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Side Chain Engineering of Sulfonated Poly(arylene ether)s for Proton Exchange Membranes

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Abstract Proton conductivity of proton exchange membranes (PEMs) strongly relies on microscopic morphology, which can be modulated by engineering the distribution of ionic groups. Herein, poly(arylene ether)s with densely distributed allyl functionalities are polymerized from a tetra-allyl bisphenol A monomer. The subsequent thiol-ene addition with sodium 3-mercaptopropanesulfonate yields comb-shaped sulfonated fluorinated poly(arylene ether)s (SFPAEs) with ion exchange capacities (IECs) ranging from 1.29 mmol·g⁻¹ to 1.78 mmol·g⁻¹. These SFPAEs exhibit superior proton conductivity over the whole temperature range, which is attributed to the enhanced hydrophilic/hydrophobic phase separation as evidenced by small angle X-ray scattering characterizations. The **SFPAE-4-40** with an IEC of 1.78 mmol·g⁻¹ shows the largest proton conductivity of 93 mS·cm⁻¹ at room temperature under fully hydrated condition, higher than that of Nafion 212. Furthermore, the vanadium redox flow battery (VRFB) assembled with **SFPAE-4-40** separator exhibits higher energy efficiency than the VRFB assembled with Nafion 212.

Keywords Proton exchange membrane; Thiol-ene addition; Side-chain engineering; Phase separation; Vanadium redox flow battery

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INTRODUCTION

Proton exchange membranes (PEMs) have gained application in more and more electrochemical devices recently,^[1–5] where they serve not only as the conducting matrix for protons, but also as the barrier for electrical insulation between the electrodes. Generally, PEMs should meet several basic requirements, such as high proton conductivity, good chemical stability, robust mechanical strength, and low cost.^[6–8] The state-of-the-art PEM is Nafion[®], a perfluorinated ionomer from DuPont, whose sulfonate groups are placed at the end of the long and flexible side chains. These sulfonate groups are capable of self-aggregating into ion-conductive channels for efficient proton transport.^[9,10] However, Nafion[®] suffers from high fuel permeability and manufacturing cost, which limit its wide application.^[11,12] Therefore, lots of works have been devoted to the development of alternative PEMs.

Recently, sulfonated hydrocarbon polymers with nonfluorinated or partially fluorinated rigid backbones, such as sulfonated poly(arylene ether sulfone)s,^[13,14] poly(arylene ether ketone)s,^[15,16] poly(phenylene)s,^[17] polyimides^[18,19] and polybenzimidazoles,^[20] have emerged as low-cost and high-performance alternatives to Nafion[®]. It has been found that the proton conductivities of the randomly sulfonated polymers

are usually low at certain ion exchange capacity, because of the lack of nanophase-separated morphology.^[21,22] To enhance the nanophase separation, many strategies on molecular design have been proposed, such as dense sulfonation at particular segments of polymers or the attachment of lengthy and flexible ionic side chain.^[23–25] Indeed, distinct nanophase separation can be achieved by such design, as evidenced by small-angle X-ray scattering, transmission electron microscopy, or atomic force microscopy, and improved proton conductivity can be obtained.^[26–28]

While many successes have been achieved for high performance PEMs, new synthetic approaches to attach lengthy, especially densely located, ionic side chains for enhanced phase separation are still highly desirable. Previously, we have reported the polymerization of sulfonated fluorinated poly(arylene ether)s (SFPAEs) featuring with (i) low polymerization temperature, (ii) 7 atoms spacing between sulfonic acid group and aromatic backbones, and (iii) two alkyl sulfonate side chains per monomer unit.^[29] To further promote the phase separation, herein, we report the synthesis of a new tetra-allyl bisphenol A monomer and the resulting sulfonated fluorinated poly(arylene ether)s copolymers containing doubled density of alkyl sulfonate side chains per monomer unit compared with the previous ones.

EXPERIMENTAL

Materials

All reactants and solvents were purchased from local chemical

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suppliers and used as received.

Synthesis of Tetra-allyl Bisphenol A (TABPA)

The reaction route to TABPA is shown in Scheme 1. 20 g of (64.8 mmol) di-allyl bisphenol A (DABPA), 17 mL (194.4 mmol) of allyl bromide, 14 g (97.2 mmol) of anhydrous potassium carbonate, 300 mL of *N,N*-dimethylacetamide (DMAC), and a magnetic stirrer were added into a 500 mL flask. The reaction proceeded at 70 °C for 48 h under the protection of Ar gas. After that, the reactants were slowly added into 2 L of ultrapure water to precipitate out the intermediate **a**, which was filtered and recrystallized from ethanol (yield 93%). Finally, the intermediate **a** was charged into one-necked round-bottom flask, and heated for 1 h at 240 °C under Ar atmosphere for Claisen rearrangement. After cooling to room temperature, the crude product was purified by column chromatography using cyclohexane as the eluent. TABPA was obtained with a yield of 65.5%. ¹H-NMR for intermediate **a** (CDCl₃, δ, ppm): 1.50 (s, —CH₃); 3.25, 4.85, and 5.88 (m, —C₃H₅); 4.37, 5.11, 5.29, and 5.88 (m, —OC₃H₅); 6.60 and 6.90 (m, —C₆H₃—). ¹H-NMR for TABPA (CDCl₃, δ, ppm): 2.03 (s, —CH₃); 5.46 (s, —OH); 3.75, 5.50, and 6.39 (m, —C₃H₅); 7.27 (s, —C₆H₂—).

