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Graphical abstract

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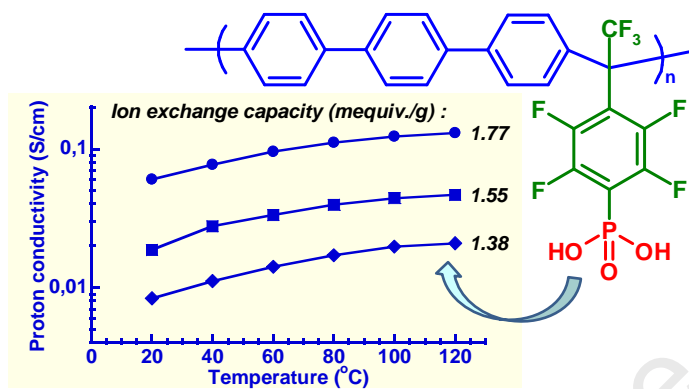
Durable and highly proton conducting poly(arylene perfluorophenylphosphonic acid) membranes

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ABSTRACT: Phosphonated aromatic polymers show several important advantages as proton exchange membranes (PEMs), including high thermal and chemical stability. However, the conductivity needs to be significantly enhanced for most electrochemical applications. Here, we have prepared a series poly(*p*-terphenyl perfluoroalkylene)s functionalized with highly acidic perfluorophenylphosphonic acid by first carrying out triflic acid mediated polyhydroxylations of *p*-terphenyl, 2,2,2-trifluoroacetophenone and perfluoroacetophenone. Subsequently, the resulting polymers were quantitatively and selectively phosphonated in the *para* positions of the pendant perfluorophenyl units by employing an efficient Michaelis-Arbuzov reaction. X-ray scattering of proton exchange membranes (PEMs) based on the phosphonated polymers showed efficient ionic clustering with the interdomain distance depending on the acid content of the polymer. Although the water uptake and swelling was moderate (even at high temperature) the PEMs showed high proton conductivity, up to 111 mS cm^{-1} at 80 °C fully hydrated, and reaching 4 mS cm^{-1} at 50% RH at the same temperature. This may be ascribed to the distinct phase separation and high acidity of the polymers. The stability of the PEMs was excellent with thermal decomposition only above ~400 °C. Moreover, no change in weight, appearance or molecular structure was detected after 5 h immersion in Fenton's reagent at 80 °C, demonstrating an excellent chemical resistance of the PEMs towards free-radical attack. The radical resistance of the present phosphonated PEMs

was found to increase with the acid content, which is contrast to corresponding sulfonated PEMs. The combination of high thermochemical stability and high conductivity implies that the present materials are attractive for use as ionomers in catalyst layers and as PEMs in fuel cells and water electrolyzer applications.

Keywords: proton exchange membranes; fuel cells; phosphonic acid; proton conductivity; stability against radicals; polyhydroxyalkylation

1. Introduction

Polymeric proton exchange membranes (PEMs) are crucial components of many electrochemical devices such as fuel cells, electrolyzer cells and flow batteries operating under acidic conditions [1-3]. The key functions of the PEM are to physically separate the electrodes and the respective reactants and to facilitate efficient transport of the charge carrier (H^+) to enable the electrochemical reactions. PEMs generally consist of sulfonated polymers such as the archetypal Nafion[TM] which features a polytetrafluoroethylene backbone with pendant perfluoroether side chains terminated by sulfonic acid [4]. This molecular structure gives many advantageous properties such as high chemical stability, acidity and efficient clustering of the acid units to provide high conductivity. Still, Nafion[TM] also have drawbacks including sensitivity towards mechanical creep above 80 °C, poor barrier properties leading to crossover of reactants, and a high price [5]. This has motivated an extensive research for alternative PEMs, mainly based on sulfonated aromatic hydrocarbon polymers [5-7]. In addition, phosphonated PEMs have received considerable attention as an alternative to the sulfonated counterparts because of a number of distinct advantages [8-18]. In comparison to sulfonated PEMs, corresponding phosphonated ones generally possess for example improved thermal and chemical stability, reduced water swelling and decreased fuel permeability [8]. Moreover, aryl and alkyl phosphonic acids are generally amphoteric and strongly hydrogen

2

bonding, and show a considerably degree of self-dissociation, giving rise to anhydrous proton conductivity in highly concentrated systems at elevated temperatures [18-25]. Still, the rather low acidity of the phosphonic acid leads to a lower water uptake and conductivity in comparison with corresponding sulfonated PEMs [25]. However, the conductivity of phosphonated PEMs can be significantly improved by synthesizing polymers with high concentrations of phosphonic acid,[26-28] or by employing perfluorophosphonic acids with enhanced acidity [29-32].

In general, aromatic polymers are more challenging to phosphonate than to sulfonate [8]. The majority of phosphonated aromatic polymers have been synthesized through classical Michaelis-Arbuzov reactions, i.e., nucleophilic substitutions involving a trialkyl phosphite and benzyl or alkyl halide groups in the polymer structure [10, 33]. In contrast, aryl halides are usually less reactive and thus a Pd catalyst is generally employed to directly phosphonate aromatic rings. However, Pd-catalyzed Michaelis-Arbuzov reactions are often incomplete, leaving residual, potentially harmful aryl halide groups in the polymer structure [8, 25]. Another route to aryl-phosphonated polymers proceeds via Michaelis-Arbuzov reactions between tris(trimethylsilyl)phosphite and perfluoroaromatic polymers. The fluorine atom in the *para* position of the perfluorophenyl moieties is highly activated by nearby electron-withdrawing fluorine atoms and readily undergoes the aromatic nucleophilic substitution. This has previously been exploited in the efficient phosphonation of pentafluorostyrene homopolymers [34] and copolymers [30, 31].

