

## Materials Science inc. Nanomaterials &amp; Polymers

Synthesis and Characterization of Poly(*m*-tolylloxy-co-4-pyridinoxy phosphazene)s and their Application as Proton Exchange MembranesBurak Yigen,<sup>[a]</sup> Mariamu Kassim Ali,<sup>[b]</sup> Betül Karatas,<sup>[a]</sup> Selmiye Alkan Gürsel,<sup>[b, c]</sup> and Yunus Karatas<sup>\*[a]</sup>

A novel set of polyphosphazenes are synthesized to produce three polymers with varying side group ratios for proton exchange membranes. The designed heterosubstituted polymers here are the rare examples of polyphosphazenes of this kind to serve as proton exchange membranes with optimized structural stability and high temperature ionic conductivity. High quality polyphosphazenes with narrow polydispersity and rather low  $T_g$  values were prepared. These poly(*m*-tolylloxy-co-4-pyridinoxy phosphazene)s are sulfonated under a range of

conditions and characterized in order to investigate the synergetic effect of the heteroatom on the proton conductivity of the proton exchange membranes. The effect of sulfonation temperature and time on the fuel cell relevant properties is also investigated. Hydrolytically stable proton exchange membranes with high thermal and chemical stabilities are achieved. Additionally, resultant membranes exhibit proton conductivity, IEC and water uptake values comparable with commercial Nafion® membranes.

## Introduction

Polymers with the ability of exchanging protons or conducting protons are an emerging class of materials for various applications. For instance, proton exchange membranes (PEMs) are utilized as both solid electrolytes and separators for fuel cells. Today the most extensively used PEMs for polymer electrolyte membrane fuel cell (PEMFC) are perfluorosulfonic acid membranes such as Nafion® membranes which reveal desirable properties including high proton conductivity, mechanical strength, chemical/thermal resistivity and reasonably low water swelling.<sup>[1]</sup> However, there are several drawbacks of Nafion® such as high cost, limiting operating temperature (below 90 °C) and problems associated with transport of water (high osmotic drag) and fuel (e.g., methanol).<sup>[2]</sup> In this context, alternative PEMs specifically designed for use in fuel cells are still needed to be improved in line with these expectations. Aside from the fully and partially perfluorinated ionomers and their modified counterpart, a series of other polymers have also

been greatly investigated. Such examples include non-fluorinated hydrocarbons,<sup>[3]</sup> acid-base complexes,<sup>[4]</sup> inorganic-organic hybrid membranes,<sup>[5]</sup> radiation grafted membranes,<sup>[6]</sup> etc. Nonetheless most of these membranes do not possess ionic conductivity like Nafion® and therefore, acid moieties have to be integrated in order to introduce acidic functionality and hydrophilicity.

In the recent years it became evident that inorganic-organic materials such as polyphosphazenes could function as membranes and numerous attempts to investigate its functionality are ongoing. Polyphosphazenes with inorganic –P=N– backbone are a potentially a useful class of base-polymers to serve as PEMs because of their thermal and chemical stability. The backbone is particularly stable to free-radical skeletal cleavage reactions. Pintauro *et al.* reported an impressive chemical resistivity of polyphosphazenes in peroxide solution at 68 °C.<sup>[7]</sup> Moreover the ease of functionalization by attaching various aliphatic and/or aromatic side chains enables the synthesis of co-substituted polymers, thus a wide range of structures with improved properties can be designed to fulfil the major drawbacks seen in traditional membranes.<sup>[8]</sup> Bulky side groups also protect the backbone under aggressive conditions at the electrode interfaces of fuel cell, thus in general, any polyphosphazene containing bulky aromatic groups can be suitable to serve as PEMs.

Reports on the polyphosphazene based PEMs revealed two general approaches for the preparation; first one includes direct synthesis of PEMs via sulfonated group containing aliphatic<sup>[9]</sup> or aromatic substituents,<sup>[10]</sup> the second one involves the sulfonation or phosphonation of aryl groups containing polyphosphazenes.<sup>[7,11]</sup> Although the former method provides more controlled polymer architecture, the latter is preferred for easiness and flexibility. The first example of this group was

[a] B. Yigen, Dr. B. Karatas, Dr. Y. Karatas  
Department of Chemistry Faculty of Arts and Sciences  
Kirsehir Ahi Evran University Department, Bagbasi Campus, Kirsehir  
40100, Turkey  
E-mail: ykaratas@ahievran.edu.tr

[b] Dr. M. Kassim Ali, Dr. S. Alkan Gürsel  
Faculty of Engineering and Natural Sciences  
Sabanci University,  
Istanbul 34956, Turkey

[c] Dr. S. Alkan Gürsel  
Sabanci University Nanotechnology  
Research and Application Center (SUNUM)  
Sabanci University,  
Istanbul 34956, Turkey

Supporting information for this article is available on the WWW under  
<https://doi.org/10.1002/slct.202103650>

(aryloxy)- and (arylamino)- polyphosphazenes sulfonated via concentrated sulfuric acid associated with polymer degradation.<sup>[11a]</sup> Monteneri *et al.* reported the reaction of (aryloxy)polyphosphazenes with sulfur trioxide with no detectable degradation.<sup>[11b,c]</sup> This degradation was mainly observed for polyphosphazenes with phenoxy side groups but not with especially methyl containing aromatic substituents. In terms of sulfonation degree, conductivity and cross-linking properties, poly(bis(*m*-tolylxy phosphazene)) was reported to be the optimum candidate among the investigated polyphosphazenes as PEM,<sup>[12]</sup> showing even superior properties to traditional Nafion<sup>®</sup>.<sup>[7b,11d]</sup>

Although these polymers fulfill most of the requirements as a PEM, they still suffer from dehydrating at above 80 °C and recent studies concentrate on the effect of heteroatom especially nitrogen containing additives or polymer architectures like polyimides<sup>[13]</sup> or polybenzimidazoles<sup>[14]</sup> to preserve the ionic conductivity at higher working temperatures, i.e. 100–140 °C. Among the various studies on polyphosphazenes, there is no example of polyphosphazenes with nitrogen or other heteroatom containing substituents for this purpose. In fact, best to our knowledge, neither the synthesis of poly(bis(4-pyridinoxy)phosphazene) nor the preparation of PEMs based on poly(bis(4-pyridinoxy)phosphazene) has been reported in the literature previously. The only example included the use for the synthesis of a chiral polyphosphazene copolymer.<sup>[15]</sup> Moreover, the several polyphosphazene derivatives were reported for their potential use as PEMs previously yet their ex-situ fuel cell relevant properties were not reported in literature.

In our study, the facts that the focus of the recent studies on the heteroatom containing polymer architectures as PEMs and the optimum polyphosphazene structure investigated up to now are combined. For this purpose, the synergetic effect of nitrogen containing side groups is targeted and the systematic syntheses of polyphosphazenes co-substituted with *m*-tolylxy and 4-pyridinoxy side groups with varying amounts were aimed. The design of the polymer structure based on *m*-tolylxy side groups as this gave the optimum PEM properties<sup>[7b,11d]</sup> and cosubstitution was completed with 4-pyridinoxy side groups with the hope to ensure reasonable ionic conductivities at higher working temperatures. Moreover, these polyphosphazenes comprises the first examples of this kind because not only they are novel but also specially designed to be used as PEMs. The targeted polyphosphazenes were synthesized and characterized in detail. Moreover, PEMs based on these polyphosphazenes were fabricated at different sulfonation conditions and investigated for ex-situ and fuel cell relevant properties.