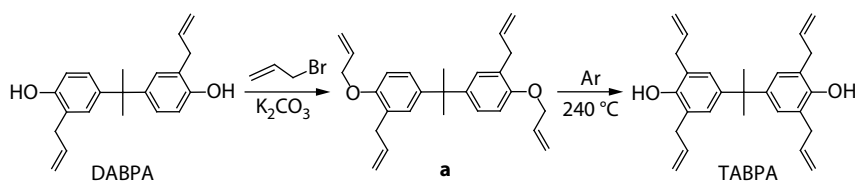
Polymerization

The polymerization of fluorinated poly(arylene ether)s (**FPAE-4-**

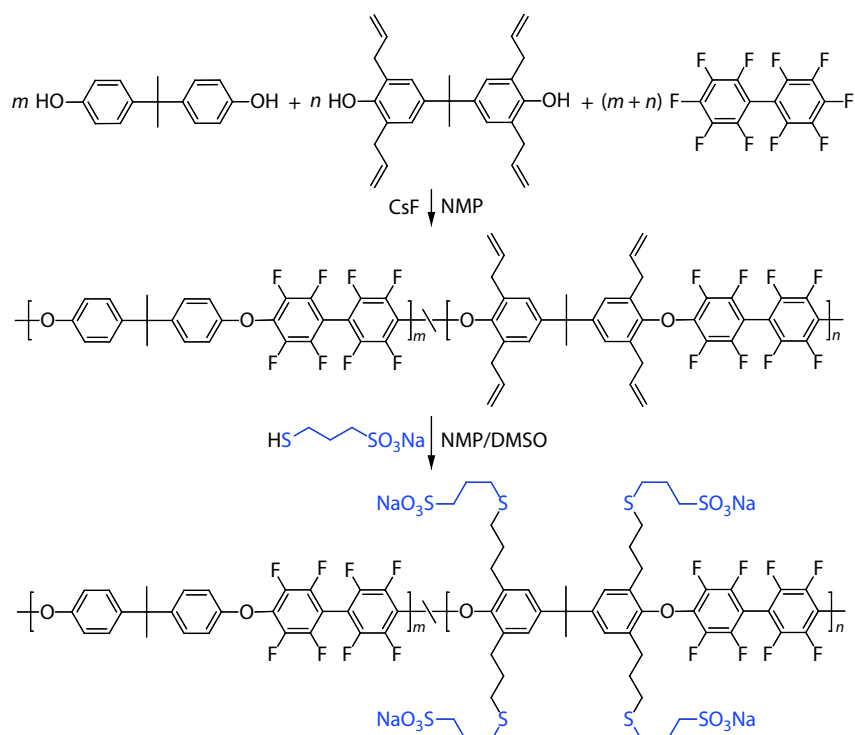
ks) is depicted in Scheme 2. Various molar ratios of TABPA were polymerized with bisphenol A and decafluorobiphenyl at room temperature to produce **FPAE-4-k**, where *k* represents the molar percentage of TABPA unit in the polymer backbone. Typically, to a 50 mL three-necked round-bottom flask were introduced 8 mL of 1-methyl-2-pyrrolidinone (NMP), 0.3886 g (1 mmol) of TABPA, 0.6849 g (3 mmol) of bisphenol A, 1.3500 g (4.04 mmol) of decafluorobiphenyl, 3.03 g (20 mmol) of anhydrous CsF (purity: 99.99%), and 0.4 g of CaH. The reaction was magnetically stirred under Ar atmosphere for 24 h. Viscous solution was yielded, which was slowly added into 500 mL of ultrapure water. The product **FPAE-4-25** was precipitated, and was purified by dissolving in 20 mL of chloroform, precipitating in 200 mL of methanol, and drying under vacuum at 60 °C for 24 h. Yield: 92%. ¹H-NMR for **FPAE-4-25** (CDCl₃, δ, ppm): 1.65 (s, —CH₃); 3.30, 4.94, and 5.83 (m, —C₃H₅); 6.99 (s, —C₆H₄—); 7.25 (s, —C₆H₂—).

Attachment of Sulfonated Side Chains

As shown in Scheme 2, sulfonated side chains were attached by thiol-ene addition to yield sulfonated fluorinated poly(arylene ether)s (**SFPAE-4-ks**). Typically, to a 25 mL three-necked round-bottom flask were charged with 0.5 g (0.89 mmol) of **FPAE-4-25**, 0.63 g (3.56 mmol) of sodium 3-mercaptopropanesulfonate, 0.94 g (3.56 mmol) of 18-crown-6, 13 mL of



Scheme 1 Reaction route to tetra-allyl bisphenol A (TABPA).



Scheme 2 Synthesis of **FPAE-4-ks** and **SFPAE-4-ks**.

