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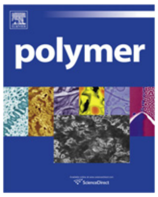

Synthesis of sulfonated poly(fluorenyl ether thioether ketone)s with bulky-block structure and its application in vanadium redox flow battery

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ABSTRACT

High-molecular-weight bulky-block poly(fluorenyl ether thioether ketone)s were successfully synthesized by a two steps one-pot protocol using *N*,*N*′-dimethy-*S*-carbamate masked dithiols for vanadium redox flow battery (VRB) application. The followed sulfonation procedure gave birth to novel sulfonated block poly(fluorenyl ether thioether ketone)s (SPFETKs) with controlled ionic exchange capacities (IEC). Membranes with proton conductivities higher than ($IEC > 1.66$ mequiv. g^{-1}) or comparable to ($IEC < 1.66$ mequiv. g^{-1}) that of Nafion117 membrane were achieved. The VO^{2+} permeabilities of SPFETKs membranes were much lower than that of Nafion117 membrane. The thermal properties, mechanical properties, oxidative stability, water uptake, proton conductivity, VO^{2+} permeability and cell performance were investigated in detail.

1. Introduction

Vanadium redox flow battery (VRB) has arisen as a promising energy storage system for renewable power sources such as solar cell and wind plant in the last decade [1]. As one of the key components, the ion conducting separator, which allows the transportation of specific ions (in most cases, H^+) at a considerable rate whilst blocks the permeation of electrolyte to a certain degree, has attracted most attention because it is the bottleneck for the VRB development. Among all the separators studied, sulfonated ionomers exhibited much more prospect for VRB application owning to their high proton conductivity and excellent mechanical integrity [2,3]. However, it is envisaged that Nafion (a benchmark material for proton exchange membrane developed by Dupont™) suffers too large electrolyte permeation when assembled in VRB, which has intrigued lots of works focusing on the modification of Nafion [4–6]. Qiu et al. have reported Nafion/organic silica modified TiO_2 composite membrane for VRB application [7]. The electrolyte permeation of Nafion could be decreased significantly after doping. However, Nafion is considered as high cost and environmental unfriendly membrane for use in proton exchange membrane fuel cells [8]. Therefore, the non-fluorinated ionomers as alternative candidate to Nafion for VRB application is also of great interest.

Poly(arylene thioether)s are important classes of high performance engineering thermoplastics with a favorable combination of physical, chemical and mechanical properties. It can be prepared by the nucleophilic displacement of aromatic dihalides with activated dithiols [9]. However, thiols are difficult to work with because of their unpleasant odor and oxidative unstable nature even at room temperature. We have previously synthesized novel sulfonated poly(arylene thioether)s for VRB application by one-pot polymerization of *N*,*N*′-dimethy-*S*-carbamate masked dithiols with aromatic dihalides, followed by post-sulfonation using chlorosulfonic acid as sulfonation agent in dichloromethane solution [10]. The as-made membranes, similar to SPFEK [2], exhibited comparable proton conductivity and much lower VO^{2+} permeability than Nafion117. The proton conductivity dominates the voltage efficiency of the battery while the VO^{2+} permeability influences the coulombic efficiency. Since low VO^{2+} permeability could be easily achieved using these aromatic ionomers, their proton conductivity is of most concern.

Generally, the proton conductivity can be enhanced by increasing the ionic exchange capacity (IEC) of the material. However, it is always accompanied with some drawbacks such as decreased mechanical integrity and increased electrolyte permeation. It has become an increasingly sophisticated endeavor to synthesize sulfonated ionomers with high proton conductivity at low IEC values. The edge-cutting strategies includes anchoring the sulfonic acid groups as

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many as possible to specific domains of the polymer by molecular design [11,12], control the segment arrangement of a polymer to facilitate hydrophilic-hydrophobic phases separation by synthesizing block copolymers [13–16], increasing the acidity of sulfonic acid groups by the introduction of fluorine [17], and so on. Of which first two strategies are employed in this manuscript. The physicochemical properties and electrochemical properties are investigated in detail, and the structure–morphology–property relationships are discussed.

2. Experimental section

2.1. Materials

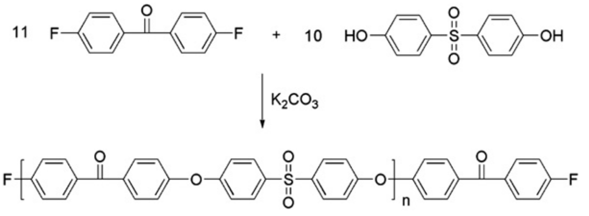
4,4′-Difluorobenzophenone was purchased from Aldrich Chemical Co. and recrystallized from ethanol prior to use. Bis(4-hydroxylphenyl)sulfone (99.9% purity) was bought from Aladdin reagent Co., China. Benzophenone was purchased from Aldrich Chemical Co. *N,N*′-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), toluene, chloroform, dichloromethane, methanol, concentrate sulfuric acid (95–98%), chlorosulfonic acid, hydrochloric acid, potassium hydroxide, *tert*-butylamine, anhydrous potassium carbonate, calcium carbonate and aqueous hydrogen peroxide (30%) were obtained from commercial sources. 9,9′-S,S′-bis(*N,N*′-dimethyl-4-thiocarbamoyl-phenyl)fluorene was synthesized according to the literature [18].