## Results and Discussion

### Synthesis of Monomer (trichloro-(trimethylsilyl) phosphoranimine) and Precursor Polymer (poly(dichloro phosphazene))

For the synthesis of precursor polymer, ambient temperature living cationic polymerization of the monomer with  $\text{PCl}_5$  as

initiator was used (Scheme S1). The monomer to initiator ratio was 350:1 and since two initiators were used for a complete polymer chain, statistically polymer chains with 700 repeating units were expected. This method is particularly favored to other classical thermal ring opening polymerization as it allows the controlled molecular weight with high purity and a narrow molecular weight distribution (PDI below 1.5). The detailed explanations for the syntheses of monomer<sup>[16]</sup> and precursor polymer<sup>[17]</sup> can be found elsewhere.

### Synthesis of Poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s (P1, P2, P3)

The polymerization of the poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s with varying *m*-tolylxy- and 4-pyridinoxy-substituents (Scheme S2) was performed via macromolecular substitution. Mixed substituent polyphosphazenes were synthesized by sequential macromolecular replacement of chlorine atoms in PDCP with required amount of sodium *m*-tolylxyoxide, followed by the addition of slight excess of sodium 4-pyridinoxy to yield the fully substituted P1, P2 and P3. Although less bulky nucleophiles like aliphatics can be reacted with PDCP at lower temperatures, the bulky aromatic substituents requires more forcing reaction conditions to maintain the complete replacement of chlorine atoms. The attempt of reacting excess sodium aryloxy with PDCP in THF, for example, resulted in only partial substitution of precursor polymer and longer reaction time did not help for this case,<sup>[18]</sup> however higher boiling dioxane as the solvent ensured the completeness of the macromolecular substitutions.

Polymers with varying *m*-tolylxy- and 4-pyridinoxy- substituents (P1, P2 and P3) were prepared in order to investigate the synergic effect of heteroatom on the conducting properties of the PEMs. 4-hydroxypyridine was chosen for this purpose and the syntheses of polymers with 10% (P1), 20% (P2) and 30% (P3) 4-pyridinoxy- substituents in total were aimed so that statistically 40% (P1), 60% (P2) and 80% (P3) of repeating units on the polymer chains contained heteroatom (Scheme S2).

### Sulfonation of Poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s (P1, P2, P3)

Sulfonation serves to promote the proton conductivity of membranes by addition of sulfonic acid groups. Depending on the polymer in context different sulfonation agents such as chlorosulfonic acid, fuming sulfuric acid, concentrated sulfuric acid, and sulfur trioxide complexes may be utilized.

In this study, we employed three different sulfonation methods named as chlorosulfonic acid, mild concentration sulfuric acid sulfonation and concentrated sulfuric acid sulfonation to sulfonate the poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s. Mild concentration sulfuric acid sulfonation (0.1–0.2 M sulfuric acid) yielded membranes with no signs of dissolution and after rinsing it was observed that membranes hardened and became brittle. Proton conductivity and FT-IR studies of these membranes showed insignificant proton conductivity and weak signal of side groups resulted in

discarding of mild concentration sulfuric acid sulfonation method.

Other attempts included use of chlorosulfonic acid since previous works<sup>[19]</sup> reported successful sulfonation of polyphosphazenes using chlorosulfonic acid to produce membranes with promising fuel cell characteristics. However, our attempts in this work for the sulfonation of our polymers by chlorosulfonic acid did not achieve a rigid form. The sulfonated products were observed to be robust and underwent dissolution during the preconditioning stage that followed the sulfonation. The robustness was due to the crosslinking that resulted in incorporation of the sulfonyl chloride group to the aromatic structure.<sup>[20]</sup> It is thought that the crosslinked compound entered into reaction during the preconditioning stage thereby resulting in dissolving of the products. Moreover any residual acid may have aggressively reacted with water and decomposed. Triggering an attack on the polymer backbone and by doing so, contribute to the hydrolysis of the sulfonated products. This behavior is in agreement with some reports in the literature which suggested that polymer degradation and crosslinking are the major problems associated with sulfonation using strong agents like chlorosulfonic acid and 100% H<sub>2</sub>SO<sub>4</sub>.<sup>[21]</sup>

We determined that concentrated sulfuric acid (97%) sulfonation much more successful than the other two methods (mild sulfuric and chlorosulfonic acid as explained above) in terms of lower degree of crosslinking. While P1 polymer gave some promising results P2 and P3 polymer did not perform well. The amount of the 4-pyridinoxy- substituents were generally slightly higher and this increase in nitrogen in the structure resulted in extreme attack by the sulfonating agent increasing the dissolution of the P2 and P3 products. Although the backbone nitrogen is protected from hydrolysis by the bulky side groups the nitrogen at the pyridinoxy side group may have succumbed to attack. Its electronegative nature attracts hydrogen from surroundings therefore increasing hydrophilicity of the membranes.

At this point of our study, we established that only P1 could be sulfonated and the results of sulfonated membranes presented hence forth will only constitute that from this polymer.

#### Characterization of Pristine and Sulfonated Poly(*m*-tolylloxy-*co*-4-pyridinoxy phosphazene)s (P1, P2, P3)

The compositions of the target polymers were determined using <sup>1</sup>H and <sup>31</sup>P NMR spectra. Figure 1 shows the stacked <sup>1</sup>H NMR spectra of the target polymers and the assigned polymer structure. The assignments were done according to the NMR spectra of the substituents and the varying signal intensities of the polymers. First of all, there was no alcohol signals of the substituents expected to be seen around 5 ppm, indicated that there were no residual left in the polymer. The polymer spectra were normalized to the signal of the *m*-tolylloxy that was assigned as g. As the amount of 4-pyridinoxy- substituents gradually increased from P1 to P3, the intensities of its signals assigned as b' and c' increased as expected. In the <sup>1</sup>H NMR spectra, the almost all signals of *m*-tolylloxy- assigned