NMP/dimethyl sulfoxide (DMSO) mixed solvent (2/1, V/V), and a magnetic stirrer. Under the protection of argon, the reaction temperature was increased to 80 °C. Then, 0.45 mmol of 2,2'-azobis(2-methylpropionitrile) (AIBN) was dissolved in 4 mL of DMSO and added dropwise. After 48 h of reaction, the mixture was subjected to dialysis at room temperature for 2 days. Water was removed by freeze-drying, and 0.57 g of **SFPAE-4-25** was obtained with the yield of 87.7%. Similar to the nomenclature of **FPAE-4-k**, the *k* in **SFPAE-4-k** also represents the molar percentage of TABPA unit in the polymer backbone. ¹H-NMR for **SFPAE-4-25** (DMSO-*d*₆, δ, ppm): 1.65 (s, —CH₃); 1.75–1.91, 2.60 and 2.69–3.00 (m, —C₃H₆SC₃H₆—); 6.69 (s, —C₆H₂—); 7.12–7.27 (d, —C₆H₄—).

Membrane Formation

Solution-casting method was employed to prepare the membranes. 0.08 g/mL of SFPAEs in DMAc were cast onto leveled glass plates, which was conditioned in an oven at 80 °C. After 24 h of drying, the membranes were peeled off the glass surface by immersing in ultrapure water. Then, the membranes were immersed in 1 mol·L^{−1} H₂SO₄ solution to change the counter cation to proton. The excess H₂SO₄ in the membranes was removed by immersing in ultrapure water at 80 °C with replacing fresh water several times until pH of water is neutral. The thickness of all samples is ~50–55 μm.

Characterizations

The small angle X-ray scattering (SAXS) was measured on an Anton Paar SAXSess mc² instrument. The ¹H-NMR spectra were obtained on a Bruker AVANCE 400 spectrometer. The thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C analyzer with a ramping rate of 10 °C·min^{−1} and under the protection of N₂ atmosphere (100 mL·min^{−1}). FTIR spectra were achieved on a Thermo Nicolet 5700 FTIR spectrometer. The tensile properties were measured on a Suns universal testing instrument UTM 6502X with stretching rate of 5 mm·min^{−1}. Gel permeation chromatography (GPC) analysis was performed on a Waters Breeze system equipped with a Waters Styragel column, Waters 515 HPLC pump, and Waters 2414 refractive index detector. Tetrahydrofuran was used as elution solvent (flow rate: 1 mL·min^{−1}) and polystyrene as standard for calibration. Inherent viscosities of ionomers in NMP (0.5 g·dL^{−1}) were measured by an Ubbelohde viscometer. Electrochemical impedance spectroscopy (EIS) of membranes was measured by a Solartron 1260A impedance/Gain-phase analyzer in the frequency range from 1 Hz to 10 MHz at the voltage amplitude of 10 mV. Samples are fully hydrated in bulk water during measurements. Proton conductivity (σ) of membranes was calculated by

$$\sigma = \frac{L}{RA} \quad (1)$$

where *L* is the distance between electrodes, *R* is the resistance of the sample, which was obtained from the diameter of semicircle in EIS, and *A* is the transverse area of the sample.

The ion exchange capacity (IEC) was determined by acid-base titration according to literature protocol.^[29] The water uptake and swelling ratio were defined as the weight and length changes of the dry membranes, respectively, after being soaked in ultrapure water at each testing temperature for 24 h. The oxidative stability was evaluated by immersing in

Fenton's reagent (3% H₂O₂ + 2 ppm FeSO₄) at 80 °C with regular shaking and recording the time for the samples starting to break. VO²⁺ permeability was measured according to previously established method.^[30] The concentration of VO²⁺ was determined by a UV-5800HPC UV-Vis spectrophotometer. The vanadium redox flow batteries (VRFBs) were assembled according to literature.^[31] 100 mL of 1.0 mol·L^{−1} VO²⁺ in 2.0 mol·L^{−1} H₂SO₄ solution was used as the anolyte; 50 mL of 1.0 mol·L^{−1} V²⁺ in 2.0 mol·L^{−1} H₂SO₄ solution was used as the catholyte. The flow rate is 200 mL·min^{−1}. The voltage window for testing VRFBs was 0.7–1.7 V. The membrane active area in the VRFBs was 15 cm². The electrolytes were pumped unceasingly through the cell during the tests. The Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the VRFBs were calculated by the following equations:

$$CE = \frac{\int I_d dt}{\int I_c dt} \times 100\% \quad (2)$$

$$VE = \frac{V_{d,avg}}{V_{c,avg}} \times 100\% \quad (3)$$

$$EE = VE \times CE \quad (4)$$

where *I_d* and *I_c* are the discharge and charge currents, respectively; *V_d* and *V_c* are the average discharge and charge voltages, respectively; *t* is the time taken for charge/discharge.

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

Claisen rearrangement has been widely used to make di-allyl bisphenol monomers;^[32,33] however, repeated Claisen rearrangement is seldom reported, probably because of the potential difficulty of the second step reaction in the presence of large steric hindrance. In order to develop multi-allyl bisphenol monomers as dense reaction sites for the introduction of sulfonic acid groups, a tetra-allyl bisphenol monomer TABPA was designed from repeated Claisen rearrangement, *i.e.* reacting DABPA with allyl bromide to yield the intermediate **a**, which was then subjected to a second Claisen rearrangement (Scheme 1). The proposed structures of compound **a** and TABPA were confirmed by ¹H-NMR, as shown in Fig. 1. In the spectrum of compound **a** (Fig. 1a), the signals at 5.08, 5.27, and 5.88 ppm have an integral ratio of 2:2:1, which suggest the presence of O—CH₂—CH=CH₂. After thermal rearrangement, a new signal at 5.47 ppm is observed (Fig. 1b), which can be assigned to the protons of phenol groups (Ar—OH). Also, the signals for the allyl ether groups disappear. All the other protons are well assigned in the ¹H-NMR spectroscopy (Fig. 1b), suggesting the successful synthesis of TABPA.