2.2. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in a Bruker DRX NMR instrument and the chemical shifts were listed in parts per million (ppm) downfield from tetramethylsilane (TMS). 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, chloroform as an elution solvent at a flow rate of 1 mL min^{-1} and polystyrene as standards for calibration. FT-IR spectra were recorded on a Perkin–Elmer Spectrum 100 Fourier transform spectrometer with membrane samples. Inherent viscosity of ionomers was determined using an Ubbelohde viscometer in DMAc at 25 °C. Thermal stability was analyzed using a PerkinElmer Pyris Diamond TG/DTA analyzer. The temperature was increased from room temperature to 150 °C and hold for 10 min., and then increased to 600 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere. The glass-transition temperature (Tg) was determined on a Seiko 220 DSC instrument at a heating rate of 10 °C min^{-1} under N_2 protection. The tensile properties were determined by SANS (Shenzhen, China) electromechanical universal test machine (model CMT-4014) at 25 °C. Samples were cut into dumbbell shape and immersed in deionized water prior to test. Morphology was observed on a JEM-2010HR Transmission electron microscope (TEM) using an accelerating voltage of 200 kV. Samples were stained with silver ions by proton exchange in a large excess of 1 M $AgNO_3$ aqueous solution, rinsed with deionized water and conditioned at atmosphere overnight.

2.3. Synthesis of F terminated telechelic oligomer *a*

The synthetic route is depicted in Scheme 1. To a 25 mL three necked round bottom flask, equipped with a Dean-Stark trap, a nitrogen inlet, a condenser and a magnetic stirrer, 0.2040 g (0.935 mmol) of 4,4′-difluorobenzophenone, 0.2127 g (0.85 mmol) of bis(4-hydroxylphenyl)sulfone, 0.207 g (1.5 mmol) of anhydrous potassium carbonate, 3 mL of DMAc and 4 mL of toluene were introduced. The reaction was first carried out at 140–150 °C for 3 h to remove the produced water by refluxing toluene, and then the temperature was raised to 165 °C and kept at that temperature for another 3 h. Oligomer **a** was obtained for the next step reaction without separation.



Scheme 1. Synthesis of F terminated telechelic Oligomer **a**.

In order to characterize oligomer **a**, another reaction was conducted with the same procedure. After the reaction, the resulting viscous mixture was poured into 80 mL water solution containing 0.5 mL of concentrated hydrochloric acid with magnetic stirring to precipitate out the polymer. The product was collected by filtration and redissolved in chloroform. The solution was filtered to remove residue inorganic salts, then concentrated to 5 mL and poured into 50 mL of ethanol to precipitate out the final product. The white fabric resultant was obtained after vacuum drying at 80 °C for 24 h.

2.4. Synthesis of poly(fluorenyl ether thioether ketone)s (PFETKs)

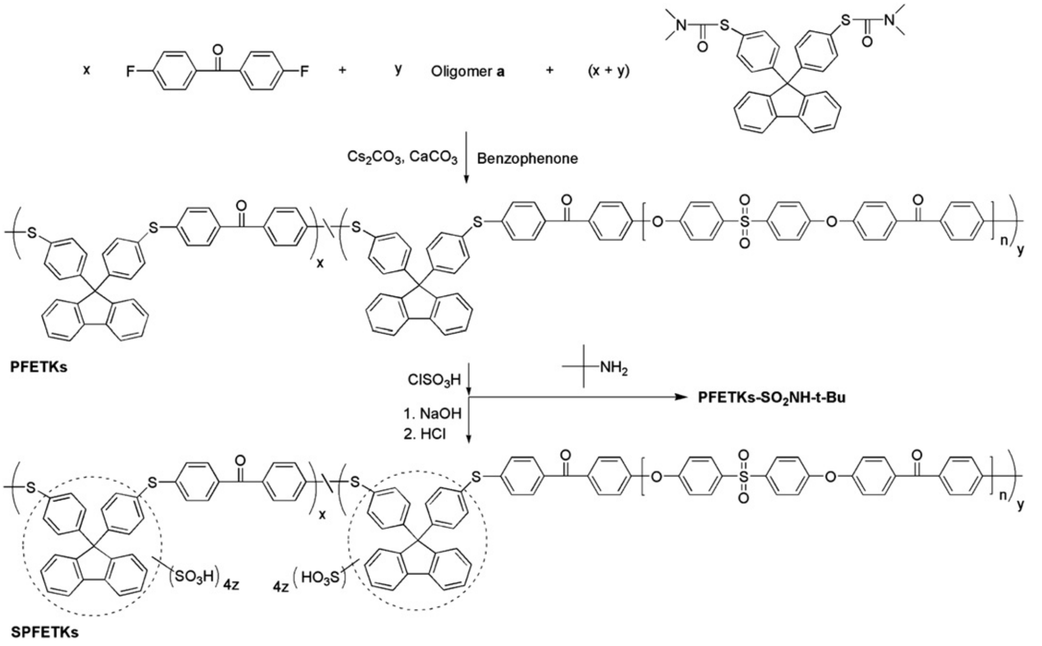
The synthesis procedure of PFETKs and their sulfonation were depicted in Scheme 2. The typical procedure is as follows (synthesis of PFETK-1): to the above reaction flask, 0.0142 g (0.065 mmol) of 4,4′-difluorobenzophenone, 0.0787 g (0.15 mmol) of 9,9′-S,S′-bis(*N,N*′-dimethyl-4-thiocarbamoyl-phenyl) fluorene, 0.0245 g (0.075 mmol) of cesium carbonate, 0.0225 g (0.225 mmol) of calcium carbonate and 3.5 g of benzophenone were charged. The mixture was first heated at 180 °C to evaporate out DMAc, elevated to 200 °C for 3 h, then brought up to 240 °C for another 3 h. After cooling down to about 80 °C, the viscous mixture was poured into acetone to precipitate out the polymer which was collected by filtration. The polymer was purified by redissolving it in $CHCl_3$, filtrated and precipitated out in acetone for three times. The product was vacuum dried at 120 °C for 24 h.