We have recently reported on a series of PEMs based on poly(*p*-terphenyl perfluorophenylsulfonic acid)s [35]. These polymers were prepared in metal-free superacid catalyzed Friedel-Crafts type polycondensations of *p*-terphenyl and 2,2,2-trifluoroacetophenone and perfluoroacetophenone. The resulting poly(*p*-terphenyl perfluorophenyl)s were then sulfonated in the *para* position of the fluorophenyl ring by a

quantitative and selective thiolation-oxidation process to obtain the target materials. The PEMs showed effective ionic clustering, moderate water uptake, remarkable radical resistance and high conductivity [35]. In the present work we have employed the same precursor polymers to prepare a series of phosphonated poly(p-terphenyl perfluorophenyl)s through Michaelis-Arbuzov reactions with tris(trimethylsilyl)phosphite followed by hydrolysis. Just as in the case of the sulfonated polymers, the substitution of the F atoms in the *para* position was complete and selective. Hence, the two series of polymers were functionalized with the same concentration of acid groups in the same position of the identical polymer structure. This allows a direct comparison and benchmarking of phosphonic acid *versus* sulfonic acid in PEMs when it comes to, e.g., morphology, stability and conductivity. This comparison is rarely possible because the typical differences in sulfonation and phosphonation reactions gives variations when it comes to how and where the acid groups are incorporated in the polymer structure. After casting the phosphonated PEMs were studied with respect to morphology, water uptake, proton conductivity, thermal stability and resistance against radical attack.

## 2. Results and discussion

2.1. Polymer synthesis and characterizations

Four poly(arylene perfluorophenylphosphonic acid)s with varying ion exchange capacity (IEC) were successfully synthesized according to Scheme 1. First, a series of poly(p-terphenyl perfluorophenyl) precursor polymers were synthesized by straightforward Friedel–Crafts type polyhydroxyalkylations of commercially available p-terphenyl (pTP), perfluoroacetophenone (PFAp) and 2,2,2-trifluoroacetophenone (TFAp) in super-acidic media, as described previously [35]. The composition of the resulting precursor polymers was conveniently controlled by balancing the PFAp : TFAp ratio in the monomer feed. The samples were
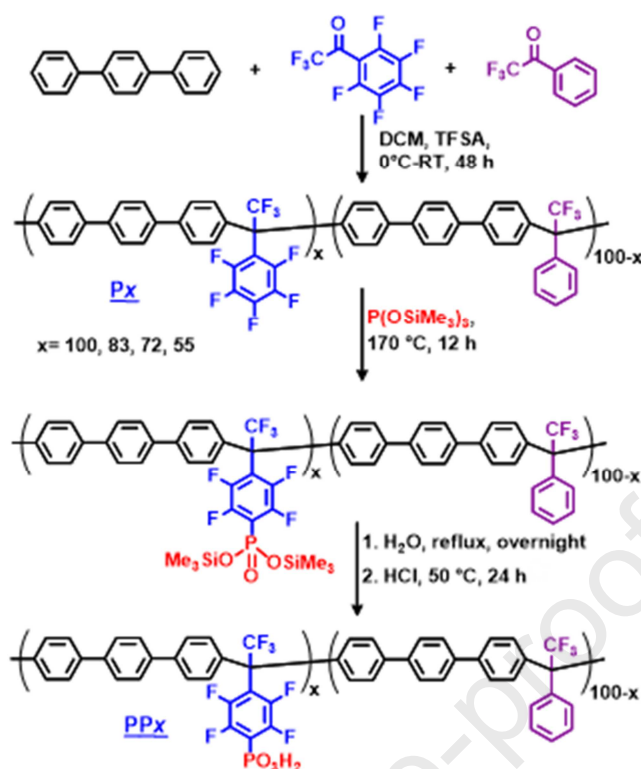
designated P*x*, with *x* = 55, 72, 83 and 100, denoting the mol% of PFAp residues in the respective polymers [36]. Hence, homopolymer P100 was result of the polymerization of only pTP and PFAp with no TFAp added. The chemical structure of the precursor polymers was confirmed by ^{1}H and ^{19}F NMR spectroscopy (Fig. 1a and c). The possibility of preparing copolymers with varying compositions enabled control of the acid content and fine-tuning of the properties of the final phosphonated PEMs. In general, the high chain rigidity combined with the alkylene units of the polymer backbone resulted in excellent solubility and film forming ability, as well as high thermal stability and high glass transition temperature (T_g). The series of P*x* precursor polymers decomposed only above $T_{d, onset}$ = 414 - 422 °C and no glass transition was detected below 400 °C, as revealed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively [35].

Scheme 1. Synthetic pathway to the poly(arylene perfluorophenylphosphonic acid)s in the PP*x* series by superacid-mediated polycondensation, phosphonation *via* a Michaelis-Abuzov reaction and hydrolysis.
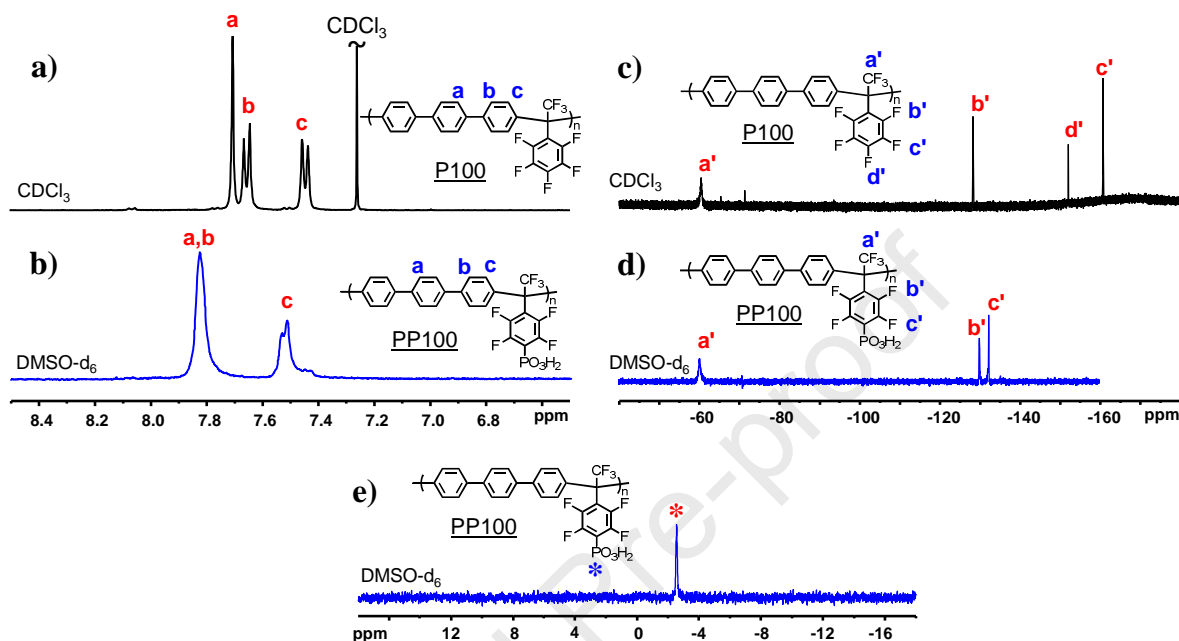
Using a previously reported method [34] after modification, the series of precursor P*x* were converted to the poly(*p*-terphenyl perfluorophenylphosphonic acid)s (denoted PP*x*) by the introduction of trimethylsilyl ester groups, followed by a hydrolysis of the ester intermediates to yield the desired PP*x* series of polymers in the acid form (Scheme 1). In the first step, a selective displacement of the F atoms in the *para* position to the phosphonate ester groups was achieved by a Michaelis-Abuzov reaction with tris(trimethylsilyl)phosphite (TSP) at 170 °C. Because the fluorine atoms in the *para* position are highly activated by neighboring electron-withdrawing fluorines, they readily undergo nucleophilic substitution with the phosphite. The reaction was highly selective as confirmed by ^{19}F NMR spectroscopy (Fig. 2b). The volatile byproduct fluorotrimethylsilane formed gas bubbles and quickly left the reaction mixtures, thus shifting the equilibrium towards the formation of the desired trimethylsilyl phosphonate esters.

