new alkyl signals (a – c) resulting from the formed N-(3-sulfopropyl) group but also by residual NH signal indicating incomplete conversion with 1,3-propanesultone. The new signals in the aromatic protons' and carbons' region (Figure S3) were assigned by combination of 1D and 2D NMR techniques. Complete ^1H and ^{13}C signal assignments are given in the Supporting Information. The degree of alkylation can be calculated from the signal intensities of NH and alkyl signals. However, signal overlap with signals from (H_2O + $-SO_3H$), from DMSO-d_5 and/or from residual solvent from synthesis hampers accurate integration. Thus, the intensity ratios NH_0/H_{Ar}(HPPQ) for the parent HPPQ and NH_{PS}/H_{Ar}(HPPQSH PS) for the PS sample were determined (Figure 1). Because the number of aromatic protons remains unchanged in post-sulfonation reaction, the degree of alkylation can be calculated according Eq. 1.

$$\text{degree of alkylation} = 1 - [(NH_{PS} * H_{Ar}(\text{HPPQ})) / (NH_0 * H_{Ar}(\text{HPPQSH PS}))]. \quad \text{Eq. 1.}$$

Replacing quadriphenyl (Q) units partially by sulfonated diphenylsulfone (SDPS) units results in the copolymer series HPPQSH-XX. The alternating structure of HPPQ changes to a random terpolymer with a characteristic microstructure. Typically, the ^1H and ^{13}C NMR signals of the 4-oxyphenyl moiety of the phthalimidine unit show a dyad splitting due to the different neighboring units (Q or SDPS).[35] In fact, such a splitting can be observed both in the ^1H and in the ^{13}C NMR spectra of HPPQSH-XX samples (Figure 2a-c and Figure 3). Additionally, the NH signal of the HPP unit shows a splitting due to the three different HPP centered triads (Figure 2a-c). Relating the content of the three triads to the polymer composition a good agreement with a random distribution of Q and SDPS units can be stated. The copolymer composition itself was calculated from integral values of regions S (H_{26} of SDPS), Q (H_{15} and H_{17} of Q), and P (H_3 of HPP). It was found for all samples that the SDPS content is lower than expected from the monomer feed (Table 1). The appearance of weak signals at 6.74 ppm resulting from *ortho* protons of phenolic groups of HPP and complete conversion of fluorine groups as proved by ^{19}F NMR analysis point to a slight excess of HPP monomer in the final copolymer. Whereas the ^1H and ^{13}C NMR spectra of

HPPQSH-XX samples could be completely assigned (see also SI), the NMR spectra after partial alkylation are too complex (Figure 2d-f). Thus, only the degree of alkylation was calculated according Eq. 1 using the signal integrals of NH protons and all aromatic protons of the parent HPPQSH-XX sample and the corresponding PS sample. The degree of alkylation was 82 (±2)% for all samples.

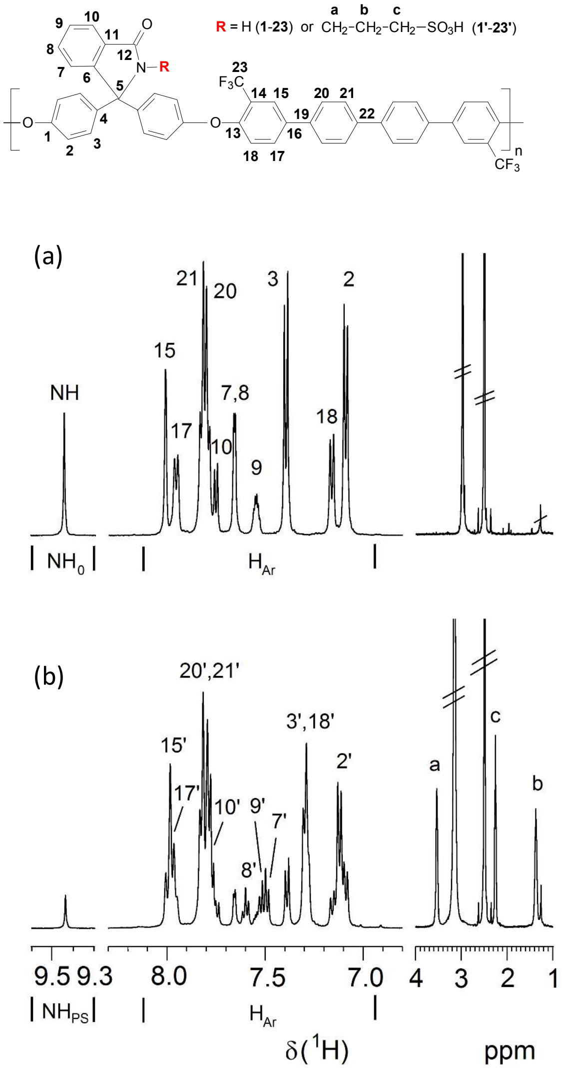


Figure 1. ^{1}H NMR spectra of (a) **HPPQ** and (b) **HPPQSH PS** (only new signals resulting from 73(±2)% alkylation are labelled) recorded at 90°C in DMSO-d$_6$. NH$_0$,NH$_{PS}$, and H$_{Ar}$ are integral regions used for calculation of the degree of alkylation.

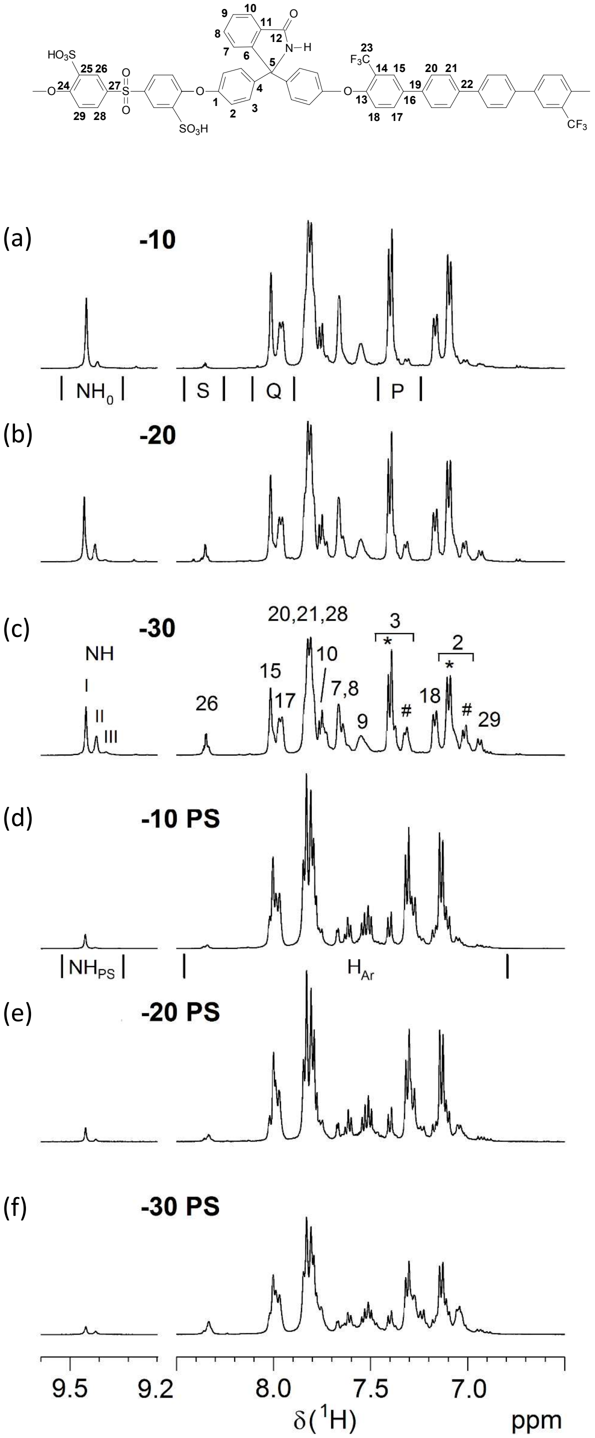


Figure 2. ^{1}H NMR spectra (regions of NH and aromatic protons) of **HPPQSH-10**, **-20** and **-30** (a-c) and its post sulfonated forms **HPPQSH-10 PS**, **-20 PS** and **-30 PS** (d-f) measured at 90°C in