2.5. Sulfonation of the synthesized polymers

The typical procedure is as follows (sulfonation of PFETK-1): To a 150 mL round bottom flask, 75 mL dichloromethane and 0.448 g (1 mmol) PFETK-1 were introduced. After PFETK-1 was dissolved completely, 6 mL of 1 M chlorosulfonic acid in dichloromethane (0.6 mmol) was added dropwise under the vigorously stirring over 3 h. The reaction was continued for another 5 h. The resulting pale purple product precipitated out from the solution during the course. The precipitates were washed with hexane three times and then with water three times.

(a) Synthesis of sulfonated poly(fluorenyl ether thioether ketone)s (SPFETKs).

90 wt.% of above synthesized solid was dissolved in 20 mL DMAc. To the solution 20 mL of 3 wt.% potassium hydroxide aqueous solution was added to react for 5 h, then the reaction mixture was acidified with 50 mL of 5 vol.% hydrochloric acid for another 5 h. The resulting solution was dialyzed for 3 days (molecular weight cut off: 6000) and the solvent was removed by rotary evaporator. SPFETK-1 was typically obtained after vacuum drying at 80 °C overnight.



Scheme 2. Synthesis of PFETKs and their sulfonation.

(b) Synthesis of *t*-butyl bearing poly(fluorenyl ether thioether ketone)s (PFETKs-SO_2NH-*t*-Bu)

The above remaining 10 wt.% polymer after sulfonation was dissolve in 5 mL NMP, then excess amount of *tert*-butylamine was added and magnetically stirred for 24 h. The solvent was removed in vacuum. The resulting solid was wash in boiling ethanol and boiling water both for 1 h with changing the solvent twice. PFETK-1-SO_2NH-*t*-Bu was typically obtained after vacuum drying at 80 °C overnight.

2.6. Membrane preparation

The sulfonated ionomers were dissolved in DMAc solution with concentrations about 15 wt.% and cast into membrane on a glass plate by drying them at 60 °C for 10 h before eventually dried at 120 °C under vacuum for 24 h. The yellowish membranes were peeled off from glass plate, immersed in 1 M H_2SO_4 solution at 80 °C for 1 h, washed by deionized water several times and then keep in deionized water until use.

2.7. Ionic exchange capacity (IEC)

The dried membrane was weighed and immersed in 1 M HCl solution at 80 °C for 5 h to protonize the sulfonic acid groups and was then immersed in deionized water to remove the excess acid absorbed in the membrane. The membrane was then immersed in 2 M solution of NaCl (aq) for 24 h to replace the protons of sulfonic acid groups with sodium ions. The amount of replaced protons was titrated using 0.1 M NaOH (aq) solution, with phenolphthalein as indicator.

2.8. Proton conductivity

Proton conductivity of the membrane was determined by electrochemical impedance spectroscopy. The measurements were carried out on a Solartron 1255 B frequency response analyzer coupled with a Solartron 1287 electrochemical interface in the frequency range of 1 Hz to 1 MHz. The conductivity was calculated from the impedance plot with a computer curve-fitting technique according to the electrode area of the cell and the thickness of the membrane, which was measured with a micrometer. The proton conductivity (σ) of the specimen in the transverse direction was calculated from the impedance data according the following equation:

$$\sigma \ (\mathrm{s/cm}) = \frac{d}{RS} \tag{1}$$

where d and S are the thickness and area of the specimen, respectively, and R is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re (Z') axis. The film samples were cut into a circle with a diameter of 1 cm and soaked in deionized water overnight prior to test. Samples were sandwiched between two gold electrodes and placed above liquid water in a temperature-controlled vessel that afforded saturated water vapor environment.