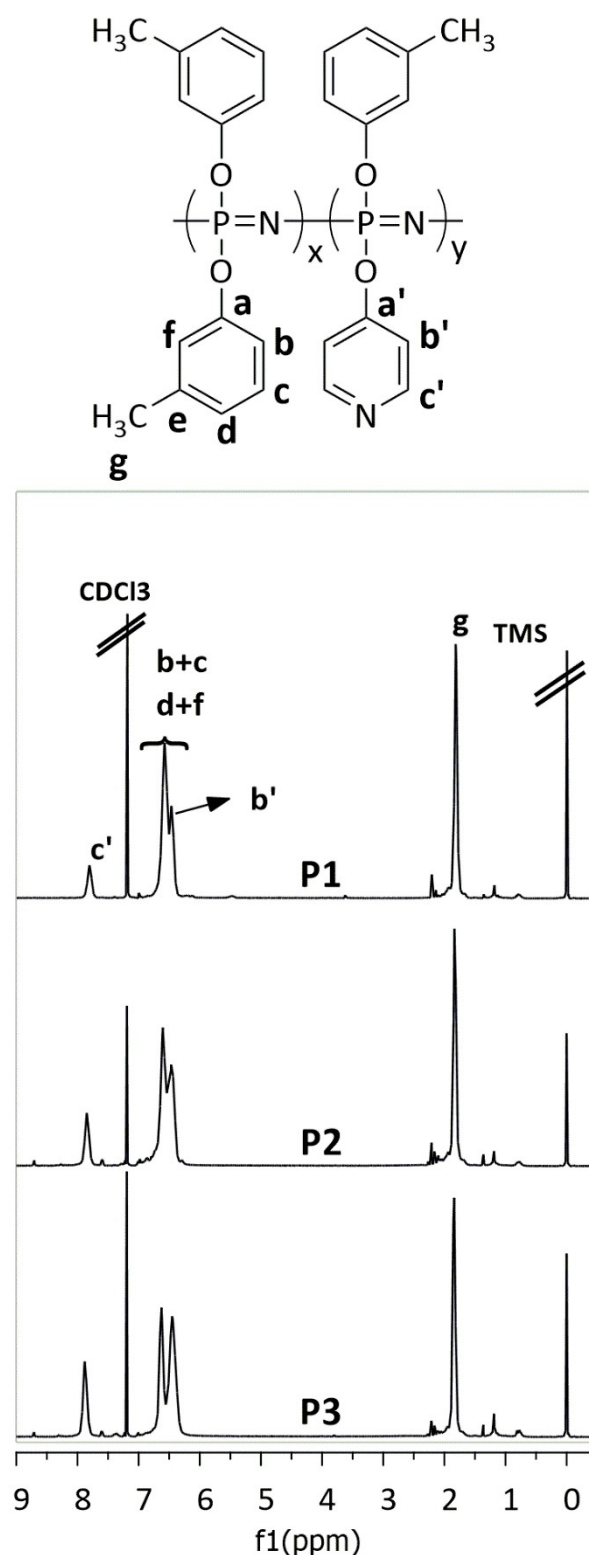


Figure 1. Stacked <sup>1</sup>H NMR of poly(*m*-tolylloxy-*co*-4-pyridinoxy phosphazene)s (P1, P2, P3).

as b, c, d and f overlapped with the signal of 4-pyridinoxy- assigned as b'. Fortunately, the methyl signals (assigned as g)

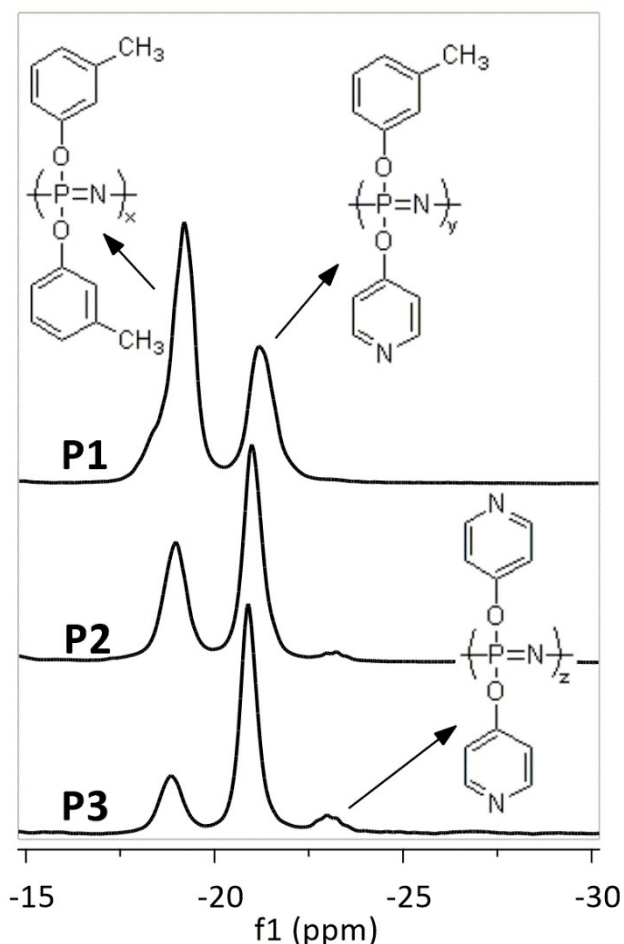
of the *m*-tolylxy- and the signals of 4-pyridinoxy- assigned as *c'* could be clearly observed. Thus, these bare signals could be used to calculate the polymer compositions and the mol percentages of *m*-tolylxy- substituents were found to be 84% (P1), 72% (P2) and 61% (P3). However,  $^{31}\text{P}$ NMR signals are more accurate for this purpose as they do not interfere with the other atoms.

$^{31}\text{P}$ NMR of the precursor polymer and the target polyphosphazenes gave more significant results in terms of substitution pattern and the completeness of the macromolecular replace-

ment. The stacked spectra of the polyphosphazenes are given in Figure 2.

First of all, the disappearance of the single sharp peak of PDCP at around  $-18$  ppm was accompanied by the expected two relatively broad signals of the synthesized polyphosphazenes at around  $-19$  ppm and  $-21$  ppm. This showed the complete replacement of the chlorine atoms of the precursor polymer. The substitution patterns of the target polyphosphazenes were calculated from these peak integrals (Table 1). The signal at around  $-19$  ppm was assigned for the repeating units fully substituted by *m*-tolylxy- (denoted by "x") and the intensity of this signal decreased from P1 to P3 as the ratio of this substituent decreased. The signal at around  $-21$  ppm was assigned for the mixed substituted repeating units (denoted by "y") and the intensities of this signal increased gradually as expected from P1 to P3 as the amount of 4-pyridinoxy- increased. The small signal at around  $-23$  ppm not shown in P1 but shown in P2 (3% contribution) and P3 (8% contribution) was attributed to repeating units fully substituted by 4-pyridinoxy- (denoted by "z"). Although statistically not expected, this would be due to some unreacted fully chlorine substituted left in the initial stage of the substitution displaced fully with 4-pyridinoxy- groups or probably due to partial replacement of *m*-tolylxy- substituent by the excess 4-pyridinoxy- during the final stage of the substitution. The polymer compositions were calculated by taking these three signals into consideration and are listed in Table 1. The calculated polymer compositions were quite close to the target polymer compositions. The amount of the 4-pyridinoxy- substituents were in general slightly higher than expected and these results were in accordance with the explanation above. The NMR spectrum of P1 membranes sulfonated at room temperature is shown in Figure 3 below. A decrease in the signals corresponding to b, c, d and f and the splitting of these signals was a clear indication of  $\text{SO}_3\text{H}$  integration at the tolyloxy side group. The newly introduced  $\text{SO}_3\text{H}$  group induces steric hindrance thereby resulting in the number of neighbouring hydrogens and also the number of signals increasing. More signals can now be observed downfield as a result of the deshielding of these protons. However sulfonation carried out at longer durations revealed disappearance of signals an outcome resulting from the degradation of the structure.