DMSO-d$_6$. Dyad signals were denoted by * (QB-HPP) and # (SDSP-HPP) whereas triad signals were denoted by I (QB-HPP-QB), II (QB-HPP-SDSP), and III (SDSP-HPP-SDSP). NH$_0$,NH$_{PS}$, S, Q, P, and H$_{Ar}$ are integral regions used for calculation of polymer composition.

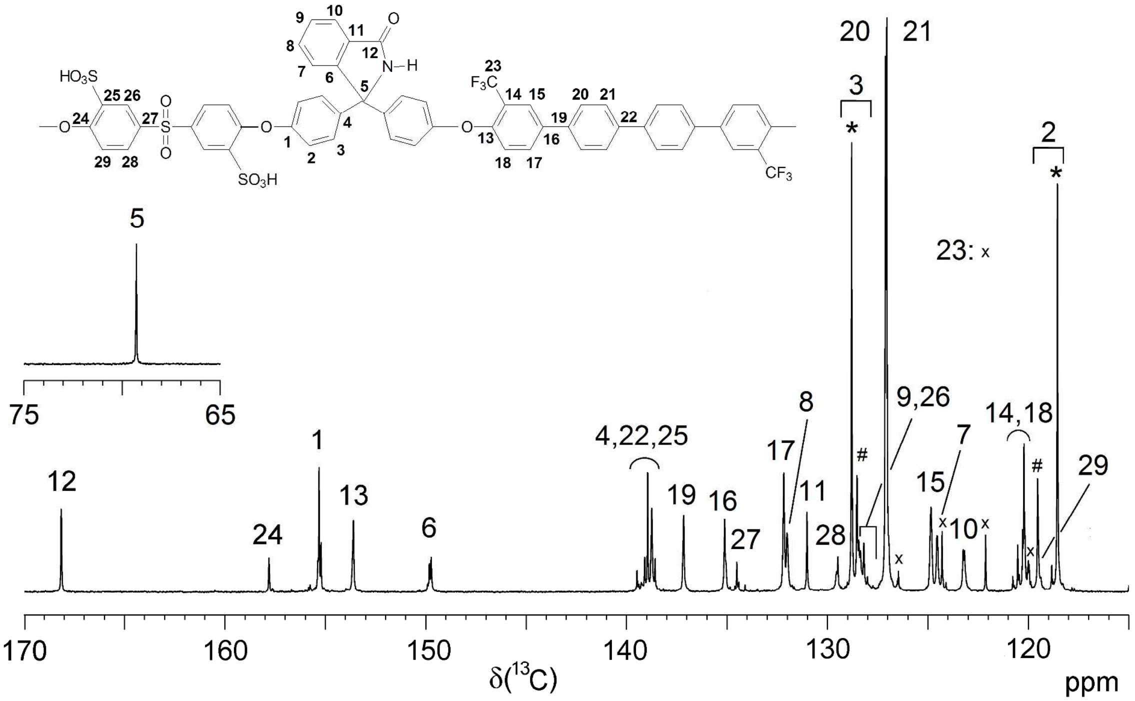


Figure 3. ^{13}C NMR spectrum of **HPPQSH-30** copolymer with signal assignment (60°C, DMSO-d$_6$). Symbols were used to mark QP-HPP (*) and SDPS-HPP (#) dyad signals. The formula depicts a structural fragment with atom numbering.

Thermal, mechanical, oxidative and hydrolytic stability

The thermal properties of all acid form copolymers were investigated by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. As expected the non-sulfonated HPPQ polymer showed lower glass transition temperature value (T$_g$ = 302 °C) than that of other two sulfonated copolymers HPPQSH-10 and HPPQSH-20 (T$_g$ = 310 °C and 322 °C, respectively) shown in Figure S4. This is due to the inter-ionic interaction (ionomer effect) of hydrophilic sulfonic acid groups in sulfonated copolymers which were absent in case of non-sulfonated one. Typically the T_g value of sulfonated copolymers also increases with increase of DS which may be attributed to the higher extent of intermolecular interaction of SO_3H groups. The rest of the sulfonated copolymers (including post-sulfonated) showed no obvious signature for glass transitions in the temperature range of 100–350°C probably due to the locking of segmental motion caused by ionic interaction.[36]

All the acid form of copolymer membranes including their post-sulfonated analogues showed two step degradation profiles in TGA analysis (Figure 4). The 10% degradation temperatures are listed in table 2. The first weight loss was found around 240-300 °C, which is allied with the degradation of labile sulfonic acid moiety. However, these initial weight loss values are gradually decreases with increasing the DS. The second degradation temperature was observed in the range of 450-530 °C and corresponds to the decomposition of the polymer backbone.

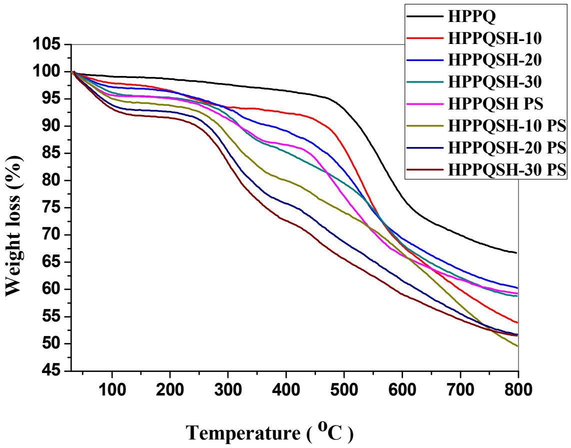


Figure 4. TGA curves of the HPPQSH-XX and HPPQSH-XX PS membranes in N_2.