The polymerization of bisphenols with decafluorobiphenyl catalyzed by CsF can be carried out at room temperature without crosslinking because of the high reactivity of decafluorobiphenyl.^[29,34] The chemical structures of **FPAE-4-ks** and **SFPAE-4-ks** were confirmed by ¹H-NMR. The representative ¹H-NMR spectrum of **FPAE-4-25** is shown in Fig. 1(c). The signals 2, 3, and 4 prove clearly the existence of allyl group after polymerization, which cannot be achieved by conventional K₂CO₃-activated polymerizations.^[35] The **FPAE-4-ks** were sulfonated *via* thiol-ene addition at 80 °C to give **SFPAE-4-ks**. The ¹H-NMR spectrum of **SFPAE-4-25** is shown

in Fig. 1(d). No resonance signals for the allyl protons can be observed, but new resonance signals corresponding to the alkyl protons appear. Therefore, the thiol-ene addition, resulting in alkyl sulfide products, is successful and efficient. ^{19}F -NMR spectra were used to confirm the structure of the decafluorobiphenyl units in **FPAE-4-25** and **SFPAE-4-25** (Fig. 2). It can be seen that both **FPAE-4-25** and **SFPAE-4-25** have two sets of signals at around -137 and -152 ppm, which demonstrate the successful incorporation of decafluorobiphenyl moieties into the linear chain of the polymers in the manner depicted in Scheme 2.

The attachment of sulfonated side chains was also valid-

ated by the FTIR, as shown in Fig. 3. Compared with the control sample **FPAE-0** without allyl group, the **FPAE-4-25** shows a new absorption band at 914 cm^{-1} in the FTIR spectrum, which can be attributed to the vibration of the allyl groups. After the attachment of sulfonated side chains (**SFPAE-4-25**), the band for allyl groups disappears, while two absorptions bands at 1238 and 1045 cm^{-1} show up, which are the symmetric and asymmetric vibration of the sulfonate groups. Therefore, these FTIR results are consistent with the above NMR results, demonstrating the successful synthesis of **SFPAE-4-ks**.

Four **FPAE-4-ks** with TABPA loadings being 25%, 30%, 35%,

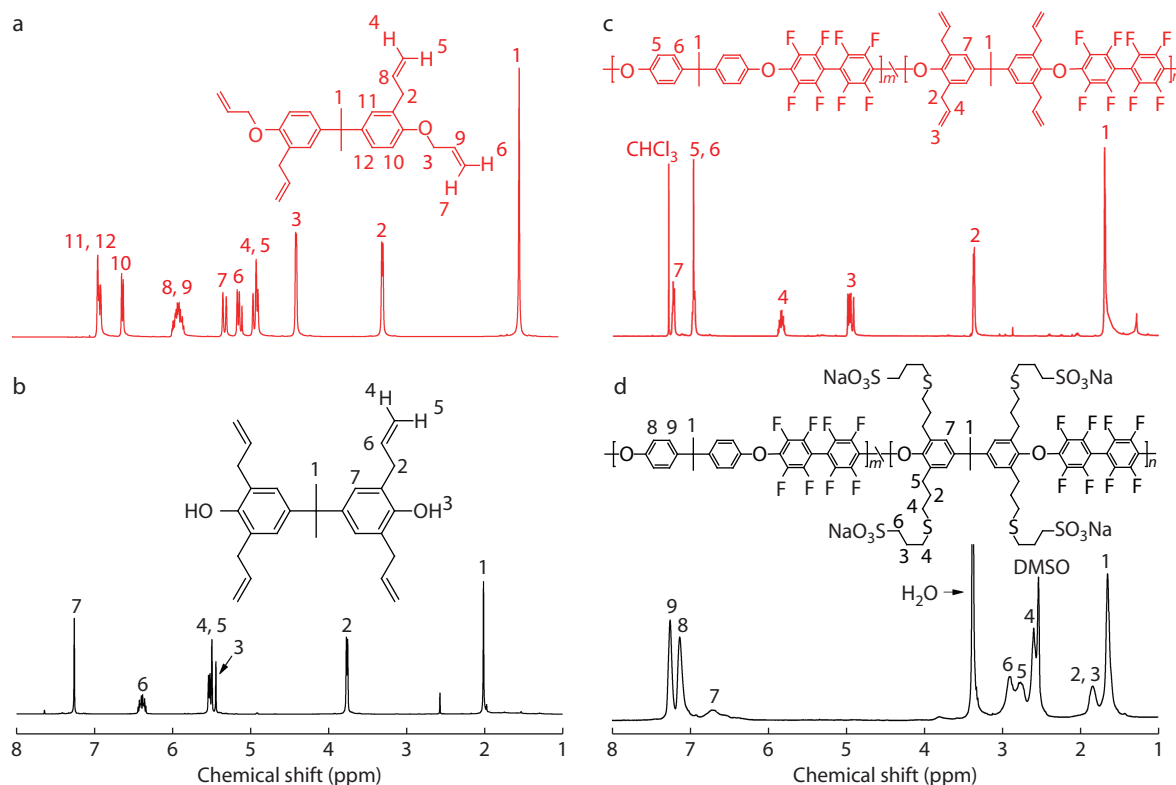


Fig. 1 ^1H -NMR spectra of (a) compound **a** (solvent: CDCl_3), (b) TABPA (in CDCl_3), (c) **FPAE-4-25** (solvent: CDCl_3), and (d) **SFPAE-4-25** (solvent: $\text{DMSO}-d_6$).