There were observable structural changes between the pristine and membranes sulfonated under different conditions as portrayed from Figure 3 and 4. A new peak which could be



**Figure 2.** Stacked  $^{31}\text{P}$ NMR of poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s (P1, P2, P3).

**Table 1.** The results of poly(*m*-tolylxy-co-4-pyridinoxy phosphazene)s (P1, P2, P3).

Sample	Target Polymer Composition		Polymer Composition <sup>c</sup>		Isolated Yield <sup>[b]</sup>	$M_n$ <sup>[d]</sup>	$M_w$ <sup>[d]</sup>	$M_w/M_n$ <sup>[d]</sup>	$T_g$ <sup>[e]</sup>
	<i>m</i> -tol (mol %) <sup>[a]</sup>	4-pyr (mol %) <sup>[b]</sup>	<i>m</i> -tol (mol %) <sup>[a]</sup>	4-pyr (mol %) <sup>[b]</sup>					
P1	80	20	82	18	100	638,200	699,200	1.10	$-16.2$
P2	70	30	68	32	98	550,400	719,200	1.31	$-14.0$
P3	60	40	58	42	97	1,391,000	1,564,000	1.13	$-10.5$

[a] *m*-tol = *m*-tolylxy- side chain. [b] 4-pyr = 4-pyridinoxy- side chain. [c] Determined by  $^{31}\text{P}$ NMR. [d] Determined by GPC (eluent = THF, polystyrene standards). [e] Determined by DSC.

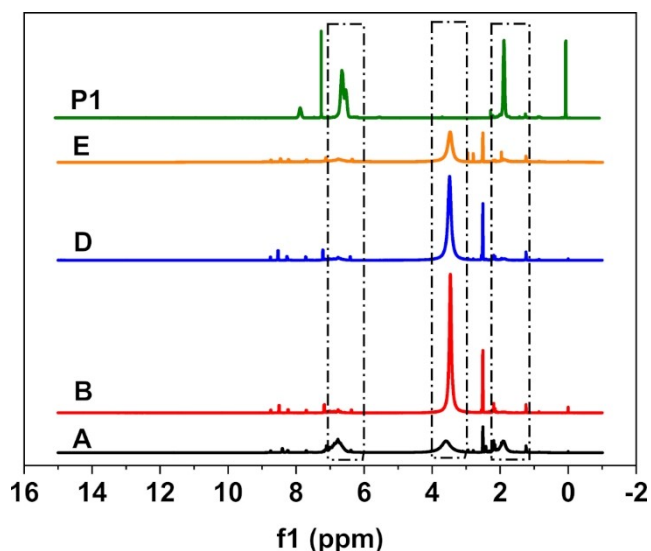


Figure 3. Stacked  $^1\text{H}$ NMR spectra of sulfonated membranes at RT. Sulfonation time (min); A:30, B: 45, D: 90, E:120.

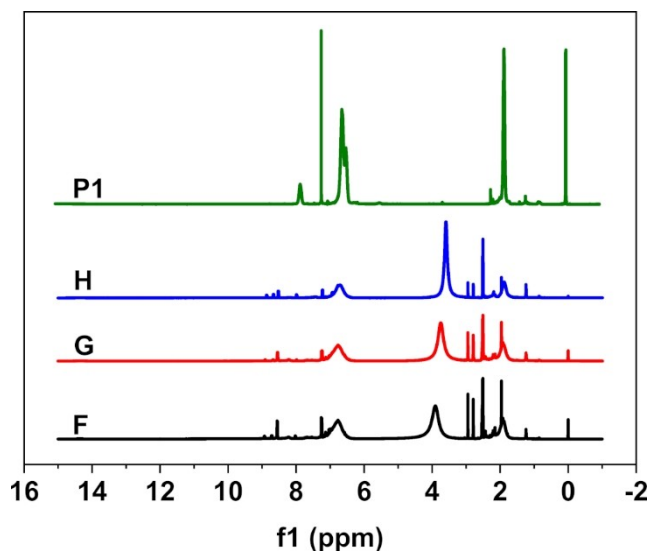


Figure 4. Stacked  $^1\text{H}$ NMR spectra of sulfonated membranes at 65 °C. Sulfonation time (min); F:15, G:30, H:45.

attributed to the  $\text{SO}_3\text{H}$  for both room temperature and sulfonation done at 65 °C is clearly seen.

Possibilities of backbone degradation for severe sulfonation conditions could not be underestimated and were checked using the  $^{31}\text{P}$ NMR as shown in Figure 5 below. The broadening in the peaks is an indication of the overall backbone degradation that is occurring in the membranes. The decreased intensities in the NMR spectra also showed how aggressively the *m*-tolylxy side group (denoted by "x") was attacked. This finding is in agreement with model described by Gleria<sup>[22]</sup> who found that under harsh sulfonation conditions polyphosphazene backbones do undergo degradation as a result of  $\text{SO}_3$  attack. New signals at around 10 ppm may be associated to the

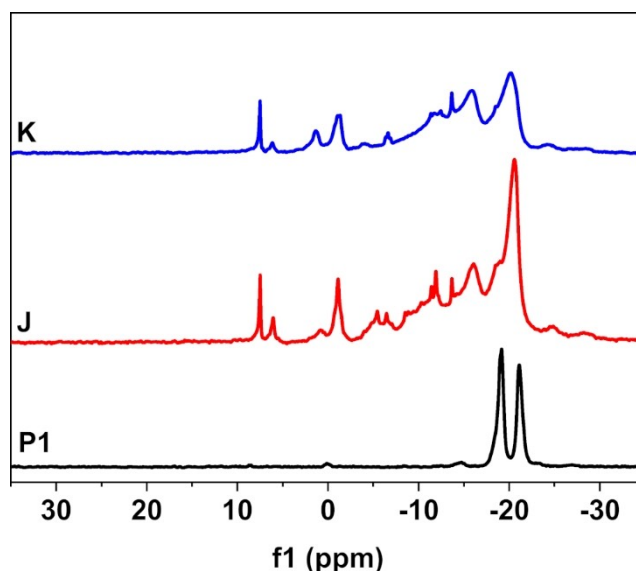


Figure 5. Stacked  $^{31}\text{P}$ NMR showing backbone degradations for harsh sulfonation conditions for membranes, J and K.

P–O–H related products resulting from attack of the backbone by hydrolysis.

The representative FT-IR spectrum of P1 with the characteristic signals of both inorganic polymer backbone and the substituents and together with different sulfonated membranes were shown in Figure 6 below. No evidence was found for the presence of –OH units around  $3500\text{ cm}^{-1}$  and P–O–H units between  $2100\text{--}2500\text{ cm}^{-1}$ , which could be the result of hydrolysis of the precursor polymer during substitution reactions. Moreover, the disappearance of the P–Cl stretching of the precursor polymer in  $1300\text{ cm}^{-1}$  and the appearance of P–O–C aromatic stretching in  $1226\text{ cm}^{-1}$  supported that the macromolecular substitution reactions were complete.

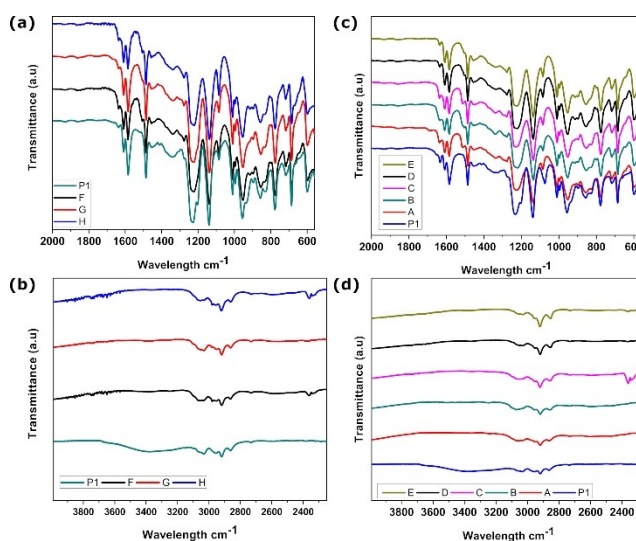


Figure 6. The FT-IR of sulfonation for different durations at a) 65 °C b) RT.