Mechanical stability is one of the essential requirements for the electrolyte membranes under extreme conditions in light of membrane electrode assemblies (MEAs) to be used in fuel cells. The synthesized copolymers exhibited very good mechanical properties both in salt and acid form under dry state at room temperature and the results are summarized in Table 2 with those of Nafion® 117. The change of mechanical behaviour was also exposed by considering the stress stain plot shown in Figure 5. It is clear that the tensile strength of the salt form of copolymers HPPQS-XX (XX = 10, 20, 30) was gradually decreased with increase of DS due to simultaneous increment of aromatic SO_3H group in the polymer backbone and was found to be in the range of 40–78 MPa with Young's modules of 1.45–2.15 GPa. Similar observation was also found for the post-sulfonated copolymers HPPQS-XX PS with tensile strength varied within 29–72 MPa, Young's modules of 1.01– 1.89 GPa, and elongation at break of 4–36%. The HPPQSH-XX and HPPQSH-XX PS membranes (acid form) had tensile strength in the range of 37–70 MPa, Young's modules of 1.35–2.55 GPa, and elongation at break of 4–20%. The acid form of the post-sulfonated copolymer (HPPQSH-XX PS) membranes showed better mechanical properties than their corresponding salt forms as can be seen from Table 2. This was somewhat contrary to the literature findings.[17,36] Possibly, the sulfonated flexible aliphatic side chains in post-sulfonated copolymers (HPPQSH-XX PS) participated in intermolecular hydrogen bonding with backbone SO_3H groups as well as the unreacted –NH groups as depicted schematically in Figure 6. Such type of protonic cross linking was not feasible in the salt form membranes due to the unavailability of H^+ ions and in case of backbone sulfonated rigid HPPQSH-XX copolymers due to steric congestion. Compared to the soft fluorocarbon based Nafion® 117 these copolymers showed higher tensile strength and Young's modulus but lower elongation attributed to the presence of rigid aromatic backbone structure (rigid quadriphenyl and bulky phthalimidine moiety).

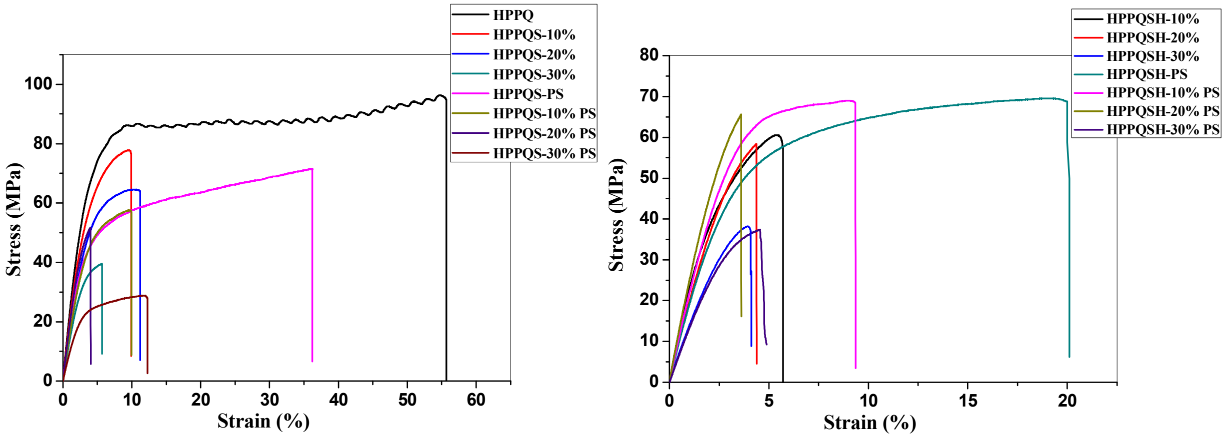


Figure 5. Stress-strain plot of all copolymer membranes in (a) salt form and (b) acid form.

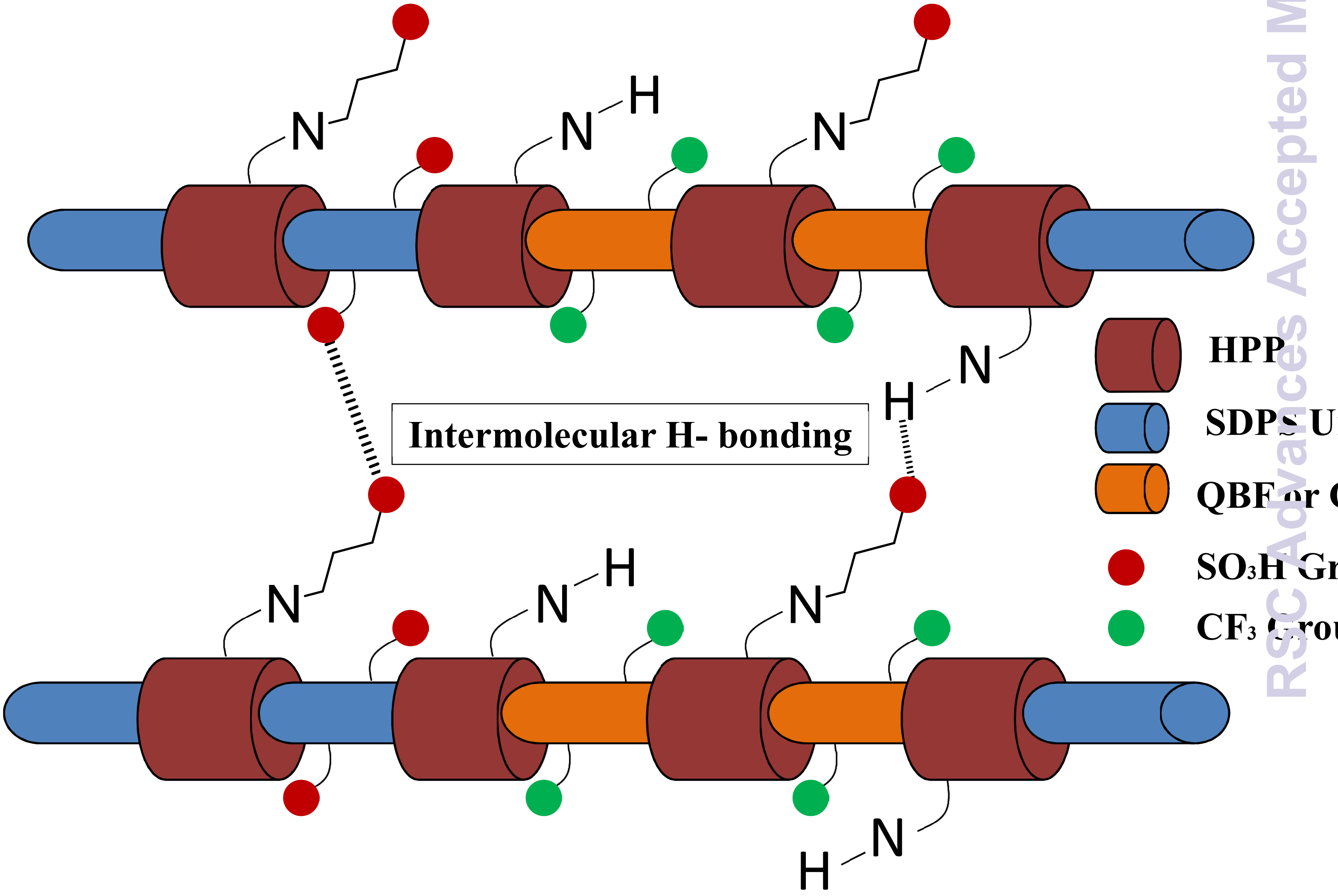


Figure 6. Architectural representations of protonic cross linking in acid form of grafted copolymers.