Fig. 1. ^{1}H (a, b), ^{19}F (c, d) and ^{31}P (e) NMR spectra of P100 and PP100 indicating quantitative and selective phosphonation at the *para* positions of the perfluorophenyl groups (spectra of P100 and PP100 recorded using CDCl$_3$ and DMSO-d_6, respectively).

Because of the low solubility of the Px polymers in TSP, a large excess of TSP (15-25 eq.) and a 12 h reaction period were employed to ensure complete conversion. In the second step, the resulting ester intermediates were first partly converted to phosphonic acids under reflux in water. According to previous reports, the hydrolysis of, e.g., trimethylsilyl ester derivatives of polypentafluorostyrene is straightforward and a reflux in water during 5 min is usually sufficient [35]. However, in the present case complete hydrolysis was more difficult because of the high T_g and low water uptake of the PPx ester derivatives, even at high temperature. Consequently, an additional treatment with HCl solution at 50 °C overnight was necessary to ensure complete hydrolysis. After this procedure, a quantitative and selective conversion of Px to PPx was confirmed by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy (Fig. 1 and 2). Hence, the signal arising from the fluorine atoms in the *para* position (*d'*) completely disappeared in the ^{19}F spectra (Fig. 1c and d, Fig. 2b) and instead a signal (*) from the phosphonic group appeared in the ^{31}P spectra (Fig. 1e).
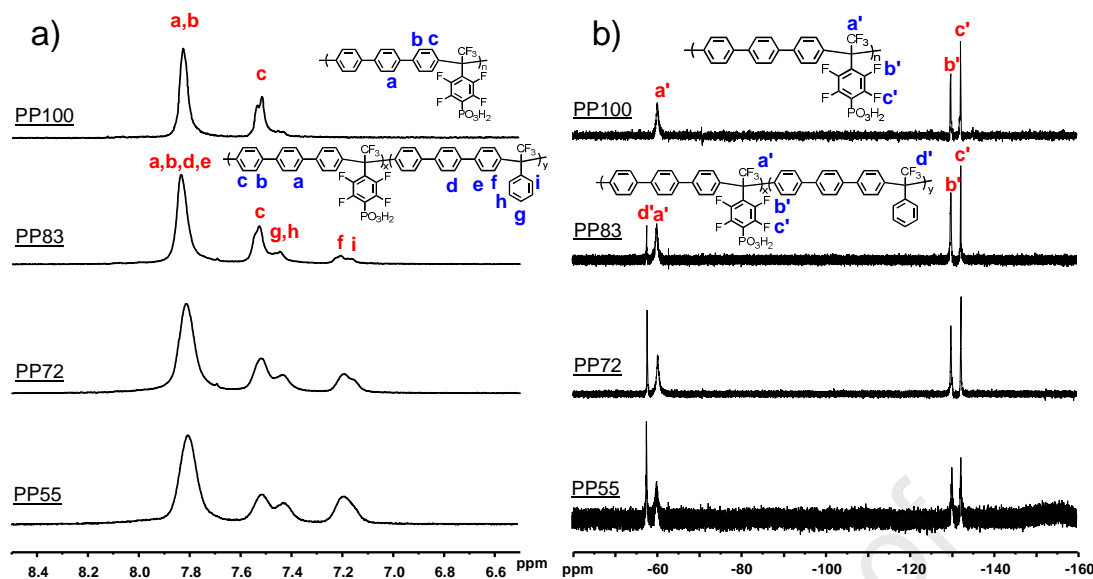
Fig. 2. ^{1}H (a) and ^{19}F (b) NMR spectra of the PPx polymers.

2.2. Membrane preparation & morphology

Transparent and flexible PEMs were prepared by solvent casting the PPx polymers from 10 wt% polymer solutions in dimethyl sulfoxide (DMSO). To ensure complete conversion to the acidic form, the membranes were conditioned in boiling 1 M aq. H$_2$SO$_4$ solution for 2 h, and then washed thoroughly with boiling water to remove excess acid until the water reached neutral pH. Throughout the present work, the properties of the phosphonated PEMs in the PPx series will be compared with those of the corresponding series of sulfonated PEMs (denoted SPx, where x gives the mol% of sulfonated PFAp residues) based on the same Px precursor polymers [35]. In contrast to the SPx PEMs, which were flexible when humidified but more brittle when dried, the PPx membranes retained an excellent flexibility also in the dry state (Fig. 3). The IEC of the PPx PEMs measured by acid-base titration was quite close to the theoretical values obtained from ^{1}H NMR spectra (Table 1), assuming that the perfluorophenylphosphonic acid is a monoprotic acid in the titrations. This further confirmed the completness of the phosphonation and hydrolysis reactions.
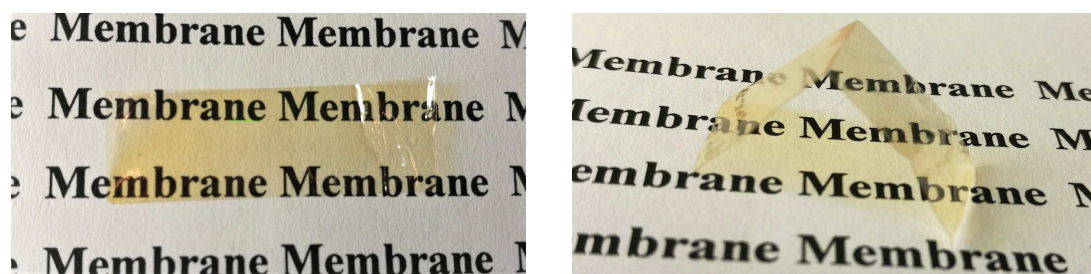
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Fig. 3. Photographs of a PP100 PEM showing its transparency and foldability.