2.9. Water uptake

The dry membranes were weighed and immersed in deionized water at different temperature for 24 h. The water uptake was defined as weight change to that of the dry membrane.

2.10. Oxidative property

Oxidative stabilities were tested in Fenton's reagent (3 wt.% $H_2O_2 + 2$ ppm $FeSO_4$) at 80 °C. The membranes with the thickness ranging from 100 μm to 140 μm were immersed in Fenton's reagent and conditioned at 80 °C Water Bath Shaker. The values for each sample were determined from the times of commencement to break.

2.11. VO^{2+} permeability

The permeation of VO^{2+} was measured by the method similar to the literature [19]. A total of 40 mL of 1 M $VOSO_4$ in 2 M H_2SO_4

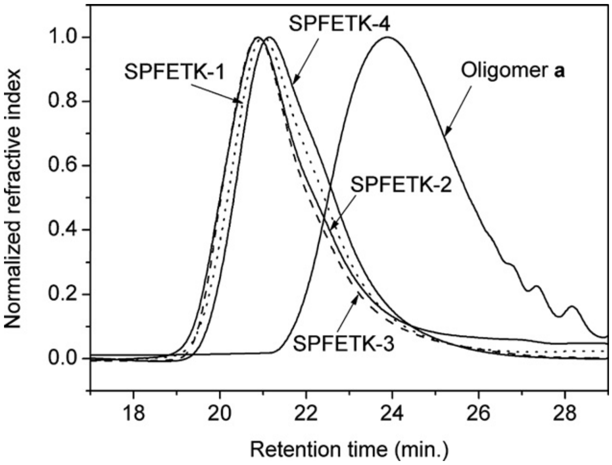


Fig. 1. GPC profiles of Oligomer **a** and PFETKs

solution and 40 mL of 1 M $MgSO_4$ in 2 M H_2SO_4 solution were filled in two reservoirs respectively. The membrane area exposed to electrolytes was 5.3 cm^2. $MgSO_4$ was used to equalize the osmotic pressure. The two solutions were continuously magnetic stirred and the concentration of VO^{2+} was measured by UV-Visible spectrophotometer (Model: 752-P, Shanghai Xianke Co., China) at a regular time interval (1 h) at room temperature.

The VO^{2+} permeability was defined as VO^{2+} diffusion coefficients (D) of membranes calculated by Fick's first law of diffusion on the assumption of pseudo-steady-state condition inside the membrane, and is calculated by the following equation:

$$J = -D\frac{|C_1 - C_2|}{d} \tag{2}$$

where J is the flux of VO^{2+}, C_1 and C_2 are the concentrations of VO^{2+} in each side reservoir, d is thickness of the membrane.

2.12. Cell performance

Samples for discharge tests were sandwiched in two pieces of carbon paper before being clamped in the graphite bipolar with serpentine flow field. The anodic electrolyte was 40 mL of 1 M VO_2^+ in 2 M H_2SO_4 solution and the cathodic electrolyte was 40 mL of 1 M V^{2+} in 2 M H_2SO_4 solution. They were pumped through the cell unceasingly during the test at room temperature. The effective area of membrane was 4.86 cm^2 and the limit voltage was set to 0.75 V. The coulombic efficiency (CE) was calculated by the following equation:

$$CE = \frac{C_d}{C_{tc}} \times 100\% \tag{3}$$

where C_d is the discharge capacity and C_{tc} is the theoretic charge capacity (where we assume the charge efficiency is 100%) of the cell.

3. Results and discussion

3.1. Synthesis of oligomer *a* and polymerization

Electron deficient telechelic oligomer **a** was successfully synthesized by the polycondensation of 4,4′-difluorobenzophenone and bis(4-hydroxylphenyl) sulfone in *N,N′*-dimethylacetamide (DMAc) solution at 165 °C in the presence of K_2CO_3. It is designed as the hydrophobic block in the resulting polymer after sulfonation, which will inevitably while indirectly cause the aggregation of the other components, namely hydrophilic domains. After the synthesis of oligomer **a**, the reaction mixture was cooled down to room temperature, and charged with other monomers, catalysts and solvent. It is necessary to add the polymerization solvent before the distillation of DMAc to avoid the precipitation of oligomer **a** during the procedure. Cs_2CO_3 is chosen in this step for the cleavage of C–S bond in the thiocarbamoyl group of mononer. Successful synthesis of poly(fluorenyl ether thioether ketone)s (PFETKs) were achieved as demonstrated in the GPC profiles in Fig. 1. The molecular weight of oligomer **a** and PFETKs were listed in Table 1. It can be seen that the number average molecular weight increased from 7 kDa of oligomer **a** to higher than 30 kDa of PFETKs after the polymerization.