The typical P=N stretching around  $1240\text{ cm}^{-1}$  (appeared as a shoulder of the strong P–O–C stretching) and the  $777\text{ cm}^{-1}$  was assigned for the polymer backbone.

Relatively weak P–O–H stretching between  $2100\text{--}2500\text{ cm}^{-1}$  showed that the polymer backbone was rather protected by bulky substituents and no extensive chain cleavage occurred under highly aggressive conditions of sulfonation. These results are in accordance with the  $^{31}\text{P}$ NMR interpretations for Figure 5. The appearance of the new signal around  $1300\text{ cm}^{-1}$  was attributed to the asymmetric O=S=O stretching that is an indication of sulfonic acid integration. Sulfonation processes carried out at higher temperatures and longer durations also exhibited doublet peaks at around  $2350\text{ cm}^{-1}$  which was associated with the P–O–H. It is seen that the intensities of the O=S=O peaks increases as the duration of the process increases (from F to H in Figure 6(a) and from A to E in Figure 6(c)), a trend which is expected because the polymer interaction with the sulfonation reagents increases. It can be assumed that longer timed sulfonation processes will maximize the  $\text{SO}_3\text{H}$  group integrated however it brings about more hydrolysis attack to the polymer backbone as indicated in Figure 6 above. Therefore a fine tune of the sulfonation conditions is required.

Number and weight average molecular weights of the obtained polyphosphazenes were estimated by GPC relative to polystyrene. The results are listed in Table 1. The living cationic polymerization with the monomer to polymer ratio of 350:1 implied a narrow molecular weight distribution and the polymer chains of the polyphosphazenes ought to contain around 700 repeating units (as two initiator species were used per chain). This assumption mean the molecular weight should be around  $2 \times 10^5$  D, however much higher molecular weights were estimated by the measurements. Although, the over estimation of the molecular weight of the polyphosphazenes is known, such a high molecular weight jump could be resulted either from the loss of the initiator during the course of the polymerization (as the monomer to initiator ratio increases, the molecular weight increases but the narrow distribution is maintained) or the partial crosslinking of the polyphosphazene chains during the macromolecular displacement reactions due to impurities mainly water (both the molecular weight and the polydispersity increases).

The former explanation could be taken into account as the molecular weight distributions of the polymers were estimated to be very close to unity. No crosslinking was observed and the polymers were soluble in common solvents like THF, dioxane, chloroform.

The glass transition temperature ( $T_g$ ) of the synthesized polyphosphazenes were listed in Table 1. They were all opaque products with  $T_g$  values around  $-20$  to  $-10^\circ\text{C}$ . The DSC thermograms of the polyphosphazenes were given above in Figure 7 The lowest  $T_g$  value was determined to be  $-16.2^\circ\text{C}$  for P1 (the highest *m*-tolylxy- content) and increased gradually with increasing 4-pyridinoxy- amount up to  $-10.5^\circ\text{C}$ . This is in good agreement with the fact that asymmetry of the substituent decreases the  $T_g$  values of a polymer. Although the  $T_g$  value of the poly[bis(*m*-tolylxy)phosphazene] was reported

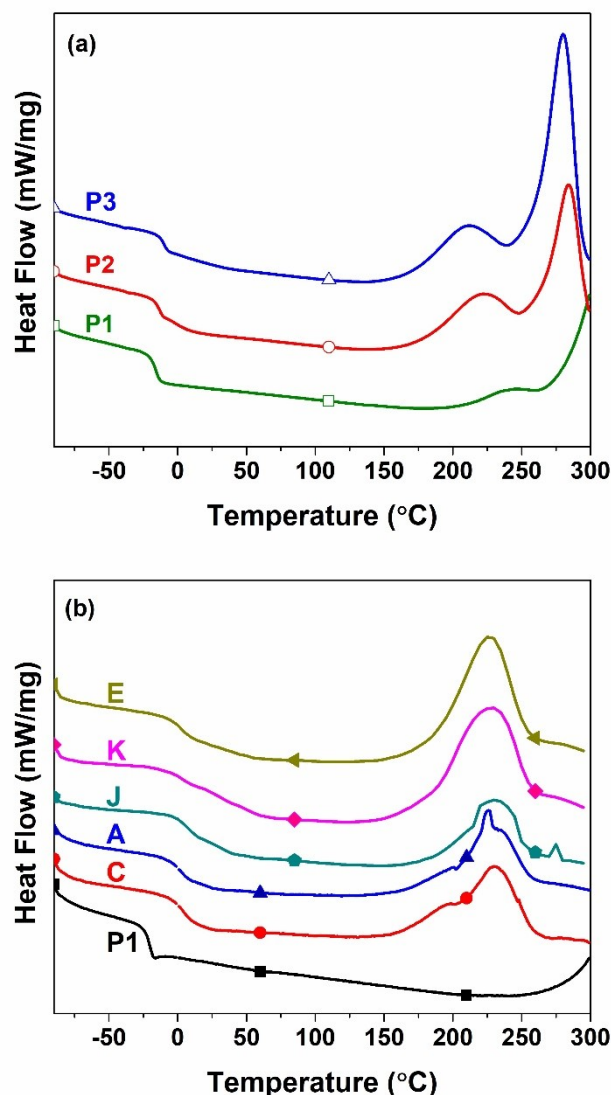


Figure 7. DSC thermograms of a) pristine polymers, P1, P2 and P3 b) sulfonated P1 polymer's membranes.

to be  $-25^\circ\text{C}$ ,<sup>[8]</sup> there was no record for the synthesis of poly[bis(4-pyridinoxy)phosphazene] but the trend in the  $T_g$  values of the cosubstituted polymers here implies a much higher  $T_g$  value for this polymer.

For most of the aryloxyphosphazenes were reported a  $T(1)$ -type liquid crystalline transition and a melting temperature around  $300\text{--}350^\circ\text{C}$  with a subsequent decomposition, however mixed aryloxyphosphazenes were essentially amorphous elastomeric-type materials with only glass transition at lower temperatures due to the random disposition of the different side groups.<sup>[8]</sup> Our polymers fall also in this type and showed mainly secondary transition. Moreover, two endothermic peaks were observed at higher temperatures. They could be attributed to the packing of the aromatic groups at these temperatures.

The sulfonation process resulted in the polymers undergoing structural changes which affected their thermal properties. The thermograms in Figure 7 above depicted an increase in the ( $T_g$ ). This increase is attributed to the restriction in the polymer chains of the modified polyphosphazene polymers usually induced by the intermolecular interactions by hydrogen bonding which hinder rotations of polymers. The effects of duration and temperature of sulfonation was investigated to determine optimum conditions. Very long time durations and higher temperatures were seen to result in much higher  $T_g$  values. This is in agreement with the literature<sup>[23]</sup> since the polymer had a longer interaction with the reagent resulting in more incorporation of the sulfonic acid group which is responsible for causing an increase in the structural rigidity of the polymer. As much as this property is desired, too much sulfonation results in degradation of the mechanical properties<sup>[24]</sup> and thus renders the membranes unsuitable for the desired application.