The morphology of the phosphonated PEMs in dry state was studied by small angle X-ray scattering (SAXS) measurements and the results are displayed in Fig. 4. As can be seen in the figure, PP100 showed an intense ionomer peak, as expected from its high ionic content, well-defined polymer structure and precise ionic sequencing along the polymer backbone. As the ionic content decreased, the scattering intensity decreased and the characteristic interdomain distance *d* increased. This is consistent with the expected decrease in domain size and/or decrease in the domain concentration in the PEMs. The *d* values of PP100, -83, -72 and -55 were 21, 21, 22, 24 Å, respectively (Table 1). These values appoximately correspond with the distance between two neighboring phosphonic acid groups (19 Å), as calculated from the chemical structure. The results show that the phosphonic acid groups cluster efficiently to induce the phase separation necessary to form a percolating hydrated phase for high conductivities [5, 6]. The SAXS results

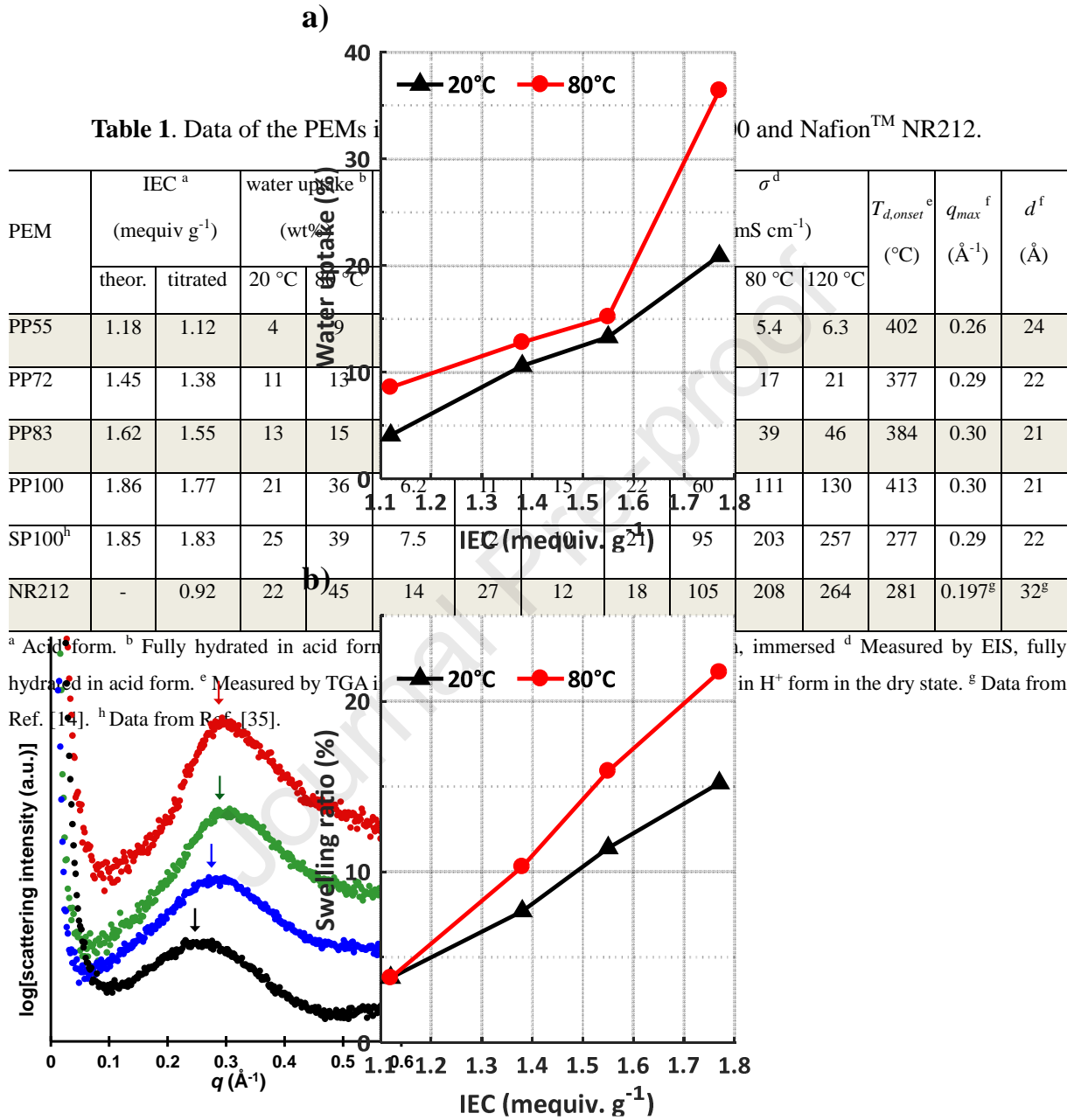are also similar to those of the corresponding SP*x* series of PEMs [35].

a)

Table 1. Data of the PEMs in the PP*x* series, SP100 and Nafion[TM] NR212.