The chemical structures were characterized by ^1H NMR and FT-IR as shown in Figs. 2 and 3 respectively. Since the simple structure and low molecular weight of oligomer **a**, its ^1H NMR spectrum is quantitatively acquired. After the incorporation of 9,9′-S,S′-bis(*N,N′*-dimethyl-4-thiocarbamoyl-phenyl) fluorene monomer, new peaks in ^1H NMR are observed which are consistent with the phenyl protons resonance of the monomer. The peaks in FT-IR spectrum at 1730 cm^{-1} and 1449 cm^{-1} for PFETK-2, which are absent in the FT-IR spectrum of oligomer **a**, can be assigned to the carbonyl vibration of *N,N′*-dimethyl-thiocarbamoyl group in the polymeric chain end and C=C vibration in fluorenyl group respectively. Both the ^1H NMR and FT-IR results validate the successful synthesis of PFETKs from oligomer **a**.

3.2. About sulfonation

The possibility of sulfonating aromatic polymers in CH_2Cl_2 using $ClSO_3H$ as sulfonation agent has paved the way for the tactical synthesis of sulfonated aromatic ionomers which are also of interest for the proton exchange membrane in fuel cells [20], direct methanol fuel cell [21], actuator [22], electyrolyzer [23], and so on. Previously, we have controlled the concentration and feed ratio of $ClSO_3H$ in CH_2Cl_2 solution to sulfonate the side chain of phenyl rings on polymers with the aim at improving the thermal stability of the products [10]. The 5% weight loss temperatures increased from about 250 °C for the main chain sulfonated polymers (sulfonic acid groups attached to the ortho-position of ether or thioether groups) to higher than 300 °C. However, the thermal stability of main chain sulfonated polymers is acceptable for the low or mediate temperature applications. Therefore, it is accessible to create large ion cluster by sulfonating both on the main chain

Table 1
Properties of Oligomer **a** and PFETKs.

Sample	k^a (%)	Yield (%)	M_n (kDa)	M_w (kDa)	Polydispersion index	T_g (°C)	$T_{d-5\%}$ (°C)
Oligomer **a**	0	99	7	12	1.6	171	482
PFETK-1	15	96	34	54	1.6	178	492
PFETK-2	20	97	36	58	1.6	179	485
PFETK-3	25	95	37	60	1.6	207	492
PFETK-4	30	96	31	49	1.6	211	452

[a] The total loaded molar ratio of 9,9′-S,S′-bis(*N,N′*-dimethyl-4-thiocarbamoyl-phenyl) fluorene to 4,4′-difluorobenzophenone.

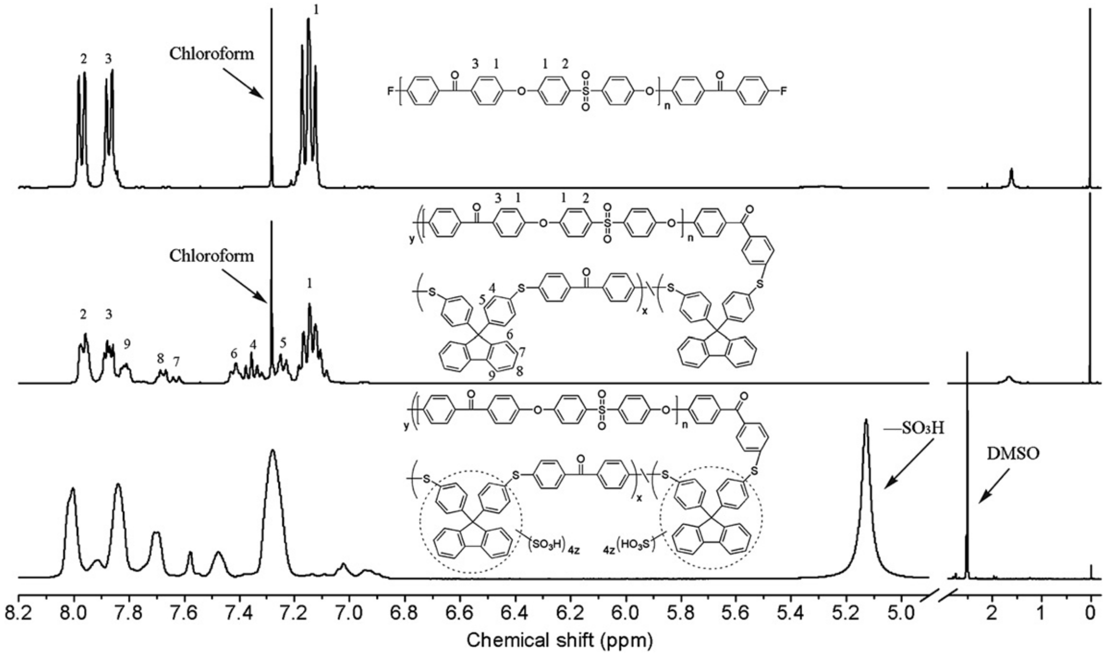


Fig. 2. ^{1}H NMR spectra of Oligomer **a** ($CDCl_3$), PFETK-2 ($CDCl_3$) and SPFETK-2 (DMSO-d_6).

and side chain of the polymer through appropriate molecular design.