The oxidative stability of HPPQSH-XX and HPPQSH-XX PS copolymers was evaluated by observing the breaking time (τ_1) of the membranes in Fenton's reagent (3 wt% H_2O_2, 2 ppm $FeSO_4$) at 80 °C. All the polymer films exhibited high oxidative stability, as shown in Table 2. The trend of oxidative stability was quite similar to our previous work;[36] it was decreased with increasing the sulfonation degree of the membranes. Naturally, in this series, a maximum oxidative stability (τ_1 = >24 h) was found in HPPQSH-10 copolymer whereas the minimum oxidative stability (τ_1 = 5.5 h and τ_2 = 15.2 h) was found in HPPQSH-30 PS copolymer. Compared to our previous set of copolymers, these post-sulfonated membranes showed higher oxidative stability value even at higher IEC value.[36] In fact, oxidative attack mainly occurs at the hydrophilic domains of the polymer. But in post-sulfonated membrane the oxidative stability is highly influenced by considering the following three factors – one is due to the wholly aromatic nature of the copolymers, next is the presence of sulfonic acid group in already electron deficient aromatic sulfonic acid moieties, and finally the aliphatic side chains separated the polymer main chain from hydrophilic sulfonic acid groups to keep the main chain in a hydrophobic surrounding. These three factors together minimized the degradation of polymer chain during oxidative attack. In addition, these membranes showed higher oxidative stability due to the presence of hydrophobic trifluoromethyl groups which can protect the polymer backbone by the attack of hydroperoxy and hydroxyl radicals.[23]

The hydrolytic stability of all membranes (before and after post-sulfonation) was investigated by immersing membranes in water at 100 °C for 24 h. But no obvious changes were observed on the basis of their appearance, weight, and IEC_W value which indicates an excellent hydrolytic behaviour of all synthesized copolymers.

Table 2. Thermal and mechanical properties of PTAQSH-XX copolymers.

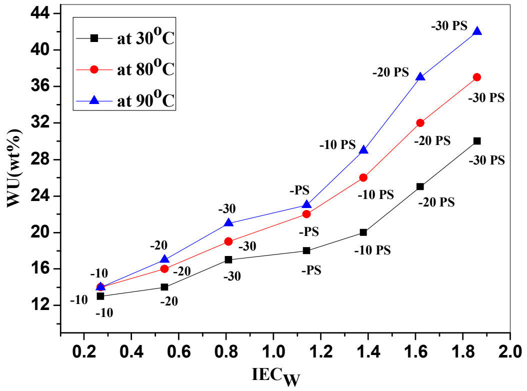
Polymer	**$T_g{}^a$ (°C)**	**$T_{d10\%}{}^b$ (°C)**	**TS^c (MPa)**	**Y^d (GPa)**	**EB^e (%)**	**Oxidative stability τ^f (h)**	
						τ_1	τ_2
HPPQ	302	524	96	2.37	56		-
HPPQSH-10	310	466	61(78)	2.52 (2.15)	6 (10)	> 24	-
HPPQSH-20	322	373	58 (65)	2.03 (1.79)	4 (11)	> 24	-
HPPQSH-30	-	317	38 (40)	1.42 (1.45)	4 (6)	> 24	-
HPPQSH-PS	-	310	70 (72)	1.97 (1.89)	20 (36)	> 24	-
HPPQSH-10 PS	-	285	69 (52)	2.20 (1.67)	9 (7)	22	> 24
HPPQSH-20 PS	-	263	65 (51)	2.55 (1.64)	4 (4)	10.2	> 24
HPPQSH-30 PS	-	245	37 (29)	1.35 (1.01)	4 (12)	5.5	15.2
Nafion® 117	-	-	21.9	0.16	288	-	-

Data in bracket ( ) refer to the salt (–Na) form. [a] Glass transition temperature determined by DSC, heating rate 10 °C/min under nitrogen. [b] 10% degradation temperature measured by TGA, heating rate 10 °C/min under nitrogen atmosphere. [c] Tensile strength, at a strain rate: 5%/min, 65 ± 2% RH and 30 °C. [d] Young's modulus. [e] Elongation break. [f] τ_1 and τ_2 refers to the initial breaking time and the complete dissolution in Fenton's reagent (2 ppm $FeSO_4$ in 3% H_2O_2) at 80 °C respectively.

IEC(wet and volume based), water uptake and dimensional swelling

The IEC_W can be calculated either theoretically by applying the traditional formula[18] or experimentally by considering the ^1H NMR spectroscopy and back titration method.[14,19,36] Table 3 compares the IECs and some other properties of the copolymer membranes in comparison to Nafion® 117. The experimental (from titration) IEC_W were found in the range of 0.20–1.67 mequiv/g which was close to the theoretical value derived from monomer feed ratio. In addition, the IEC_W (0.16–1.51 mequiv/g) as it was also calculated from ^1H NMR spectroscopy indicated that the sulfonic acid monomer (DADSDB) was successfully incorporated into the polymer (HPPQSH-XX and HPPQSH-XX PS) backbones via direct polycondensation and the sulfoalkyl group in grafted copolymer as side chain through post-sulfonation technique.

The preparation of sulfonated polymers with ideal water uptake value (WU) along with acceptable mechanical property is one of the critical demands for their application as PEMs. In order to facilitate a more exact, precious discussion about the water uptake among different membranes, volumetric ion exchange capacity (IEC_V, mequiv/cm^3) is more relevant (Table 3) which is defined as the molar concentration of sulfonic acid groups per unit volume containing absorbed water. In addition, as the electrochemical properties like proton conductivity is directly related with the length scale (independent on mass), more reasonable explanations are obtained when IEC_V (dependent on length) was considered rather than IEC_W. The water uptake [WU(wt%) and WU(vol%)] of copolymer membranes (before and after grafting) was measured by varying the temperature at 30 °C, 80 °C and 90 °C. Figure 7 represents the variation of IEC_W against WU(wt%) of the ionomer membranes at three different temperature. As shown in Table 3, the WU(wt%) increases with increasing sulfonation degree at a given temperature, thus HPPQSH-30 PS showed the highest WU(wt%) of 37% at 80 °C and 42% at 90 °C among all the copolymer membranes. Compared to Nafion® 117 membrane, this new set of copolymers showed much lower value of WU(wt%) at all temperature except HPPQSH-30 PS which may be attributed to the higher IEC_W value of HPPQSH-30 PS than that of Nafion® 117 membrane. On the other hand, this new set of copolymers HPPQSH-XX and its post sulfonated form HPPQSH-XX PS showed also much lower WU(wt%) values than our previous set of main chain type sulfonated copolymers[36] (maximum 44% for PAQSH-60 at 80 °C) even at higher degree of sulfonation which indicates the hydrophobic nature of the aliphatic group as a side chain in the grafted copolymers. Additionally, the lower WU(wt%) values of the copolymers was also influenced by the presence of a hydrophobic $-CF_3$ group in quadriphenyl moiety and rigid aromatic polymer backbone. The volume based water uptake [WU(vol%)] was calculated according to the reported papers.[19,43] The density values of the polymers are listed in Table 3 and were used to calculate IEC_V of the dry membranes. The variation of dry and wet based IEC_V against WU(vol%) of the ionomer membranes is shown in Figure 8. At lower temperature (30 °C) the change of dry volume–based IEC_V and wet volume–based IEC_V was quite similar when they are plotted against WU(vol%) of the polymers with different DS values. But at higher temperature (80 °C) IEC_V (wet) showed wide variation from IEC_V (dry) probably due to the percolation effect. Such effect was more prominent after reaching a certain IEC_V (wet) value with raised the temperature to 90 °C.