PEM	IEC [a] (mequiv g^-1) theor.	titrated	water uptake [b] (wt%) 20 °C	80 °C		σ [d] (mS cm^-1) 80 °C	120 °C	$T_{d,onset}$ [e] (°C)	q_{max} [f] (Å^-1)	d [f] (Å)
PP55	1.18	1.12	4	9		5.4	6.3	402	0.26	24
PP72	1.45	1.38	11	13		17	21	377	0.29	22
PP83	1.62	1.55	13	15		39	46	384	0.30	21
PP100	1.86	1.77	21	36		111	130	413	0.30	21
SP100 [h]	1.85	1.83	25	39	7.5	95	203	257	277 0.29	22
NR212	-	0.92	22	45	14	27	12 18	105 208 264	281	0.197 [g] 32 [g]

[a] Acid form. [b] Fully hydrated in acid form ... immersed [d] Measured by EIS, fully hydrated in acid form. [e] Measured by TGA i... in H^+ form in the dry state. [g] Data from Ref. [14]. [h] Data from Ref. [35].

b)

Fig. 4. SAXS profiles of the PEMs in the PP*x* series measured in the dry state..

2.3. Water uptake and hydroxide conductivity

Fig. 5. Water uptake (a) and through-plane swelling (b) of the PP*x* PEMs as function of IEC.

The water uptake and swelling ratio of fully hydrated PEMs were determined at 20 and 80 °C. (Table 1, Fig. 5a). As expected, the water uptake, λ values and swelling ratio increased with the temperature and IEC. Membrane PP100, with the highest IEC, reached the highest water uptake with 21 and 36 wt% at 20 and 80 °C, respectively. Meanwhile, at 20 °C the water uptake of PP55, -72 and -83 was only 4, 11 and 13 wt%, respectively. When the temperature was increased to 80 °C, the values increased slightly but remained low at 9, 13 and 15 wt%, respectively. The through-plane swelling was highest for PP100, reaching 15 and 22% at 20 and 80 °C, respectively, and degree of swelling then decreased linearly with IEC as seen in Fig. 5b. In comparison with the PEMs in the SP*x* series having similar IEC values, PP55, -72 and -83 had significantly lower water uptake and λ values. Only PP100 displayed similar (slightly lower) water uptake as the sulfonated counterpart (SP100, Table 1). While PP100 had similar water uptake as NR212, the λ values of the former was much lower due to the its higher IEC. The low level of water uptake compared to sulfonated membranes is typical for phosphonic acid-functionalized PEMs [25]. This behavior can be explained by the lower acidity and extensive intrinsic hydrogen bonding of the phosphonic acid groups, which leaves few acid sites available for hydrogen bonding with water [25]. Furthermore, the intrinsic hydrogen bonding also increases T_g which further restricts the water uptake.

A sufficient water uptake is crucial for the formation of a percolating network of water-filled channels to facilitate the transport of the protons. Given the efficient ionic clustering and moderate water uptake (low λ values), the PEMs in the PPx series were efficient proton conductors. At 120 °C under fully hydrated conditions, PP100 reached very high proton conductivity, e.g., 60, 111 and 130 mS cm^{-1} at 20, 80 and 120 °C, respectively (Fig. 6). As expected, the conductivity decreased with decreasing IEC value and water uptake. At 120 °C, fully hydrated PP55, -72 and -83 PEMs reached 6.3, 21 and 46 mS cm^{-1}, respectively. In comparison, the conductivity of a recently reported non-fluorinated aryl-phosphonated poly(ether sulfone) with IEC = 2.75 mequiv g^{-1} under fully hydrated conditions reached just above 7.5 and 25 mS cm^{-1} at 20 and 80 °C, respectively [17]. The significantly higher conductivity of PP83 and PP100, despite lower IEC values, can most probably be ascribed to the efficient ionic clustering and the higher acidity of the perfluorophenylphosphonic acid. The present conductivity values may also be compared with previous results on PEMs functionalized with perfluorophenyl phosphonic acid. For example, a triblock copolymer with a central polysulfone block and flanking blocks of phosphonated polypentafluorostyrene (IEC = 2.3 mequiv g^{-1}) had a conductivity of 80 mS cm^{-1} fully hydrated at 80 °C [27]. Still, the conductivity of the present PEMs was significantly lower than the corresponding perfluorophenylsulfonated materials due to the considerably lower water uptake and acidity of the perfluorophenylphosphonated materials. For example, SP100 reached 203 mS cm^{-1} at 80 °C fully hydrated (Table 1) [35]. The apparent activation energy of the proton conductivity (E_a) was between 7.5-9.8 kJ mol^{-1} for the membranes in the PPx series, which was quite similar to the sulfonated PEMs in the SPx series (9.6-10.0 kJ mol^{-1}) and NR212 (9.0 kJ mol^{-1}). These values are close to those of approximately 9 kJ mol^{-1} previously measured on Nafion 117 and Flemion membranes under fully hydrated conditions [37]. This indicates that the

proton conductivity occurs by both Grotthuss and vehicle mechanisms in all these perfluoroacid PEMs [6].
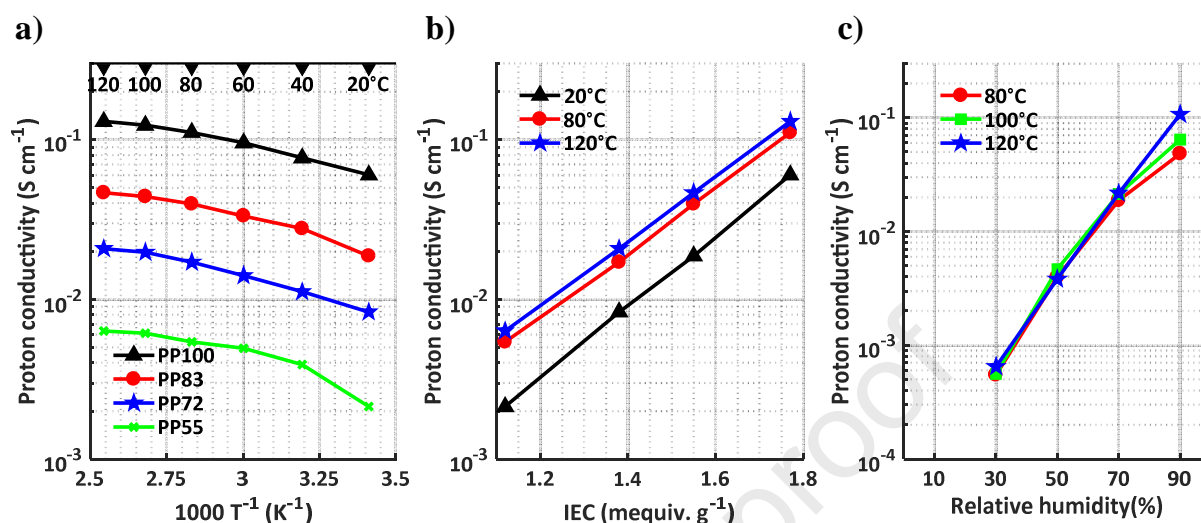
Flemion Fig. 6. Proton conductivity of the fully hydrated PEMs in the PP*x* series as function of temperature (a) and IEC (b) and proton conductivity of PP100 as function of relative humidity (c).