Since the biphenyl fluorene segment has four electron-rich phenyl rings (two at the main chain and two at the side chain) for sulfonation, it was carefully chosen for the fabrication of larger ion clusters over the conventional two sulfonic acid groups bearing segment. The sulfonation procedure was depicted in Scheme 2. Successful sulfonation is achieved as confirmed by ^{1}H NMR and FT-IR spectra which are shown in Figs. 2 and 3 respectively. For the FT-IR spectrum of SPFETK-2, new peak at 1032 cm^{-1} in comparison with that of PFETK-2 is observed, validating the existence of sulfonic acid group in SPFETK-2. The introduction of sulfonic acid groups changed the electron density of PFETK-2. Therefore, the ^{1}H NMR spectrum of SPFETK-2 is different from that of PFETK-2. Furthermore, the resonance peak of proton in sulfonic acid group was detected as shown in Fig. 2. The inherent viscosities of SPFETKs are listed in Table 2. It can be seen that high viscosity ionomers are obtained, which could be a result of high molecular weight of PFETKs.

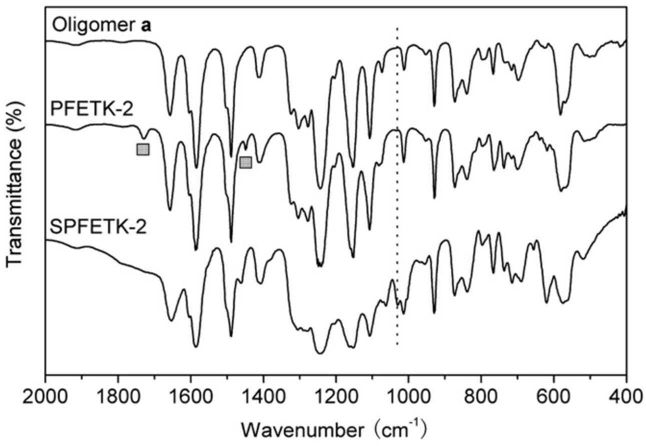


Fig. 3. FT-IR spectra of Oligomer **a**, PFETK-2 and SPFETK-2.

From Table 2 it can be seen that, ionomers with different IEC values ranged from 0.92 to 1.89 mequiv. g^{-1} were synthesized. The IEC value is controlled by tuning the feed ratio of 9,9′-S,S′-bis(*N*,*N*′-dimethyl-4-thiocarbamoyl-phenyl) fluorene monomer. It is calculated that the sulfonation degree (*z* value in polymer structure depicted in Scheme 2) is higher than 75%, suggesting both the main chain and side chain phenyl rings are successfully sulfonated. The IEC values can also be calculated from the integral ratio of all aromatic protons to protons in methyl group in the ^{1}H NMR spectrum of corresponding t-butyl containing polymer (see Fig. S1) as listed in Table S1.

3.3. Thermal properties

The thermal properties were investigated by DSC and TG/DTG analysis. The glass-transition temperatures (T_g) are listed in Table 1 for PFETKs and Table 2 for SPFETKs. PFETKs are designed to consist of oligomer **a** block randomly distributed in the polymeric main chain. There is only one T_g observed which should be arisen from the chain movement of this block. It can be seen that high T_g polymers are achieved due to their aromatic backbone. The T_g increased with the increasing content of the biphenyl fluorene segment. After the attachment of sulfonic acid groups, the T_g shifts to higher temperatures because of the chain confinement by the ion clusters. Considering the fact that sulfonated random copolymers don't have T_g prior to its decomposition, the existence of T_g for SPFETKs validates the designed block architecture.

The TG/DTG curves of oligomer **a** and PFETKs were shown in Fig. 4. It can be seen that PFETKs showed two decomposition stages

Table 2
Properties of SPFETKs.

Sample	Yield (%)	Viscosity ($g\,dL^{-1}$)	Titrated IEC (mequiv. g^{-1})	T_g (°C)	$T_{d-5\%}$ (°C)
SPFETK-1	82	1.5	0.92	189	346
SPFETK-2	85	1.7	1.15	208	342
SPFETK-3	81	1.8	1.53	221	336
SPFETK-4	83	2.0	1.89	240	337

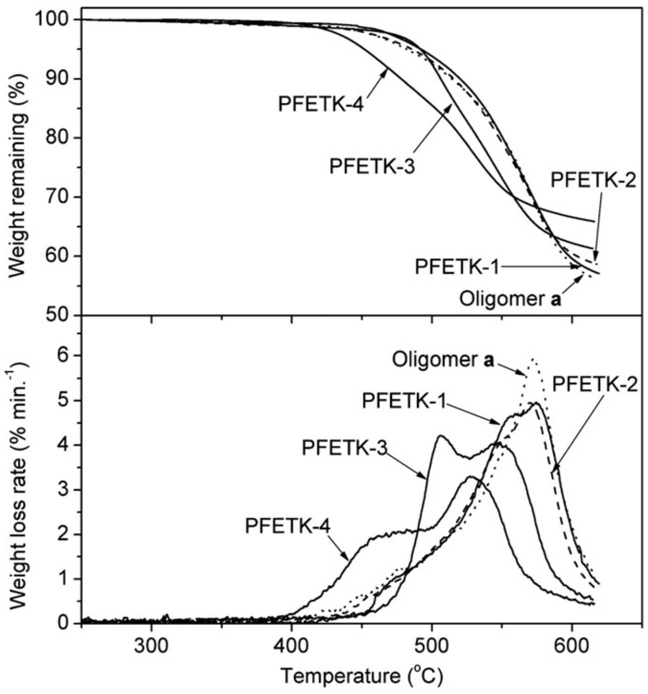


Fig. 4. TG/DTG profiles of Oligomer **a** and PFETKs.