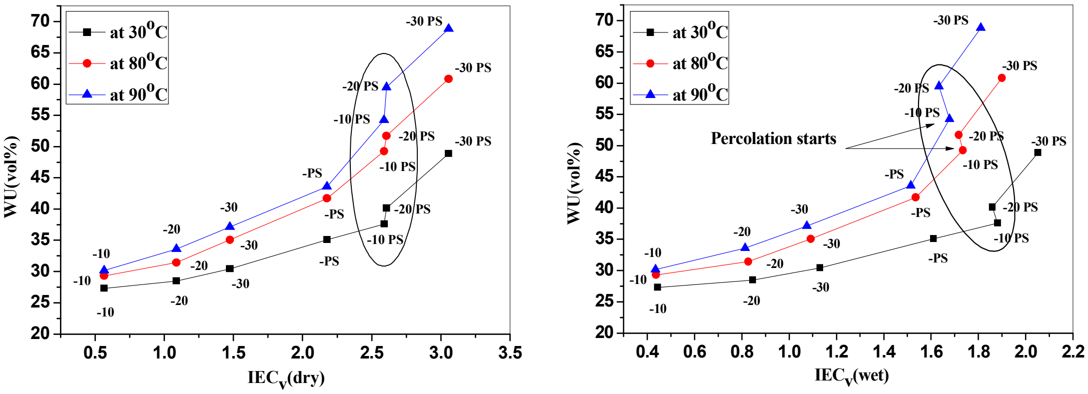


Figure 7. Water uptake (wt%) as a function of IEC_W and temperature for HPPQSH-XX and HPPQSH-XX PS copolymers.

Figure 8. Water uptake (vol%) dependence of IECv (dry), and IECv (wet) values of HPPQSH-XX and HPPQSH-XX PS membranes.

Table 3. Density, IEC, and water uptake (wt. and vol. based) of PTAQSH-XX membranes

Polymer	**d_M[a] (g/cm^3)**	**IEC$_W$ (meq/g)**			**IEC$_V$[d] (meq/g)**				**Water uptake (wt%)[e]**	**Water uptake (vol%)[f]**
					dry	wet				
		Theo.[b]	Titr.	NMR[c]		30 °C	80 °C	90 °C	90 °C	90 °C
HPPQSH-10	2.12	0.27	0.20	0.16	0.57	0.44	0.44	0.43	14	30
HPPQSH-20	2.02	0.54	0.51	0.46	1.09	0.85	0.83	0.81	17	34
HPPQSH-30	1.81	0.81	0.72	0.65	1.47	1.13	1.09	1.08	21	37
HPPQSH-PS	1.91	1.14	0.98	0.83	2.18	1.61	1.54	1.52	23	44
HPPQSH-10 PS	1.88	1.38	1.13	1.08	2.59	1.88	1.73	1.68	29	54
HPPQSH-20 PS	1.61	1.62	1.49	1.35	2.61	1.85	1.71	1.63	37	59
HPPQSH-30 PS	1.64	1.86	1.67	1.51	3.06	2.05	1.90	1.81	42	69
Nafion® 117	1.96	0.91	0.90	-	1.77	1.29	1.10	-	-	-

[a] density of membrane calculated from the weight and dimension of dry sample. [b] $IEC_{W,\ Theo.}$ = (1000/$MW_{repeat\ unit}$) x DS_{Theo} x 2, where $DS_{Theo.}$ is calculated theoretically from monomer feed ratio. [c] $IEC_{W,\ NMR}$ = (1000/ $MW_{repeat\ unit}$) x DS_{NMR} x 2, where DS_{NMR} is calculated from NMR peak ratio. [d] IECv(dry) = ($IEC_{W,\ Theo}$) xd_M and IECv(wet) = IECv(dry)/(1+ 0.01WU). [e] WU(wt %) = [(W_{wet} -W_{dry})/ W_{dry}]×100. [f] WU(vol %) = [{(W_{wet} -W_{dry})/d_w}/ (W_{dry}/dm)] ×100. [g] $\lambda = WU_W$ (%)/(100 x $IEC_{W,\ Theo.}$ x $M_{W,\ H2O}$), where $M_{W,\ H2O}$ = 18 g/mol.

Swelling ratio of the membranes was increased with increasing DS and temperature, as expected. Figure 9 represents the in plane (length) and the through plane (thickness) dimensional change of different copolymers at fixed temperature together with data for Nafion® 117. The results are listed in Table 4 and were found to be lower than that of Nafion® 117. Compared to the many main chain type copolymers, the side chain ionomer membranes generally showed much lower dimensional swelling due to the presence of flexible hydrophobic alkyl groups as a side chain which is more effective to repeal the polar water molecules. [6,7,9,42] Similar results were found in HPPQSH-XX PS copolymers where the grafted membranes showed much lower swelling ratio than main chain type sulfonated copolymers. In addition, the in plane dimensional swelling was quite lower than through plane dimensional swelling ratio.[43]

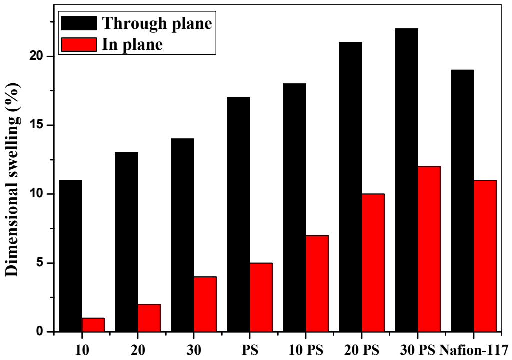


Figure 9. Dimensional swelling of HPPQSH-XX and HPPQSH-XX PS membranes along with Nafion 117 at 80 ^{o}C.

Table 4. Dimensional swelling and proton conductivity of PTAQSH-XX copolymers

Polymer	**Swelling ratio (%)**		**σ^{a} (mS/cm)**	**E$_{a}^{b}$ (kJ/mol)**
	In plane	Through plane		
	90 ^{o}C	90 ^{o}C	90 ^{o}C	
HPPQSH-10	3	21	15	10.6
HPPQSH-20	5	24	24	14.8
HPPQSH-30	8	28	27	12.5
HPPQSH-PS	10	33	32	14.9
HPPQSH-10 PS	13	36	45	12.1
HPPQSH-20 PS	18	45	90	12.4
HPPQSH-30 PS	22	48	142	14.0
Nafion® 117	-	-	150	13.6

[a] Proton conductivity was measured under fully hydrated condition(in water).
[b] Activation energy determined in the temperature range: 30-90 ^{o}C and heating rate 1-2 K/min.

Morphological nature of the membranes

Grafting is a common method to alter the morphological behaviour of polymer matrix. Microstructural study has been extensively done by considering AFM and TEM experiments in order to explain the morphological change of the copolymer membranes after side chain grafting. Atomic force microscope (AFM) study was recorded in tapping mode under ambient condition on 10 μm × 10 μm size scales for further inspection of surface morphology of the ionomer membranes shown in Figure 10. In polymer matrix the bright region corresponds to the hard hydrophobic part of the polymer and dark regions signify the soft hydrophilic region made by sulfonic acid group. Figure 10 revealed a clear hydrophobic/hydrophilic phase separation in each sulfonated polymers (except the HPPQ) and the proportion of soft dark region increases after grafting due to incorporation of –SO_3H group as a pendent side chain. At higher DS, the interconnectivity of the ionic domain appears to be more pronounced which finally resulted in high proton conductivity value.