Thermal stability of the polymers was examined by TGA and the results reported in Figure 8 above. No decomposition temperatures up to 300 °C were determined for the polymers. A two-step weight loss was observed from 47–148 °C and 330–520 °C. They were attributed to the decomposition of the two different side groups. The polyphosphazenes are considered to be inherently flame retardant due to the inorganic back bone, thus the decomposition ended with expectedly high char yield (around 40%).

In Figure 9(a) it was observed that the 1<sup>st</sup> stage mass loss was not very pronounced and there was little observable difference for the various sulfonation conditions as opposed to graph 9b where the mass losses were distinct. This particular region can be attributed to the water loss in the membrane. Higher degrees of sulfonation were obtained from higher temperature sulfonation which explains this behaviour. An additional weight loss associated with  $\text{SO}_3\text{H}$  dissociation starting from around 240 °C was also seen and this is in agreement with the literature.<sup>[23,25]</sup> As observed, this mass loss seems to increase as the sulfonation time increases because

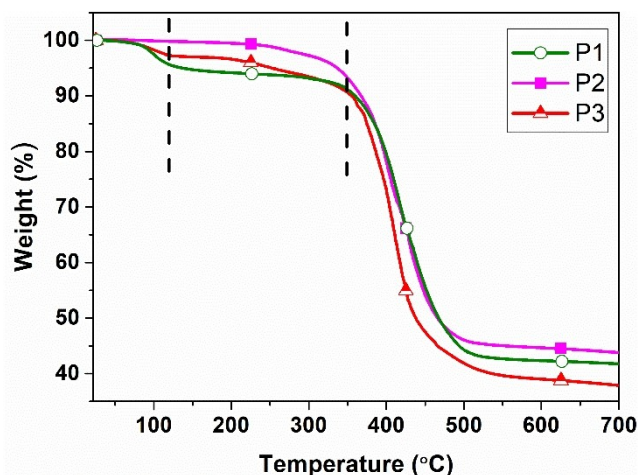


Figure 8. TGA thermograms of the pristine polymers, P1, P2 and P3.

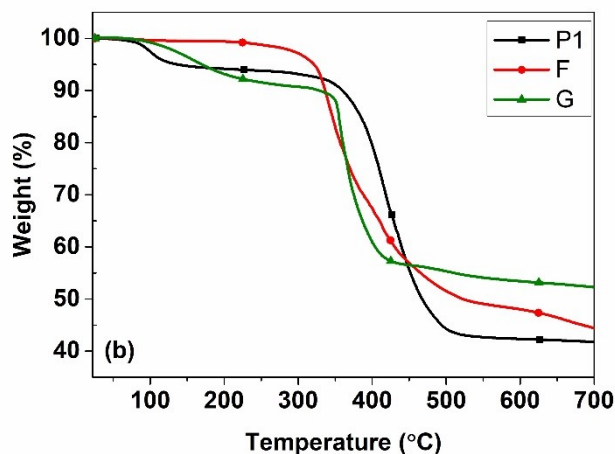
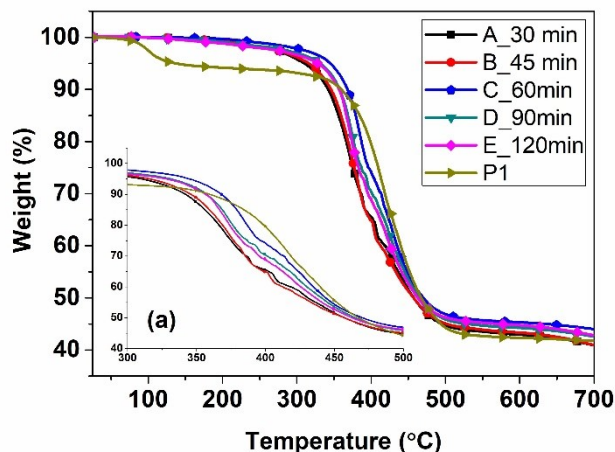
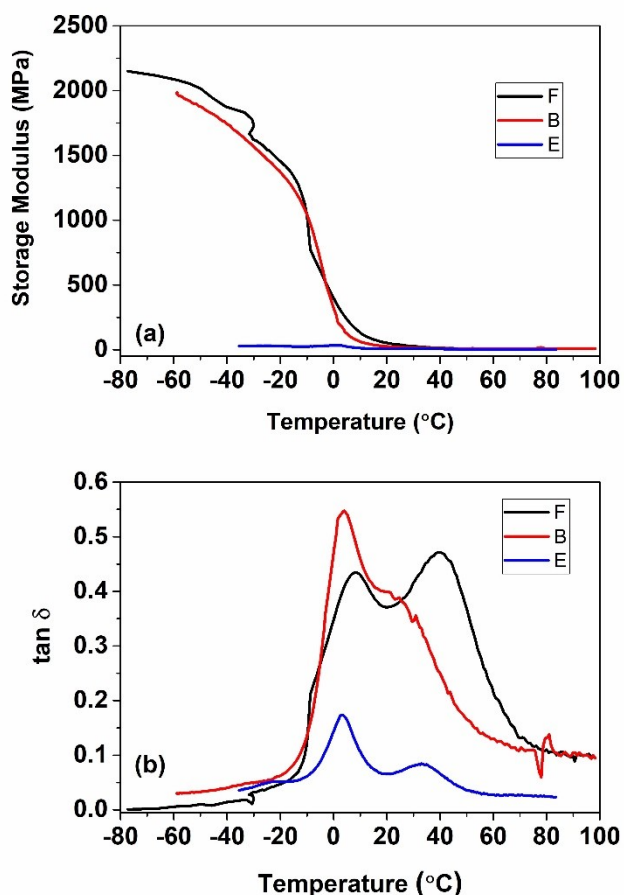


Figure 9. TGA thermograms of P1 polymer's membranes (a) RT (b) 65 °C.

sulfonic acid group integrated increases with increase in sulfonation time. In some instances, it was difficult to distinguish between the mass loss associated with the evolution of water and that of the sulfonic acid groups possibly as a result of their overlap and also due to low degrees of sulfonation. Additionally, residual masses were close to those of the pristine polymer which is a good indication that sulfonation did not deteriorate the membrane properties and that they possessed good thermal characteristics.

Mechanical property is a significant parameter for the tunability of the structure-property-performance of fuel cell membranes. However, coupling of both high modulus and conductivity to produce suitable membranes remains a challenge for most researchers. In this study, the temperature dependence of the storage modulus ( $E'$ ) and loss tangent ( $\tan(\delta)$ ) for representative samples (B, E and F) was studied and reported in Figure 10 (a) and (b). From the samples sulfonated at room temperature (B and E), B showed a higher modulus over the entire temperature range studied compared to E which was sulfonated for longer durations. Sulfonation induces structural rigidity in the polymer structure, however, extended sulfonation durations may result in the degradation of the



**Figure 10.** The dynamic mechanical analysis of selected membranes (B: 45 min RT, E: 120 min RT and F: 15 min 65 °C). (a) Temperature dependence of storage modulus and (b) loss tangent ( $\tan \delta$ ).

mechanical properties<sup>[24]</sup> which affect the membrane conductivity as portrayed for sample B and E. On the other hand, shorter sulfonation durations coupled with higher temperatures also yielded relatively high stiffness values as depicted for sample F (comparable with B) in Figure 10 (a). From Figure 10 (b), the measured samples demonstrate a glassy behavior derived from the  $T_g$  characterized by the first peak of the  $\tan(\delta)$  graph. Presence of a second peak may suggest some phase separation in the samples. Increased sulfonation time and temperature shift the peak to the right an indication that the  $T_g$  increases which agrees with our earlier discussed DSC results shown in Figure 7 (b). The increased values are ascribed to the increased structural rigidity imposed from sulfonation process.