The proton conductivity of PP100 was also measured under reduced humidity in the range 30-90% relative humidity (RH) at 80, 100 and 120 °C, respectively (Fig. 6c). At 80 °C, the conductivity was 0.55, 4.0, 19 and 48 mS cm^{-1} under 30, 50, 70 and 90% RH, respectively. Notably, between 30 and 70% RH the conductivity reached very similar values regardless of temperature, while the temperature dependence was notable at 90% RH (Fig. 6c). At this humidity, the values increased from 48 to 64 and 110 mS cm^{-1} when the temperature increased from 80 to 100 and 120 °C, respectively. Conductivity data of phosphonated PEMs measured under reduced humidity are very scarce, but the performance of PP100 can be compared with results reported for poly(1,3-phenylene-5-phosphonic acid) by Kreuer and coworkers [38]. This polymer reached 6 mS cm^{-1} at 115 °C and 1 atm water vapor pressure (corresponding to 60% RH). However, the very high IEC made it water soluble and hence unsuitable for use as a PEM.
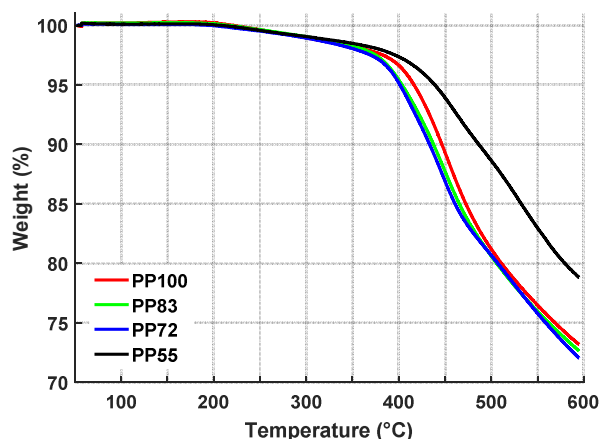
2.4. Thermal stability and radical resistance

13

Fig. 7. TGA profiles of PEMs recorded under N_2 atmosphere.

The thermal stability of the PPx membranes was studied by thermogravimetric analysis (TGA) under N_2 atmosphere (Fig. 7). The small weight loss (~2%) at approximately 200 °C most probably originated from evaporation of water formed through phosphonic acid anhydride formation. However, this process is reversible because the P-O-P bonds formed during the heat treatment may be readily hydrolyzed to restore the phosphonic acids when immersing the PEMs in water [19, 26]. The decomposition temperature $T_{d,onset}$ was determined as the onset of the irreversible weight loss occurring at around 400 °C. Hence, the PEMs in the PPx series displayed excellent thermal stability, with $T_{d,onset}$ between 377 and 412 °C. These values were slightly lower compared to the respective Px precursors (414-422 °C) but were significantly higher than the corresponding PEMs in the SPx series (277-284 °C) [35], most probably because of the higher stability of the C-P bond. The temperature range of $T_{d,onset}$ was quite narrow and there was no clear connection between the composition of the polymers and $T_{d,onset}$.

14

a)   **Before**   **After 5 h**

PP55   PP72   PP83   PP100   PP55   PP72   PP83   PP100

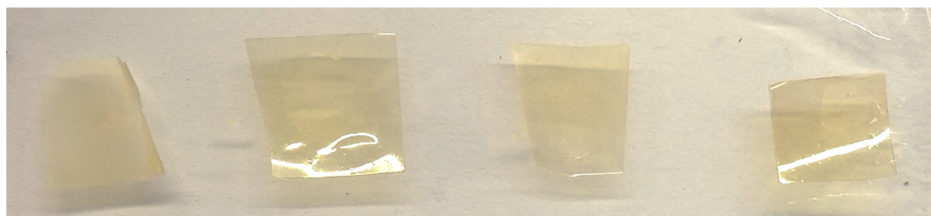**b)**   **After 260 h**

Fig. 8. Photographs showing the different PP*x* membrane samples after treatment in Fenton's reagent at 80 °C for a) 5 h and b) 260 h (note that different sample pieces were studied after these two storage times).

Low radical resistance and oxidative stability are serious obstacles against the commercialization of non-perfluorinated PEMs. In this context, the use of PEMs functionalized with phosphonic acids is beneficial as these have typically higher oxidative stability than the corresponding sulfonated SP*x* membranes [35]. In the current work, the oxidative stability of PP*x* was studied *ex situ* by immersing the PEM samples in Fenton's reagent (aq. solution containing 3% H_2O_2 and 2 ppm of Fe^{2+}). After 1 and 5 h immersion in Fenton's reagents at 80 °C, no weight loss or change in appearance was observed (Fig. 8a), suggesting an excellent chemical resistance of the PEMs toward free-radical attack. In addition, no structural changes were detected after by ^{1}H NMR analysis (Fig. 9). After immersion in Fenton's reagents during 11 days, none of the membranes fully dissolved (Fig. 8b). The change for PP55 was most obvious, this sample became very brittle and turned opaque, and the edges of the sample partly disintegrated. In contrast, the other PEMs in the series retained their shape with all edges intact. Samples PP83 and 72 turned slightly opaque and became somewhat more brittle but were still easily handled. Notably, PP100 retained its transparency and flexibility and appeared to be the most radical resistant PEM. After the