This observation is well explained on considering the transmission electron microscope analysis (TEM) of the copolymer membranes. The TEM image (Figure 11) showed an outstanding micro-phase separated morphology in all cases where the dark spherical regions correspond to the hydrophilic ionic domains (lead ion exchange –SO_3H group) and the brighter regions represent the hydrophobic domains. The distinct ionic domains were more interconnected after post sulfonation of the copolymers with gradual increment of ion exchange capacities. Only the preformed sulfonated backbone containing copolymers (HPPQSH-XX, XX=10, 20, 30) consists of a large amount of small ionic clusters (5–10 nm) that were dispersed throughout the hydrophobic polymer matrix. The particle sizes were enormously increases after post-sulfonation of the copolymer membranes indicating the possibilities of higher agglomeration of hydrophilic moiety due to insertion of additional pendent –SO_3H groups. Thus the grafted copolymers exhibited excellent phase separated morphology with greater extent of bigger ionic domains along (60–100 nm) with fewer amounts of medium ionic clusters (15–20 nm) which can provide better water channel along with good proton transport pathway. Compared to our previous set of copolymers PAQSH-XX (containing only linear backbone –SO_3H groups), this new set of post-sulfonated copolymers HPPQSH-XX PS (containing –SO_3H group both in the linear backbone and in pendant side chains) exhibited much better phase separated morphology probably due to the presence of sulfoalkyl groups as a side chain that facilitated an additional interaction with the main chain sulfonic acid groups.

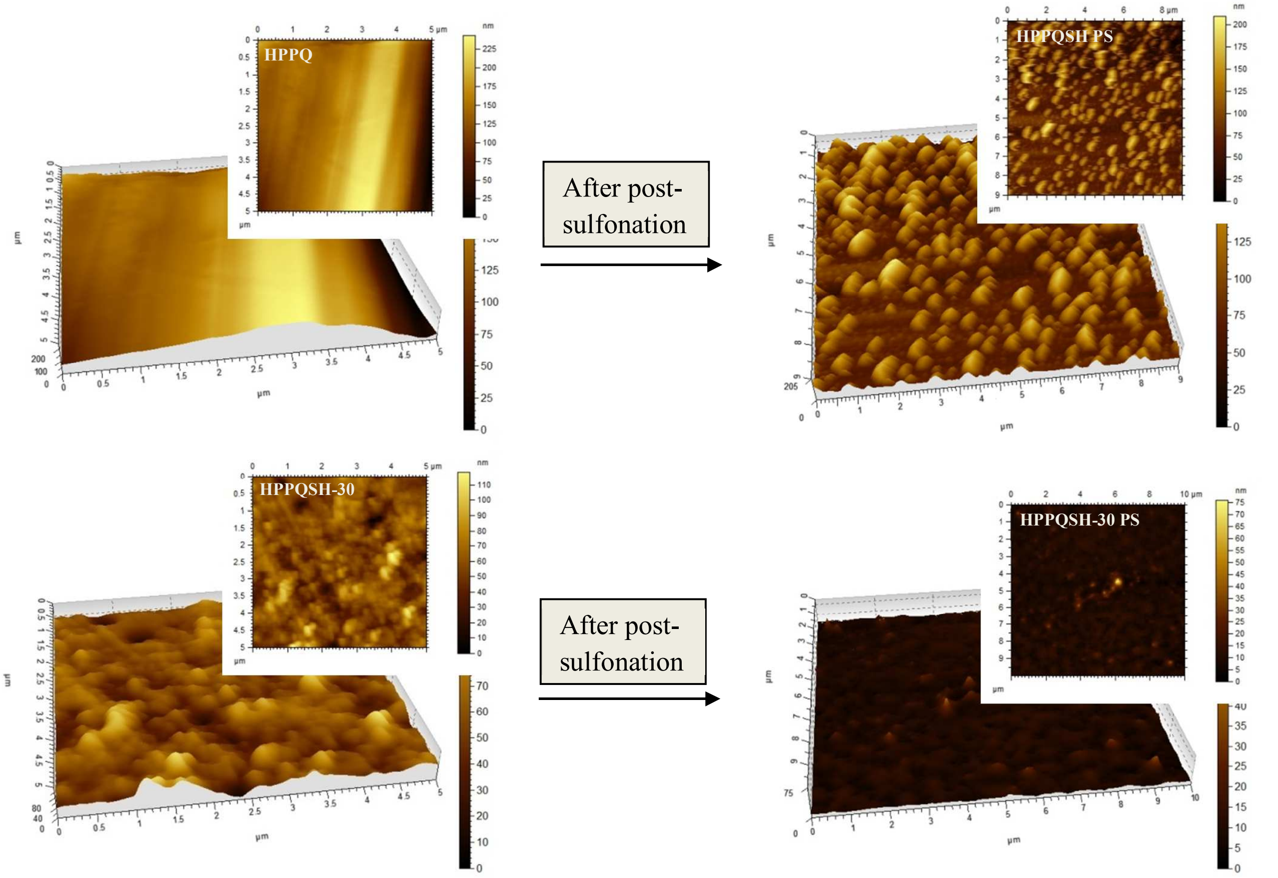


Figure 10. 2D-3D tapping mode AFM image of the polymers before and after grafting.

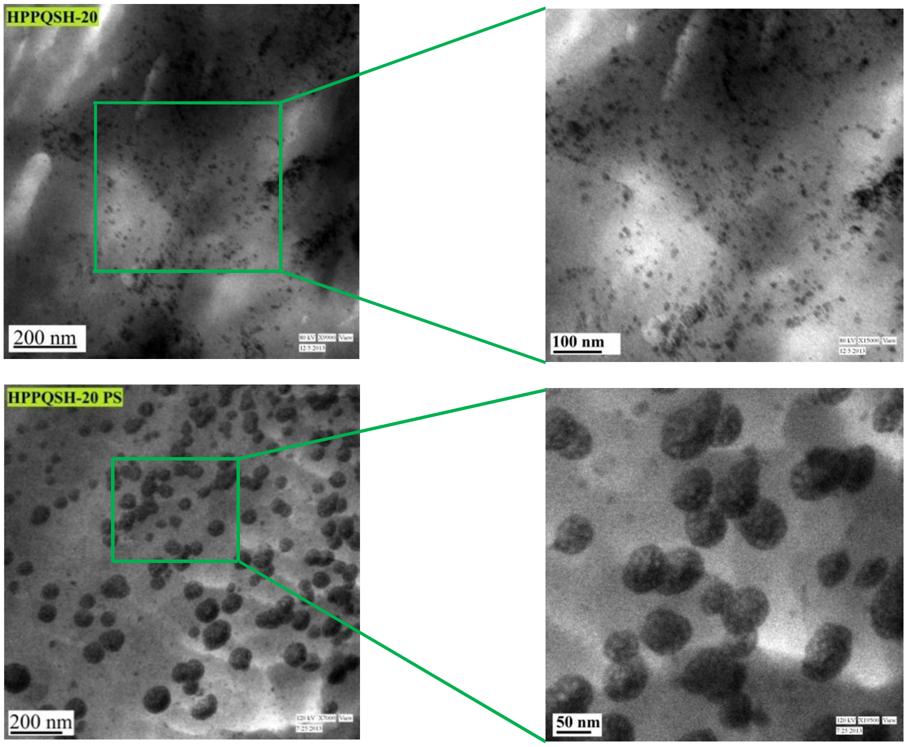


Figure 11. TEM micrographs of lead (Pb^{2+}) stained HPPQSH-20 and HPPQSH-20 PS copolymers.