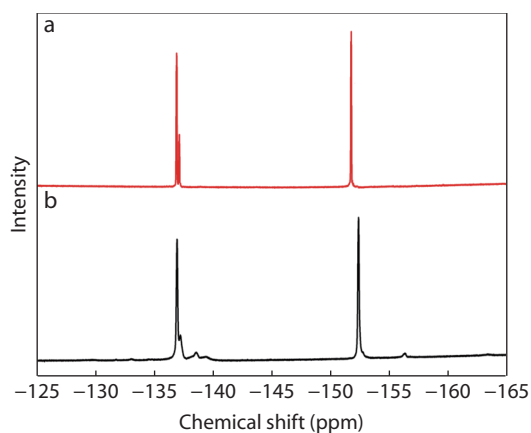


Fig. 2 ^{19}F -NMR spectra of (a) **FPAE-4-25** (solvent: CDCl_3) and (b) **SFPAE-4-25** (solvent: $\text{DMSO}-d_6$).

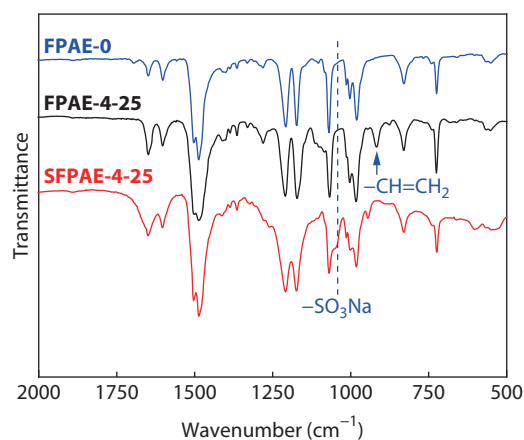


Fig. 3 FTIR spectra of **FPAE-0**, **FPAE-4-25**, and **SFPAE-4-25**.

and 40%, respectively, were polymerized. It can be seen from Table 1 that the inherent viscosities of **FPAE-4-ks** are relatively high, and the number-average molecular weights are in the range of 38 kDa to 54 kDa. After thiol-ene addition, the inherent viscosities become higher (Table 2) because of stronger intermolecular interactions. The **FPAE-4-ks** are readily soluble in CHCl_3 , CH_2Cl_2 , and aprotic solvents, while the **SFPAE-4-ks** are only soluble in aprotic solvents. The ion exchange capacities (IECs) of SFPAEs are titrated to be ranging from 1.29 $\text{mmol}\cdot\text{g}^{-1}$ to 1.78 $\text{mmol}\cdot\text{g}^{-1}$. Higher content of TABPA unit in the polymer backbones leads to higher IEC, as expected.

Table 1 Properties and molecular weights of **FPAE-4-ks**.

Sample	Loading of TABPA (%)	Yield (%)	η ($\text{dL}\cdot\text{g}^{-1}$)	M_n (kDa)	M_w (kDa)	PDI
FPAE-4-25	25	95	0.78	54	106	1.9
FPAE-4-30	30	95	0.67	50	92	1.7
FPAE-4-35	35	94	0.78	42	79	1.9
FPAE-4-40	40	93	0.82	38	68	2.1

Table 2 Basic properties of **SFPAE-4-ks** and Nafion 212 at room temperature.

Sample	η ($\text{dL}\cdot\text{g}^{-1}$)	IEC ($\text{mmol}\cdot\text{g}^{-1}$)		Water uptake (%)	Swelling ratio (%)	σ^b ($\text{mS}\cdot\text{cm}^{-1}$)
		Calculated	Titred			
SFPAE-4-25	1.7	1.35	1.29	21.7	12.5	45
SFPAE-4-30	1.8	1.53	1.50	24.8	17.6	56
SFPAE-4-35	1.9	1.69	1.60	37.1	23.3	78
SFPAE-4-40	2.1	1.84	1.78	45.0	27.9	93
Nafion 212	/	/	0.95 ^a	18.5	7.8	85

^a Obtained from commercial sample information; ^b Obtained at room temperature.

Membrane Morphology

To study the effect of side chain distribution on the properties of membranes, a previously reported sulfonated fluorinated poly(arylene ether) bearing di-alkylsulfonate side chains (**SFPAE-2-50**),^[29] which has identical backbone and same content of side chains to **SFPAE-4-25** but different distributions of the side chains, is selected as control sample, as depicted in Fig. 4(a). The aggregation of ionic groups usually leads to

the presence of an ionomer peak in SAXS patterns, which corresponds to the distance (d) between the ionic aggregates.^[25,36–38] This d can be calculated by the equation of $d = 2\pi/q$, where q refers to the scattering vector of the ionomer peaks. The impact of side chain density on the microscopic morphology of SFPAEs was investigated by small angle X-ray scattering (SAXS), as shown in Fig. 4(b). As can be seen, the q s of **SFPAE-4-25** and **SFPAE-2-50** are 1.34 and 1.84 nm^{-1} , respectively, corresponding to the d s of 4.7 and 3.4 nm, respectively. The larger d of **SFPAE-4-25** demonstrates better aggregation of its sulfonic acid groups, suggesting that the molecular design of densely distributed ionic side chains is successful.