15

prolonged Fenton test the PP*x* membranes were no longer soluble, possibly due to crosslinking via degradation products. Consequently, it was not possible to analyze the degradation by ^{1}H NMR analysis.
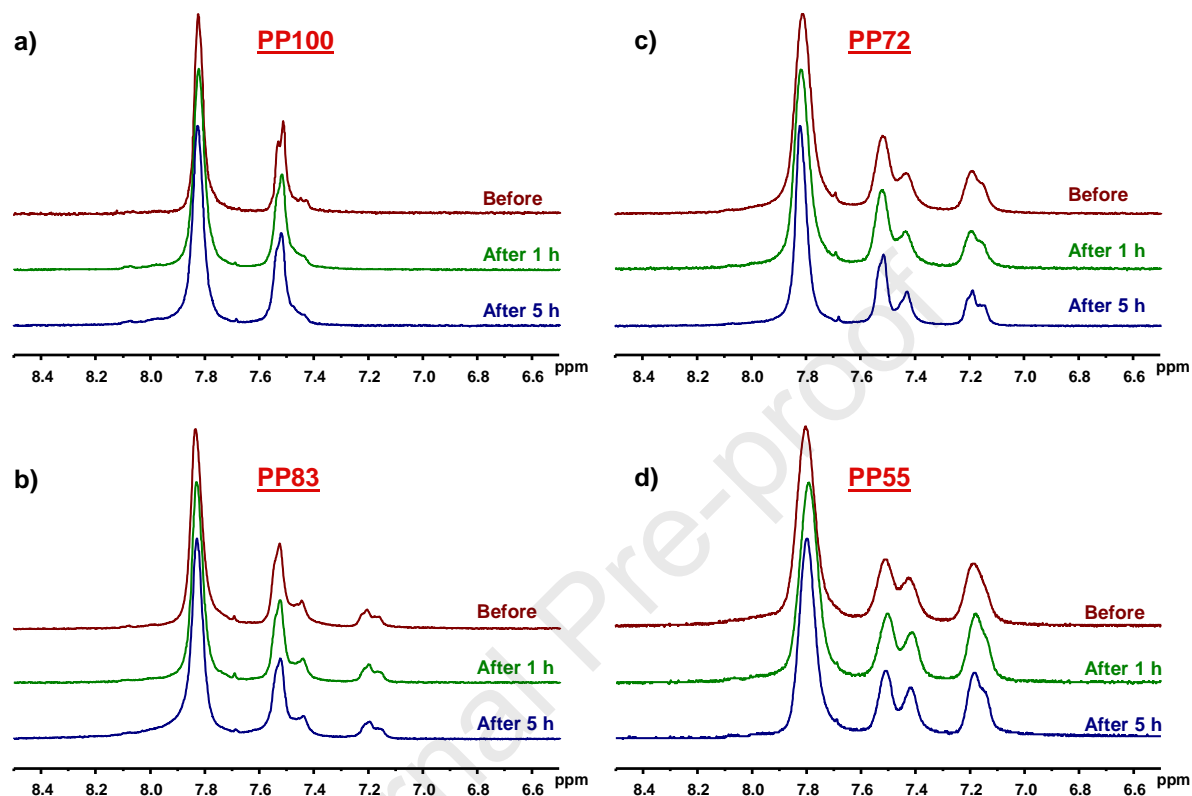

Fig. 9. ^{1}H NMR spectra of PP*x* PEM samples before and after immersion in Fenton's reagents during 1 and 5 h at 80 °C.

Notably, the PEMs in the PP*x* series displayed superior oxidative stability when compared with the corresponding SP*x* membranes, which disintegrated into small pieces already after 24 h immersion in Fenton's reagents at 80 °C [35]. Moreover, while PP100 with the highest IEC value was the most stable in the series of phosphonated membranes, SP100 with the highest IEC in the series of sulfonated membranes showed the lowest stability in that series [35]. This strongly implies that the degradation by radical mechanism is different in the two series.

3. Experimental

3.1. Materials

p-Terphenyl (99+%, Acros), 2,2,2-trifluoroacetophenone (TFAp, 99%, Sigma-Aldrich), perfluoroacetophenone (PFAp, 98%, Matrix Scientific), triflic acid (TFSA, 99%, Acros), methanol (reagent grade, VWR), *N*,*N*-dimethylacetamide (DMAc, 99+%, Sigma-Aldrich), tris(trimethylsilyl)phosphite (TSP, 95%, Sigma-Aldrich), hydrochloric acid (HCl, reagent grade 37%, VWR), tetrahydrofuran (THF, VWR, reagent grade), hexane (VWR, reagent grade), *N*-methyl-2-pyrolidone (NMP, reagent grade, Sigma-Aldrich), chloroform-*d* (99.8% D, Sigma-Aldrich), and DMSO-d_6 (99.96% D, Sigma-Aldrich) were all used as received. Dichloromethane (DCM, Analytical, VWR) was dried over molecular sieves prior to use.

3.2. Synthesis

3.2.1. Polymer synthesis. The preparation of the P*x* precursor polymers has been described previously [35, 36]. In short a 10 mL one-neck round-bottom flask was charged with anhydrous DCM (2.7 ml), *p*-terphenyl (0.46 g, 2 mmol, 1 eq.) and PFAp (1.4 eq.) or mixture of PFAp : TFAp (1.4 eq. in total). The composition of the polymers was controlled by adjusting the PFAp : TFAp molar ratio. The reaction mixture was cooled to 0 °C using an ice bath before TFSA (2.7 mL, 30.8 mmol, 15 eq.) was added dropwise using a dropping funnel. The reaction mixture was then stirred for 30 min at 0 °C followed by 48 h at room temperature. The resulting highly viscous dark-blue, inhomogeneous reaction mixtures were slowly poured into methanol to precipitate the products. Finally, the polymers were washed thoroughly with hot methanol and dried at room temperature under vacuum during 24 h. The average number molecular weight (M_n) of the resulting P55, P72, P83 and P100 precursor polymers were 29.1, 24.8, 18.4 and 87.8 kg mol^{-1}, respectively, while the polydispersity (PDI) values were 1.72, 1.50, 1.46 and 1.84, respectively, as measured by size exclusion chromatography (SEC) in chloroform using polystyrene standards [35].