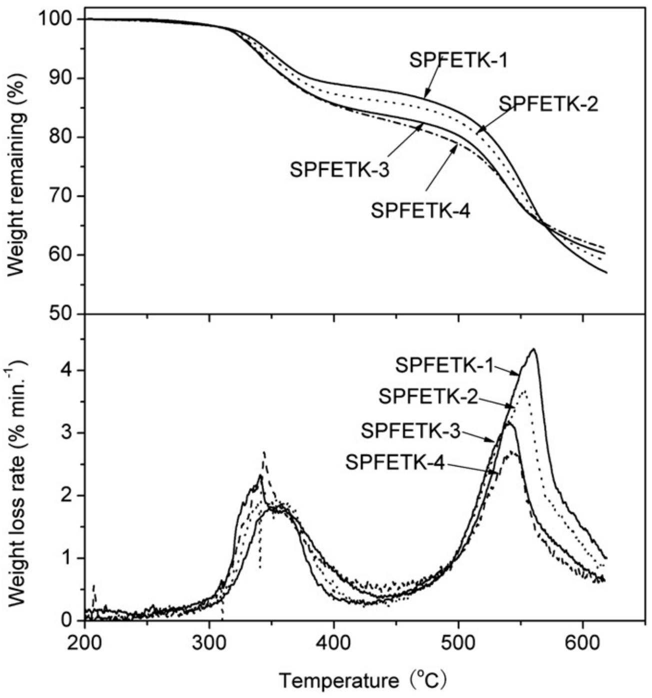


Fig. 5. TG/DTG profiles of SPFETKs.

while oligomer **a** shows only one decomposition stage. Since PFETKs is consisted of oligomer **a** block and biphenyl fluorene segment, the two decomposition stages correspond to these two segments. The 5% weight loss temperatures for oligomer **a** and PFETKs are listed in Table 1. All of the samples exhibit good thermal stability up to 450 °C.

The TG/DTG curves of SPFETKs are shown in Fig. 5. Two decomposition stages were observed, which were attributed to the decomposition of sulfonic acid groups (low temperature stage) and the decomposition of the polymeric backbone (high temperature stage). The ortho-position of ether or thioether bond at the phenyl rings is the electron-rich position under the normal circumstances. Since sulfonation is an electrophilic substitution reaction, the sulfonic acid groups are consequently attached to the ortho-positions. Generally, the decomposition temperature of sulfonic acid groups attached at the ortho-position of ether or thioether bond is less than 280 °C [24,25]. Interestingly, the 5% weight loss temperatures of SPFETKs are higher than 330 °C as listed in Table 2, suggesting that the sulfonic acid groups are not introduced to the ortho-position of thioether bond on SPFETKs. From the above titrated IEC values, it can conclude that the sulfonic acid groups have been successfully introduced to the main chain biphenyl rings. After examining the electron density of biphenyl fluorene segment by ChemDraw, we found that the electron density of the ortho-position is lower than that of the meta-position of thioether bond in this case. Therefore, we propose that the sulfonic acid groups are mainly attached to the meta-position of thioether bond. This is different with the poly(arylene ether)s where the biphenyl fluorene was connected to the polymeric main chain by ether bond [26]. However, due to the complexity of the system, it is difficult to assign the exact position of sulfonic acid groups.

3.4. Mechanical properties and oxidative stability

The mechanical properties of SPFETKs are listed in Table 3. It can be seen that all samples possess comparable tensile strength with other sulfonated aromatic ionomers with relevant IEC values [9,25]. The tensile strength increased obviously with decreasing the IEC value of the samples, implying that the higher sulfonic acid groups content in the synthesized polymer resulted in the poor tensile strength. This is because more water can swell the membrane and then decrease the cohesion of the polymer molecules.

The oxidative stabilities of the samples were investigated in Fenton's reagent (3 wt.% $H_2O_2 + 2$ ppm $FeSO_4$) at 80 °C, and the results are listed in Table 3. It can be seen that the oxidative stability deceased with increasing IEC of samples. This is attributed to the larger water uptake which results in more opportunities for the attack of radicals to the backbones of polymers. These oxidative stabilities are comparable to the results disclosed in the literature [27], and also our previously reported SPFEK which showed excellent stability for vanadium redox flow battery (VRB) application [2]. Poly(perfluorosulfonic acid) membranes, e.g. Nafion, are well known highly oxidative stable membranes due to the unprecedented hydrophobic nature of fluorine and its strong electron withdrawing effect [28]. However, it is environmental unfriendly to produce these fluorine containing compounds.