The IEC of membranes is dependent on the sulfonation conditions and number of  $\text{SO}_3\text{H}$  groups integrated. Although it does not give an indication about the distribution of the exchange sites across the membrane thickness, it is important in order to understand the total number of protons available for conductivity. These protonic sites available on the  $\text{SO}_3\text{H}$  group is what later on forms an interconnected channel for ion transfer through the various mechanisms explained in the

literature. Table 2 below displays the IEC and their corresponding calculated degrees of sulfonation for membranes. It is seen that increased duration of sulfonation for both 65 °C and room temperatures yielded increasing IEC values which is agreement with the literature. Longer durations enabled longer interactions of the polymer with the sulfonation agent thereby increasing the  $\text{SO}_3\text{H}$  group integration. However, for the latter it was observed that from 90 minutes and longer durations the IEC values decreased. Instead of the expected outcome where sulfonic acid group is integrated to the polymer these longer interactions between the polymer and the sulfonating agent may have resulted in degradation thus producing low IEC values. Comparisons into the two different temperatures revealed that higher IEC values were easily achieved at higher temperatures due to the increased thermal energy available for the process. However, very high values are discouraged due to the excessive swelling it cause in membranes.

Water uptake is also another very significant parameter for fuel cell membranes as it directly influences the physico-chemical properties of a membrane such as the proton conductivity and the mechanical stability of a membrane.<sup>[26]</sup> High IEC values usually promote high water uptake values making the membranes highly hydrophilic and which may sometimes result in hydrogel formation, something that is highly undesired.<sup>[27]</sup> It is for this reason that an optimum degree should be achieved so that the membranes contain just enough water uptake capacity to facilitate conductivity yet at the same time maintain the mechanical stability during functioning. The presence of nitrogen in the hetero-atomic structure is expected to increase the water uptake capacity of the fabricated polyphosphazene membranes. Table 2 below shows the wide range of water uptake values for the membranes fabricated in this study. Water uptake was seen to increase for both cases of temperatures, however for 65 °C sulfonation process the effect of both the temperature and time resulted in a rapid increase than that observed at room temperature. Both for the sulfonation at room temperature and 65 °C it was observed that sulfonation processes for longer durations had an increasing trend. This is expected due to the increasing number of sulfonic acid groups being integrated into the polymer. At durations longer than 90 minutes however, room temperature sulfonation showed a downward trend which agrees with previous discussions. Although we

**Table 2.** The effect of different sulfonation conditions on IEC, degree of sulfonation, water uptake and proton conductivity of membranes.

Sample Name	IEC (meq/g)	DS (%)	Water uptake (%)	Conductivity (mS/cm)
A	0.41	10.60	17.40	39
B	0.50	13.15	26.10	22
C	0.53	13.94	28.20	35
D	0.23	5.84	9.60	0.033
E	0.14	3.68	20.20	0.024
F	0.20	5.21	15.30	18
G	0.53	13.72	20.80	10
H	0.75	19.64	85.50	0.009
Nafion®	0.91	–	35.00	60



expected a higher IEC and water uptake for membranes under longer durations, degradation due to long exposure may have resulted into less integration and therefore lesser water uptake compared to their previous membranes.

Sulfonation at 65 °C also showed an increasing trend of water uptake. As much as this is preferred, very high values resulted in excessive swelling in membranes which is undesirable due to mechanical frailty of the respective membrane. Membranes sulfonated for 45 min at 65 °C yielded a much higher water uptake compared to that of Nafion® resulting from the fact that the structure of the polyphosphazene is originally a hydrophilic structures due to its backbone<sup>[28]</sup> and sulfonation process in addition also increases hydrophilicity of the membrane.

### Proton conductivity of the sulfonated membranes out of polymer

P1 is given in Table 2. High performance of PEM fuel cell membranes requires careful tuning of the sulfonation processes to achieve sufficient water uptake, high conductivity, and mechanical integrity. Within the common knowledge of such practices, extended sulfonation durations increases the number of SO<sub>3</sub>H groups incorporated in the polymer structure which translate to higher IEC hence higher conductivity values. However, the contrary is observed with membrane A (0.41 meq/g) which showed higher conductivity values compared to B (0.50 meq/g) and C (0.53 meq/g) despite the higher IEC values for the latter samples. Comparison of the loss modulus data of samples B and E from the DMA analysis (Figure 10 (b)) has shown appearance of a distinct second peak as the sulfonation time is increased, which may be attributed to phase separation in the polymer structure. This is therefore anticipated to result in presence of both conductive and non-conductive domains in the membrane structure. Subsequently this may affect the mass transport and hence the ion mobility negatively, thereby causing the conductivity to decrease despite the high degree of sulfonation in B and C. Careful tuning of the sulfonation conditions is therefore of paramount importance to achieve a compromised mechanical integrity and conductivity of membranes. Additionally, it was observed that longer durations (90 min and more for RT and 45 min for 65 °C) yielded poor conductivity values which may be linked to polymer degradation and increased water uptake which result in loss of mechanical integrity despite the high levels of sulfonic acid groups available.

Although the synthesized membranes exhibited lower proton conductivity (highest value obtained is 39 mS cm<sup>-1</sup>) than that of Nafion® (60 mS cm<sup>-1</sup> measured at the same conditions), these membranes are still promising for fuel cell application according to our previous results with (radiation grafted membranes with a maximum proton conductivity of 40 mS cm<sup>-1</sup> and encouraging fuel cell performance.<sup>[6a,c-h]</sup>

## Conclusion

We successfully synthesized and characterized three novel polyphosphazene derivatives with varying amount of *m*-tolylxy- and 4-pyridinoxy- side groups. The syntheses of these polymers were confirmed by basic spectroscopic techniques. High quality polyphosphazenes with narrow polydispersity and rather low *T<sub>g</sub>* values were successfully prepared. As prepared polymers were sulfonated under various sulfonation conditions and the synergic effect of the side group heteroatom on the proton conductivity of the proton exchange membranes were investigated. It was determined that fuel cell relevant properties of membranes can be tuned by changing sulfonation conditions. Hydrolytically stable PEMs with high thermal, mechanical and chemical stabilities, and proton conductivity, IEC and water uptake comparable with commercial Nafion membranes were achieved.

## Supporting Information Summary

Details of experimental procedures for the syntheses and characterizations of polyphosphazenes, the characterization of fuel cell related membranes, corresponding references are provided in supporting information.