Proton conductivity

High proton conductivity is one of the essential requirements of the membranes for their effective utilization in fuel cells. In-plane proton conductivity of the all copolymer membranes was investigated using AC impedance spectroscopy in deionized water. Before measuring the conductivity values of different copolymers, all the acidified membranes were immersed in deionized water for at least 72 h at room temperature to reach a fully equilibrium condition. For better rationalization, Nyquist plot (Figure S5) of ionomer membranes was considered on the basis of two facts, one was at fixed DS by varying the temperature and other was at fixed temperature by varying the DS of copolymer membranes(shown in inserted figure). It was observed that for a fixed DS the arc size gradually decreases with increase of temperature whereas for fixed temperature (90°C) the resistance value gradually dropped which makes an increment of proton conductivity value. However, in case of HPPQSH-20 PS the resistance value was suddenly dropped which may be attributed to the formation of percolated structure in the membrane morphology. Figure 12 shows the change of proton conductivity of the resultant copolymers at different temperatures. The results are listed in Table 4 along with Nafion® 117. The proton conductivity of the HPPQSH-XX (XX=10, 20, 30) membranes were found in the range of 8–12 mS/cm at 30 °C, 14–24 mS/cm at 80 °C and 15–27 mS/cm at 90 °C. In order to improve the conductivity values the backbone sulfonated membranes (HPPQSH-XX) were further modified by incorporation of sulfoalkyl groups as a side chain and the resultant post-sulfonated membranes (including HPPQSH PS) showed high conductivity values in the range of 12–56 mS/cm at 30 °C, 28–125 mS/cm at 80 °C and 32–142 mS/cm at 90 °C. Thus, the addition of sulfoalkyl groups as a side chain helped to increase the proton conductivity of the membranes. The proton conductivity of HPPQSH-30 PS copolymer was very close to that of Nafion® 117 which indicates the formation of well conductive sites in HPPQSH-30 PS copolymer membrane. In addition, HPPQSH-20 PS and HPPQSH-30 PS copolymers showed much higher proton conductivity than our previous set of copolymers[36] (PAQSH-XX, maximum conductivity is 50 mS/cm at 80 °C) which indicated that more densely populated aliphatic sulfonic acid groups along with sulfonated polymer backbone are more effective in proton conduction. The Arrhenius-type temperature dependent proton conductivity behaviour of all copolymer membranes (before and after grafting) is shown in Figure 13 and the activation energy (E_a) for proton conductivity was calculated according to Arrhenius equation.[18]

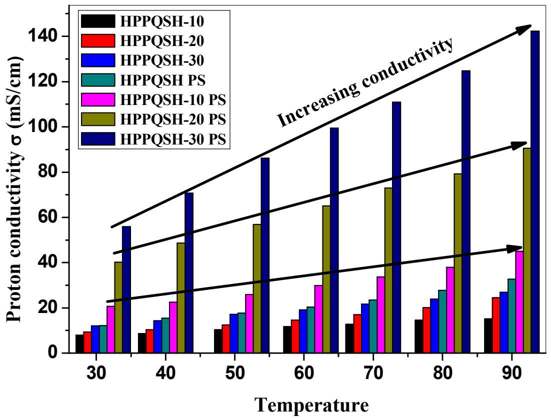


Figure 12. Proton conductivity of all copolymer membranes at different temperatures under fully hydrated conditions.

The activation energy of copolymer membranes was also calculated and was found in the range of 14.9-10.6 kJ/mol. In this regard, the activation energy (13.9 kJ/mol) of HPPQSH-30 PS membranes was quite close to the value of Nafion®117 (13.6 kJ/mol) which allowed to assume an analogous type of proton conduction mechanism involving hydronium ion. Also, there may be a possibility of more effective interaction between two polymer chains due to the formation of protonic crosslinking involving intermolecular hydrogen bonding. It can be observed from Table 4 that the activation energy values of the copolymers did not show any change rather increased as the DS value increases for some of the copolymers. This is somewhat difficult to explain as there are many factors that affect the activation energy. However, as the temperature increases the protonic crosslinking involving intermolecular hydrogen bonding breaks and that could be a reason of no change of activation energy in the threshold of percolation (between HPPQSH-10 PS and 20 PS). It could be simply stated the copolymers having activation energy in the range of Nafion®117. Furthermore, a correlation plot of proton conductivity with IEC_W and IEC_V (wet%) of all ionomer membranes is shown in Figure 14. At low IEC_W values (up to 1.38 meq/g), the hydrophilic clusters were far apart from each other that lead to a poor interconnection and lower proton conductivity value. Whereas at higher IEC_W (1.62 meq/g onwards), the isolated hydrophilic clusters came closer to build a well-connected channel by forming of large ionic cluster (validated by the microstructural evidence from TEM analysis) which resulted in high proton conductivity.

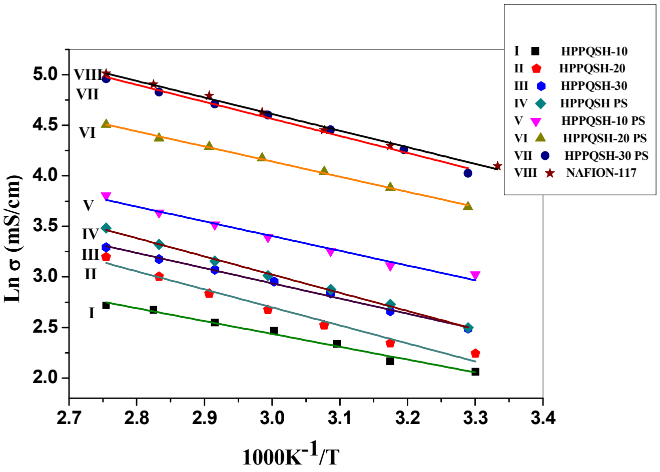


Figure 13. Arrhenius-type temperature-dependant proton conductivity (σ) behaviour of all copolymer membranes along with Nafion®117.

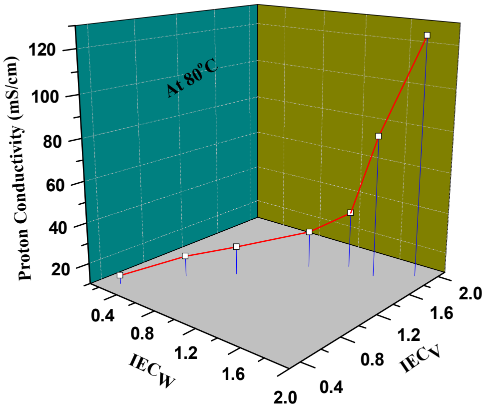


Figure 14. Correlation plot of proton conductivity with IEC_W and IEC_V (wet%) of all ionomer membranes at 80 °C.