Water Affinity and Proton Conductivity

The water uptake and swelling ratio of **SFPAE-4-ks**, **SFPAE-2-50** and Nafion 212 as a function of temperature are shown in Figs. 5(a) and 5(b), respectively. Both the water uptake and swelling ratio for **SFPAE-4-ks** increase with the increase of IEC or temperature. All of the **SFPAE-4-ks** exhibit modest water uptake (20.7%–45.0%) and swelling ratio (12.4%–27.9%) at room temperature, while these values are higher than those of Nafion 212. Notably, **SFPAE-2-50** has slightly lower water uptake and swelling ratio than **SFPAE-4-25** at all the tested temperatures. This result suggests that the increase of side chain density slightly increases the water affinity of the polymer.

The proton conductivities of **SFPAE-4-ks**, **SFPAE-2-50**, and Nafion 212 measured under fully hydrated conditions are gathered in Figs. 5(c) and 5(d). It can be seen that the proton conductivity of **SFPAE-4-ks** increases gradually either with the increase of IEC at room temperature or with the increase of temperature. The **SFPAE-4-40** with the highest IEC of 1.78 $\text{mmol}\cdot\text{g}^{-1}$ exhibits the highest proton conductivity of 93 $\text{mS}\cdot\text{cm}^{-1}$ at room temperature among all **SFPAE-4-ks**. The **SFPAE-4-25** has a nearly identical IEC to **SFPAE-2-50**; however, its room temperature proton conductivity is 24% higher than that of the latter. It has been well known that the excellent proton conductivity of Nafion 212 is a result of its highly aggregated ionic groups, which forms proton conductive channels for efficient proton transport.^[10] Indeed, the proton conductivity of Nafion 212 is measured to be as high as

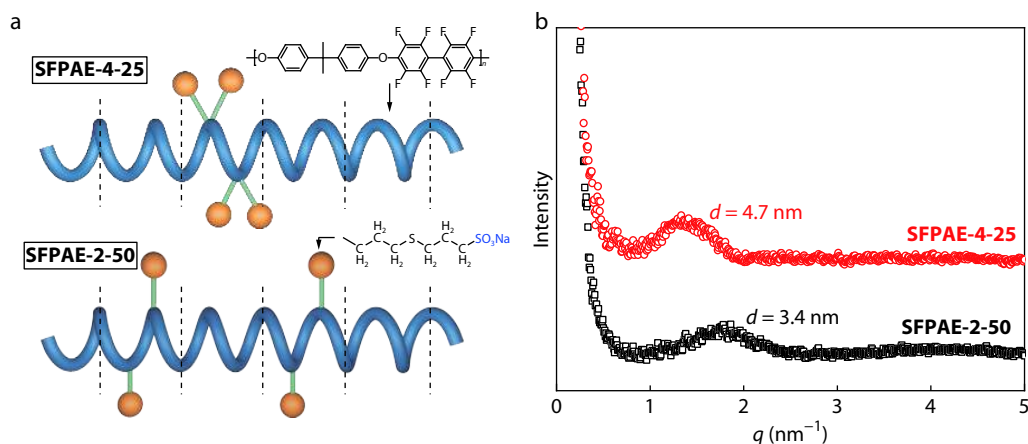


Fig. 4 (a) Schematic illustration of different side chain distributions of **SFPAE-4-25** and **SFPAE-2-50**. (b) SAXS profiles of **SFPAE-4-25** and **SFPAE-2-50**.