## Acknowledgements

We acknowledge the financial support of The Scientific and Technological Research Council of Turkey (TUBITAK) (Project number: 210T045) for the grant provided.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Aryloxy Phosphazene · Heteroatom · Sulfonation · Membrane

- [1] S. J. Paddison, *Annu. Rev. Mater. Res.* **2003**, *33*, 289–319.
- [2] a) M. Watanabe, H. Uchida, H. Igarashi, *Macromol. Symp.* **2000**, *156*, 223–230; b) V. Tricoli, N. Carretta, M. Bartolozzi, *J. Electrochem. Soc.* **2000**, *147*, 1286–1290; c) D. Rivin, C. E. Kendrick, P. W. Gibson, N. S. Schneider, *Polymer* **2001**, *42*, 623–635.
- [3] J. Roziere, D. J. Jones, *Annu. Rev. Mater. Res.* **2003**, *33*, 503–555.
- [4] B. Smitha, S. Sridhar, A. A. Khan, *J. Membr. Sci.* **2005**, *259*, 10–26.
- [5] B. P. Tripathi, V. K. Shahi, *Prog. Polym. Sci.* **2011**, *36*, 945–979.
- [6] a) L. Gubler, N. Prost, S. A. Gursel, G. G. Scherer, *Solid State Ionics* **2005**, *176*, 2849–2860; b) L. Gubler, S. A. Gursel, G. G. Scherer, *Fuel Cells* **2005**, *5*, 317–335; c) S. A. Gursel, Z. Yang, B. Choudhury, M. G. Roelofs, G. G. Scherer, *J. Electrochem. Soc.* **2006**, *153*, A1964–A1970; d) L. Gubler, H. B. Youcef, S. A. Gursel, A. Wokaun, G. G. Scherer, *J. Electrochem. Soc.* **2008**, *155*, B921–B928; e) S. A. Gursel, L. Gubler, B. Gupta, G. G. Scherer, *Fuel Cells I* **2008**, *215*, 157–217; f) H. Ben youcef, L. Gubler, S. A. Gursel, D. Henkensmeier, A. Wokaun, G. G. Scherer, *Electrochem. Commun.* **2009**, *11*, 941–944; g) L. I. Sanli, S. A. Gursel, *J. Appl. Polym. Sci.* **2011**, *120*, 2313–2323; h) L. I. Sanli, S. Tas, Y. Yurum, S. A. Gursel, *Fuel Cells* **2014**, *14*, 914–925; i) M. M. Nasef, S. A. Gursel, D. Karabelli, O. Güven, *Prog. Polym. Sci.* **2016**, *63*, 1–41.
- [7] a) R. Wycisk, P. N. Pintauro, *J. Membr. Sci.* **1996**, *119*, 155–160; b) Q. H. Guo, P. N. Pintauro, H. Tang, S. O'Connor, *J. Membr. Sci.* **1999**, *154*, 175–181; c) H. Tang, P. N. Pintauro, *J. Appl. Polym. Sci.* **2001**, *79*, 49–59.

- [8] H. R. Allcock, *Chemistry and Applications of Polyphosphazenes*, John Wiley & Sons, New Jersey, **2003**.
- [9] S. Ganapathiappan, K. Chen, D. F. Shriver, *Macromolecules* **1988**, *21*, 2299–2301.
- [10] A. K. Andrianov, A. Marin, J. Chen, J. Sargent, N. Corbett, *Macromolecules* **2004**, *37*, 4075–4080.
- [11] a) H. R. Allcock, R. J. Fitzpatrick, L. Salvati, *Chem. Mater.* **1991**, *3*, 1120–1132; b) E. Montoneri, M. Gleria, G. Ricca, G. C. Pappalardo, *Macromol. Chem. Phys.* **1989**, *190*, 191–202; c) E. Montoneri, M. Gleria, G. Ricca, G. C. Pappalardo, *J. Macromol. Sci. Pure Appl. Chem.* **1989**, *A26*, 645–661; d) H. Tang, P. N. Pintauro, Q. H. Guo, S. O'Connor, *J. Appl. Polym. Sci.* **1999**, *71*, 387–399.
- [12] R. Wycisk, P. N. Pintauro, *Fuel Cells li* **2008**, *216*, 157–183.
- [13] a) C. Genies, R. Mercier, B. Sillion, R. Petiaud, N. Cornet, G. Gebel, M. Pineri, *Polymer* **2001**, *42*, 5097–5105; b) J. H. Fang, X. X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules* **2002**, *35*, 9022–9028.
- [14] a) Q. F. Li, J. O. Jensen, R. F. Savinell, N. J. Bjerrum, *Prog. Polym. Sci.* **2009**, *34*, 449–477; b) S. Yu, B. C. Benicewicz, *Macromolecules* **2009**, *42*, 8640–8648; c) A. Verma, K. Scott, *J. Solid State Electrochem.* **2010**, *14*, 213–219.
- [15] G. A. Carriedo, F. J. G. Alonso, A. Presa-Soto, *Eur. J. Inorg. Chem.* **2003**, 4341–4346.
- [16] a) B. Wang, E. Rivard, I. Manners, *Inorg. Chem.* **2002**, *41*, 1690–1691; b) J. Paulsdorf, N. Kaskhedikar, M. Burjanadze, S. Obeidi, N. A. Stolwijk, D. Wilmer, H. D. Wiemhofer, *Chem. Mater.* **2006**, *18*, 1281–1288.
- [17] H. R. Allcock, S. D. Reeves, C. R. de Denus, C. K. Crane, *Macromolecules* **2001**, *34*, 748–754.
- [18] H. R. Allcock, M. N. Mang, A. A. Dembek, K. J. Wynne, *Macromolecules* **1989**, *22*, 4179–4190.
- [19] a) P. N. Pintauro, H. Tang, Tulane Educational Fund, USA; Administrators of the Tulane Educational Fund . **2000**, p. 49 pp; b) Y. Kurachi, M. Kajiwara, *J. Mater. Sci.* **1991**, *26*, 1799–1802.
- [20] in *Chlorosulfonic Acid: A Versatile Reagent* (Ed.: R. J. Cremlyn), The Royal Society of Chemistry, **2002**, pp. 35–145.
- [21] X. G. Jin, M. T. Bishop, T. S. Ellis, F. E. Karasz, *Brit. Polym. J.* **1985**, *17*, 4–10.
- [22] M. Gleria, R. De Jaeger, Editors, *Phosphazenes: A Worldwide Insight*, Nova Science Publishers, Inc., **2004**.
- [23] S. M. J. Zaidi, *Arab J Sci Eng* **2003**, *28*, 183–194.
- [24] M. Eikerling, A. Kulikovskiy, *Polymer Electrolyte Fuel Cells: Physical Principles of Materials and Operation*, CRC Press, **2014**.
- [25] S. A. Gursel, J. Schneider, H. Ben Youcef, A. Wokaun, G. G. Scherer, *J. Appl. Polym. Sci.* **2008**, *108*, 3577–3585.
- [26] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587–4611.
- [27] R. Naim, A. F. Ismail, H. Saidi, H. Saion, in *Regional Symposium on Membrane Science and Technology* Puteri Pan Pacific Hotel, Johor Bharu, Malaysia, **2004**.
- [28] H. R. Allcock, L. B. Steely, A. Singh, *Polym. Int.* **2006**, *55*, 621–625.

Submitted: October 13, 2021

Accepted: January 4, 2022