Conclusions

In conclusion, a new series of sulfonated poly(arylene ether sulfone)s copolymers has been successfully synthesized by direct polycondensation method, from which another set of copolymers with sulfopropyl groups pendant to the main chain were prepared by post-sulfonation technique. In comparison with Nafion® 117 membrane, these copolymer membranes showed much higher tensile strength and Young modulus value along with high thermal stability. These results corroborate to the robustness of fully aromatic copolymers with cardo HPP and quadriphenyl moiety. The membranes exhibited good oxidative and dimensional stability compared to Nafion® 117 membrane which may be due to the presence of hydrophobic -CF_3 groups and aliphatic side chain. The dimensional stability of the membranes was also in the acceptable range, but anisotropic swelling was observed which is greater in through plane direction (thickness) than in plane direction. AFM studies indicate the change of surface morphology after grafting of preformed sulfonated copolymers due to assimilation of additional sulfopropyl group as a side chain. TEM micrographs of all copolymers show a clear microphase separated morphology with different domain sizes. The HPPQSH-XX (XX= -10, -20, -30) copolymers showed much lower conductivity due to poor interconnection between the small ionic domains (5–10 nm) whereas for better interconnection between the bigger ionic clusters (60–100 nm) along with medium ionic domains (15–20 nm), the post-sulfonated copolymers HPPQSH-XX PS (XX= -10, -20, -30) showed much higher proton conductivity value. In this series the HPPQSH-30 PS copolymer with highest ion exchange capacities exhibited maximum proton conductivity of 125 mS/cm at 80 °C and 142 mS/cm at 90 °C, which was very close to the conductivity of Nafion® 117 membrane. Moreover, the facile synthetic route and the overall copolymer properties make them more attractive for further investigation in fuel cell applications.

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Electronic Supplementary Information (ESI) available [FT-IR spectra, ^{1}H, ^{13}C & ^{19}F NMR data and spectra, DSC plot of the HPPQSH-XX membranes, Nyquist plot of ionomer membranes].

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Table of Contents graphic:

High proton conducting fluorinated sulfonated poly(arylene ether sulfone)s copolymers with side chain grafting

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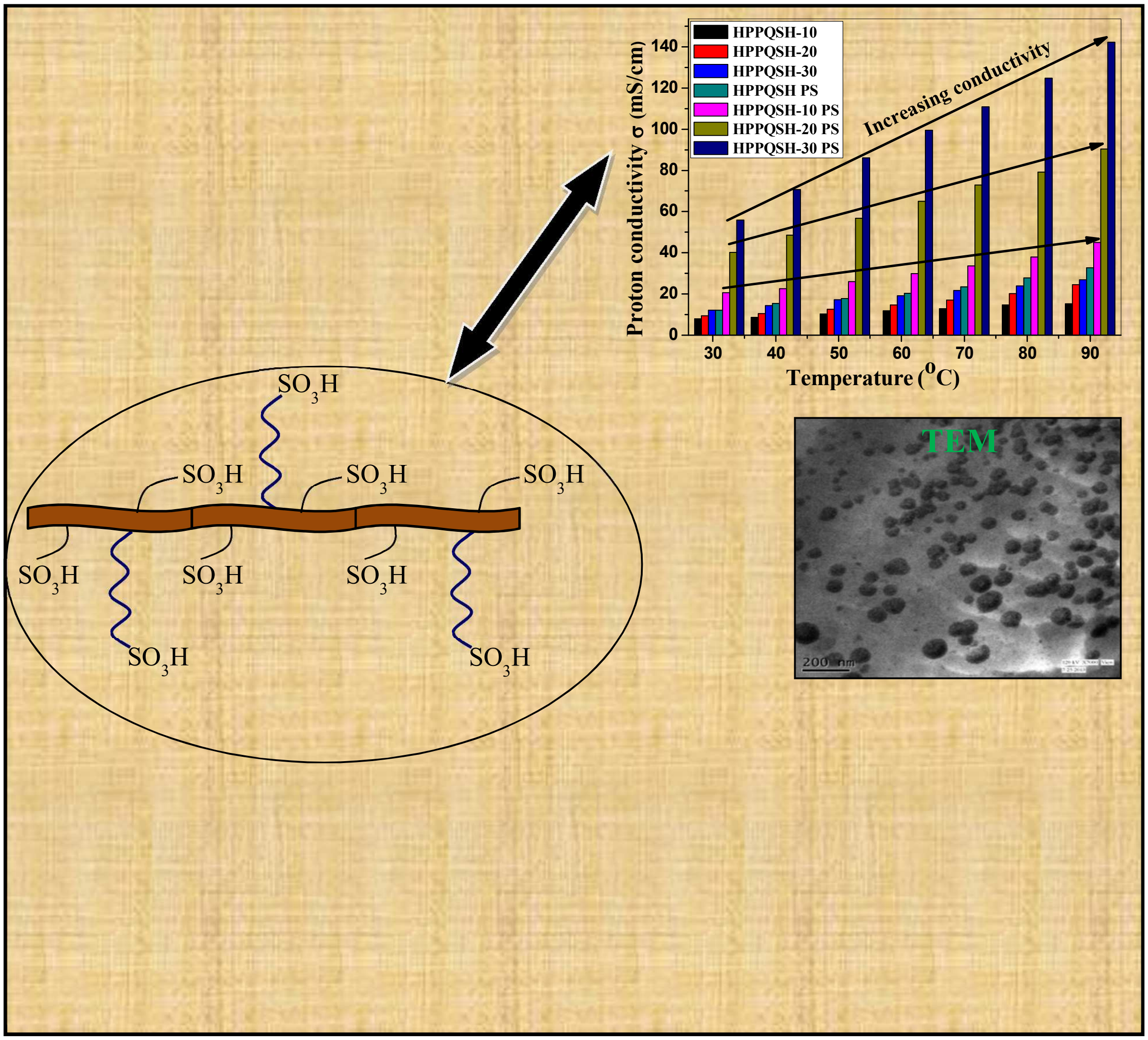

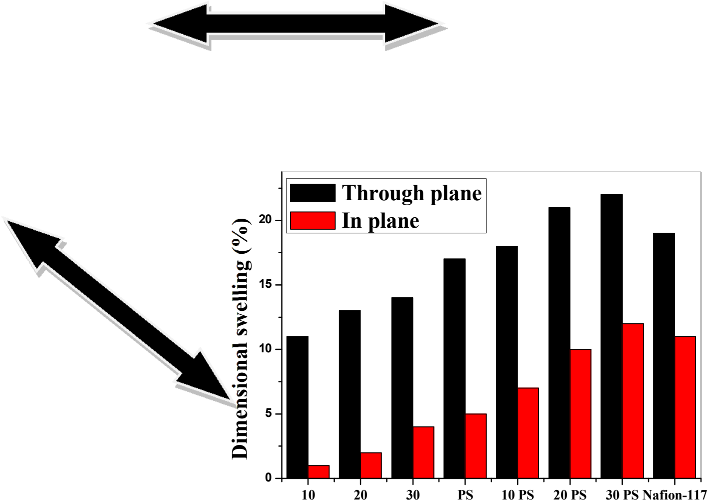
Through plane
In plane
Dimensional swelling (%)
0
5
10
15
20
10
20
30
PS
10 PS
20 PS
30 PS
Nafion-117