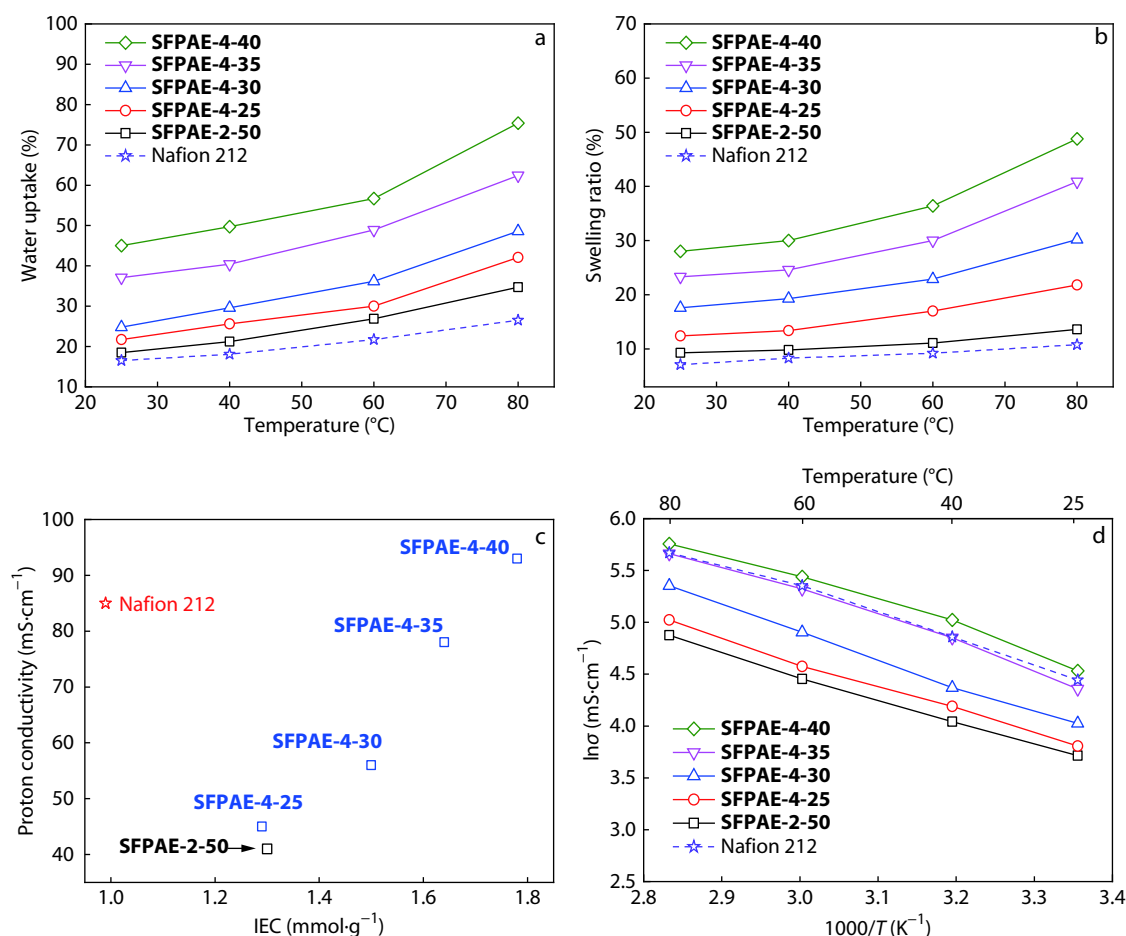


Fig. 5 (a) Water uptake, (b) swelling ratio, and (c, d) proton conductivity of **SFPAE-4-ks**, **SFPAE-2-50**, and Nafion 212 at various temperatures.

85 mS·cm⁻¹ at room temperature. Therefore, the higher proton conductivity of **SFPAE-4-25**, compared with that of **SFPAE-2-50**, can be attributed to its more aggregated ionic groups. For sulfonated poly(arylene ether)s to possess higher proton conductivity than Nafion, much larger IEC is usually required.^[1,39] The **SFPAE-4-40** achieves higher proton conductivity at an IEC of 1.78 mmol·g⁻¹, suggesting its promising prospect as alternative to Nafion.

Thermal Stability, Mechanical Property, and Oxidative Stability

The thermal stabilities of **FPAE-4-ks** and **SFPAE-4-ks** were investigated by TGA, and the 5% weight-loss temperatures ($T_{d-5\%}$) are listed in Table 3. It can be seen that all of the **FPAE-4-ks** exhibit excellent thermal stability, a typical property of the robust poly(arylene ether) backbones. The higher content of tetra-allyl groups leads to a slight reduction in $T_{d-5\%}$ for **FPAE-4-ks**. After thiol-ene addition, the $T_{d-5\%}$ s are lowered dramatically to about 240–280 °C, which is the typical decomposition temperature range of sulfonic acid groups.^[40,41] The higher content of tetra-alkylsulfonate groups leads to an obvious reduction in $T_{d-5\%}$ for **SFPAE-4-ks**, as expected. All of **SFPAE-4-ks** are thermally stable up to > 200 °C, suggesting their excellent thermal stability for applications in vanadium redox flow batteries (VRFBs) or H₂/O₂ fuel cells.

The mechanical strength of PEMs is an essential requirement for device fabrications and operations. The tensile strength and elongation at break of **SFPAE-4-ks** freshly taken out from deionized water are listed in Table 3. Both the tensile strength and elongation at break increase with the decrease of IEC. This is because more water was absorbed into the membranes at higher IEC, resulting in more loosely packed macromolecular chains. The effect of water on mechanical properties can also be supported by the significantly higher tensile strength of dry membranes than wet membranes in literature.^[42–44] All of the **SFPAE-4-ks** show good mechanical properties with tensile strength and elongation-at-break in the range of 10–17 MPa and 7%–11%, respectively.

The oxidative stability of PEMs is an essential requirement for long-term device operations. The oxidative stability of **SFPAE-4-ks** determined by immersing in Fenton's reagent (3 wt% H₂O₂ + 2 ppm FeSO₄) at 80 °C with constant shaking is listed in Table 3. It can be seen that the oxidative stability of **SFPAE-4-ks** increases with the decrease of IEC, which can be attributed to the higher uptake of degradative radicals in Fenton's reagent at higher IECs.^[29] Notably, the oxidative stabilities of the **SFPAE-4-ks** are significantly higher than those of non-fluorinated membranes under similar condi-

Table 3 Thermal, mechanical, and oxidative properties of **SFPAE-4-ks**.