3.2.2. Phosphonation. A 25 mL two-neck flask equipped with a condenser and a nitrogen inlet was charged with precursor polymer P*x* (0.5 g) and TSP (5 mL). The reaction mixture was stirred at 170 °C for 12 h, then cooled to room temperature and diluted with THF (10 mL). The solution was poured into hexane (100 mL) to yield PP*x* in trimethylsilyl ester form as a white precipitate. The polymer was filtered off, washed with fresh hexane, and dried under vacuum at room temperature for 24 h. The acid form of the phosphonated polymers was obtained by hydrolysis of the ester form in refluxing water overnight. The product was filtered off and treated with aqueous HCl solution (1M, 10 mL) at 50 °C for 24 h. The white product was filtered, washed with water, and dried at 50 °C under vacuum for 24 h.

3.3. Membrane Preparation

All membranes were prepared by casting from 10 wt% polymer solutions in DMSO. The solutions were filtrated through a 5 μm PTFE syringe filter onto a Petri dish (Ø = 5 cm) before casting in a ventilated casting oven at 85 °C for at least 24 h. The membranes were detached from the Petri dishes before soaking in deionized water to remove residual solvent. The membranes were acidified by treating in boiling 1 M H_2SO_4 solution for 2 h, and were then washed with boiling deionized water for 2 h.

3.4. Characterization

^{1}H, ^{19}F and ^{31}P spectra were obtained with Bruker DRX400 spectrometer, using either DMSO-d_6 ($\delta = 2.50$ ppm) or deuterated chloroform (CDCl$_3$, $\delta = 7.26$ ppm) as solvent.

SAXS profiles of the dry PEMs in proton form were obtained in the q-range 0.014-0.75 Å^{-1}, using a SAXSLAB instrument (JJ X-ray Systems Aps, Denmark) equipped with a Pilatus detector.

The thermal stability of the phosphonated polymer membranes was investigated by thermogravimetric analysis (TGA) using a TGA Q500 instrument (TA Instruments). The measurements were performed under nitrogen at a heating rate of 10 °C min^{-1} up to 600 °C. The degradation temperatures ($T_{d,onset}$) were determined at the onset point of the degradation.

Chemical stability was measured by submerging the membranes in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm Fe^{2+}) at 80 °C. The residual weight (RW) was calculated from the dry membrane weight before and after immersion for 1 h. Membrane samples were also dried and analyzed with NMR spectroscopy after 1 h and 5 h immersion.

Water uptake (WU) and thickness swelling (t_{sw}) was calculated based on the weights of membranes in the acid form by using the equation:

$$\text{WU (\%)} = \frac{W_w - W_d}{W_d} \times 100 \qquad (1)$$

$$t_{sw} \text{ (\%)} = \frac{t_w - t_d}{t_d} \times 100 \qquad (2)$$

where W_w and t_w represent the weight and the thickness, respectively, of the wet samples while W_d and t_d represent the weight and the thickness, respectively, of the dried samples. The weights and thickness of dry samples were obtained after drying the membranes under vacuum at 50 °C for at least 24 h. The weights and thicknesses of wet samples were measured after immersing the membranes in water at 20, 40, 60, and 80 °C for 12 h. The excess water was removed from the surface by gently wiping with tissue paper.

The IEC of the membranes in acid form was measured by acid-base titration. The dry membrane was immersed in 1.0 M NaCl solution for 1 day with vigorous stirring to exchange the counter ion from proton to sodium. The released protons were titrated with ~0.01 M

19

NaOH solution (the exact concentration was determined by titration with oxalic acid solution), using phenolphthalein as an indicator.

The proton conductivity of each membrane sample was measured under fully hydrated conditions as a function of temperature. The measurement was performed in a sealed cell (size: 1.4 cm $\times$ 1.4 cm $\times$ 1.0 cm) containing water with the membrane fully hydrated. A two-probe method was used in the range 20 to 120 °C by employing a Novocontrol high-resolution dielectric analyzer V 1.01S in the frequency range 10^0 to 10^7 Hz at 50mV. The proton conductivity of PP100 was also measured at reduced humidity (30, 50, 70 and 90% RH) at 80, 100 and 120 °C. The measurements were carried out by means of a four-probe method using a Gamry potentiostat/galvanostat/ZRA (10^{-1} to 10^6 Hz) equipped with a Fumatech MK3 conductivity cell.

4. Conclusions

We have efficiently phosphonated a series of poly(*p*-terphenyl perfluorophenylphosphonic acid)s prepared by superacid catalyzed Friedel-Crafts type polycondensations involving *p*-terphenyl and perfluoroacetophenone. The Michaelis-Arbuzov phosphonation of the *para* position of the pendant perfluorophenyl groups was both quantitative and selective, resulting in rigid and well-defined polymer backbones functionalized with highly acidic phosphonic acid groups. PEMs based on these polymers showed extensive ionic clustering and very high thermal stability. In addition, analysis of the PEMs after treatment in Fenton's reagent revealed an excellent resistance against radical attack at 80 ^{o}C. Mainly due to the combination of the distinct phase separation (ionic clustering) and the high acidity of the perfluorophenylphosphonic acid, the membranes with the highest IEC values reached high proton conductivities under fully humidified conditions immersed in water. The moderate water uptake, high conductivity and high oxidative stability suggest that poly(*p*-terphenyl

perfluorophenylphosphonic acid) should be useful as ionomers in catalyst layers and as PEMs in fuel cells and water electrolyzer applications, as well as separator materials in redox flow batteries.

CONFLICT OF INTEREST

There are no conflicts to declare.

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Highlights:

- Highly acidic PEMs functionalized with perfluorophenylphosphonic acid
- Backbone synthesized via triflic acid mediated polyhydroxylations
- Efficient phosphonation by metal-free Michaelis-Arbuzov reactions
- High conductivity, up to 111 mS cm^{-1} at 80 °C in fully hydrated state
- Excellent thermal stability and resistance against free-radical attack

Author statement: Durable and highly proton conducting poly(arylene perfluorophenylphosphonic acid) membranes

Na Rae Kang: Methodology, Data curation. **Thanh Huong Pham:** Data curation, Writing-Original draft preparation, Writing - review & editing. **Hannes Nederstedt:** Data curation, Writing - review & editing. **Patric Jannasch:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

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