Polymer	$T_{d-5\%}$ before thiol-ene addition (°C)	$T_{d-5\%}$ after thiol-ene addition (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Oxidative stability	
						t^a (min)	RW ^b (%)
SFPAE-4-25	428.5	283.9	16.9	338	10.8	213	92.3
SFPAE-4-30	426.4	276.1	13.8	324	9.9	191	90.5
SFPAE-4-35	420.1	266.8	10.8	320	8.5	132	88.4
SFPAE-4-40	415.7	240.9	10.1	309	7.2	90	85.6

^a The time when membranes first broke in Fenton's reagent (3% H₂O₂ + 2 ppm FeSO₄) at 80 °C; ^b Remaining weight after immersing in Fenton's reagent for 1 h.

tions.^[40,45,46] Therefore, the presence of fluorine in the macromolecular structures is highly beneficial to enhanced oxidative stabilities.

Flow Battery Application

To demonstrate the applicability of **SFPAE-4-ks** as high performance PEMs, the **SFPAE-4-40** was evaluated as separator for VRFB. Ideally, VRFBs requires separators to be able to completely block the permeation of vanadium ions to ensure low self-discharge rate.^[47–49] It is found that the VO²⁺ permeability of **SFPAE-4-40** is $4.1 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$, lower than the $5.36 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ of Nafion 212. The selectivity of membranes, which is defined as the ratio of proton conductivity over VO²⁺ permeability, is calculated to be $3.78 \times 10^4 \text{ S} \cdot \text{min} \cdot \text{cm}^{-3}$ for **SFPAE-4-40** and $2.64 \times 10^4 \text{ S} \cdot \text{min} \cdot \text{cm}^{-3}$ for Nafion 212. In conclusion, the **SFPAE-4-40** has higher proton conductivity, lower VO²⁺ permeability, and thus higher selectivity than Nafion 212.

The charge/discharge curves of the VRFBs assembled with **SFPAE-4-40** and Nafion 212 at a current density of 40 mA·cm⁻² are shown in Fig. 6. It can be seen that the VRFB assembled with **SFPAE-4-40** has longer charge/discharge time than the VRFB assembled with Nafion 212. The CE of the VRFB assembled with **SFPAE-4-40** is calculated to be 90.9%, higher than the 86.9% of the VRFB assembled with Nafion 212. The VE of the VRFB assembled with **SFPAE-4-40** battery is calculated to be 87.0%, also higher than the 84.3% of the VRFB assembled with Nafion 212. Thus, the overall EE of the VRFB assembled with **SFPAE-4-40** (79.1%) is higher than that of the VRFB assembled with Nafion 212 (73.3%). Therefore, the **SFPAE-4-40** can be a promising separator for VRFBs. It should be noted that the proton conductivity of **SFPAE-4-ks** may keep increasing with the increase of IEC,

but the water uptake would increase as well, which would decrease the mechanical strength and increase the vanadium permeability. Besides, the thickness of membrane, treatment of electrode, concentration of electrolyte, configuration of cell, and operation parameters of VRFB would affect the overall device performance of the membrane. Therefore, the further optimization of the separator is needed for practical applications. This study provides the synthesis of a new series of comb-shaped proton exchange membranes from a reaction route developed by our lab previously for the establishment and commercialization of potential electrochemical systems.

CONCLUSIONS

Comb-shaped sulfonated fluorinated poly(arylene ether)s bearing tetra-alkylsulfonate side chains (**SFPAE-4-ks**) were successfully synthesized from room temperature condensation polymerization of a newly developed tetra-allyl bisphenol A monomer followed by thiol-ene addition with sodium 3-mercaptopropanesulfonate. The IECs were in the range of 1.29–1.78 mmol·g⁻¹. It is found that the **SFPAE-4-25** had higher proton conductivity than a previous reported **SFPAE-2-50**, which has identical backbone and same content of side chains to **SFPAE-4-25** but different distributions of the side chains. This was rationalized by the SAXS results where the **SFPAE-4-25** had better aggregation of sulfonic acid groups to form proton conductive channels than **SFPAE-2-50**. The **SFPAE-4-40** with an IEC of 1.78 mmol·g⁻¹ exhibited higher proton conductivity, lower VO²⁺ permeability, and higher selectivity than Nafion 212. Accordingly, the vanadium redox flow battery (VRFB) assembled with **SFPAE-4-40** exhibited higher Coulombic efficiency, voltage efficiency and energy efficiency than the VRFB assembled with Nafion 212 at a current density of 40 mA·cm⁻². Therefore, side chain engineering is a versatile protocol for the development of high performance PEMs.

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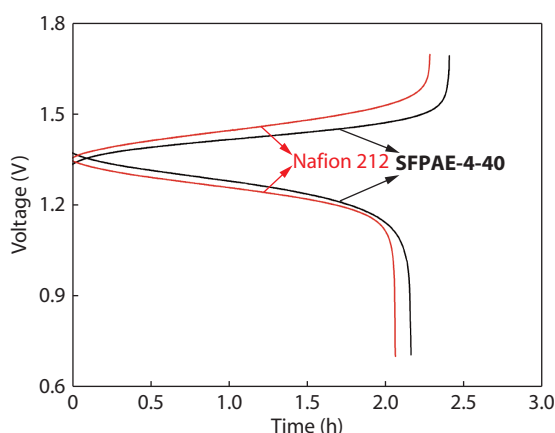


Fig. 6 Charge/discharge curves of the VRFBs assembled with **SFPAE-4-40** or Nafion 212.

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