3.5. Water uptake, proton conductivity and VO^{2+} permeability

The water uptakes of SPFETKs were measured at 35 °C and 80 °C, and are listed in Table 3. It can be seen that the water uptake increased with increasing IEC of SPFETKs or increasing temperature for each sample. The water uptakes were generally higher than the random copolymers, a same phenomenon with other literatures on the block ionomers [28].

As one of the most important parameters for SPFETKs, the proton conductivities were investigated with the influence of temperature as depicted in Fig. 6. Like water uptake, the proton conductivity increased with increasing IEC values of SPFETKs or increasing temperature for each sample. SPFTEK-3 (IEC = 1.66 mequiv. g^{-1}) exhibited equivalent proton conductivity with Nafion117, a significant improvement over our previously reported random copolymer

Table 3
Membrane properties based on SPFETKs and Nafion117.

Sample	Water uptake (%)		Tensile strength (MPa)	Elongation at break (%)	Oxidative stability (min.)	VO^{2+} permeability ($\times 10^{-12}$ m^2 s^{-1})
	35 °C	80 °C				
SPFETK-1	22	26	21	72	88	0.6
SPFETK-2	30	35	18	57	61	1.8
SPFETK-3	52	62	17	45	53	3.1
SPFETK-4	79	106	15	36	45	4.4
Nafion117	21	29	19	245	>1440	4.9

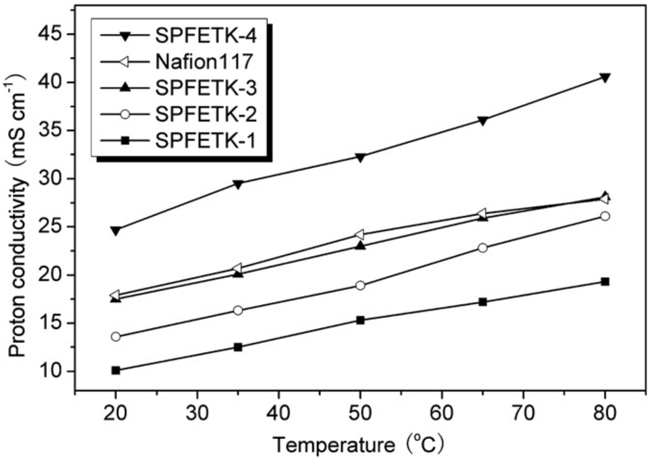


Fig. 6. The proton conductivity of SPFETKs as a function of temperature.

SPTKK which had an IEC value of 1.91 mequiv. g^{-1} and only exhibited 70% proton conductivity of Nafion117 membrane [29]. SPFTEK−4 (IEC = 1.95 mequiv. g^{-1}) exhibited about 40% higher proton conductivity than Nafion117 at all the tested temperatures. The SPFETKs were derived from SPTKK by changing random structure to block structure and amending the sulfonation strategy. These evolvements should facilitate the self-assembling of sulfonic acid groups into proton conductive channels and result in effective phase separation [25], leading to significantly improved proton conductivities.

Transmission electron microscopic (TEM) images of silver-stained representative SPFETK-2 and SPFETK-3 membranes are shown in Fig. 7. The dark areas correspond to hydrophilic domains while the brighter areas correspond to hydrophobic domains. It can be seen that both samples have obvious microphase separation. The ion cluster of SPFETK-3 is around 13 nm while that of SPFETK-2 is around 8 nm. This is because the former sample has higher IEC value than the latter sample. Nevertheless, the TEM images show poor connected hydrophilic domains, which might be the reason for their lower proton conductivities compared to Nafion117 at the same IEC level.

The VO^{2+} permeabilities of SPFETKs are listed in Table 3. It is apparent that the VO^{2+} permeability has a same trend as water uptake and proton conductivity in respect to the influence of IEC values. The higher IEC value of the membrane provides more sulfonic acid groups to absorb water and conduct ions (H^+, VO^{2+}), where the larger amount of water absorbed further facilitates the ions conduction. The slightly increased VO^{2+} permeability as compared to our previous SPTKK membrane should be attributed to the higher water uptakes in these SPFETKs membranes. The VO^{2+} permeability of Nafion117 membrane was measured under same conditions and calculated to be 4.9×10^{-12} m^2 s^{-1}, which is larger than any of SPFETKs membranes. The higher VO^{2+} permeability of Nafion117 membrane is resulted from its distinct phase separation and well connected hydrophilic channels which lead to lower ion selectivity. It is worthy to point out that Nafion also suffers too much methanol leakage when used in direct methanol fuel cell [30,31] in its native form. The hydrophilic channels for SPFETKs are more tortured and twisted as compared with Nafion117. Therefore, the proton selectivity of SPFETKs is much higher than Nafion117 membrane. SPFTEK-4, which exhibited 40% higher proton conductivity than Nafion117, showed 10% lower VO^{2+} permeability than Nafion117. This promising result is superior to our previous reported SPFEK [2], SPTK [10], and others reported SPEEK [3], where lower VO^{2+} permeability can only be achieved at lower proton conductivity when compared to Nafion.

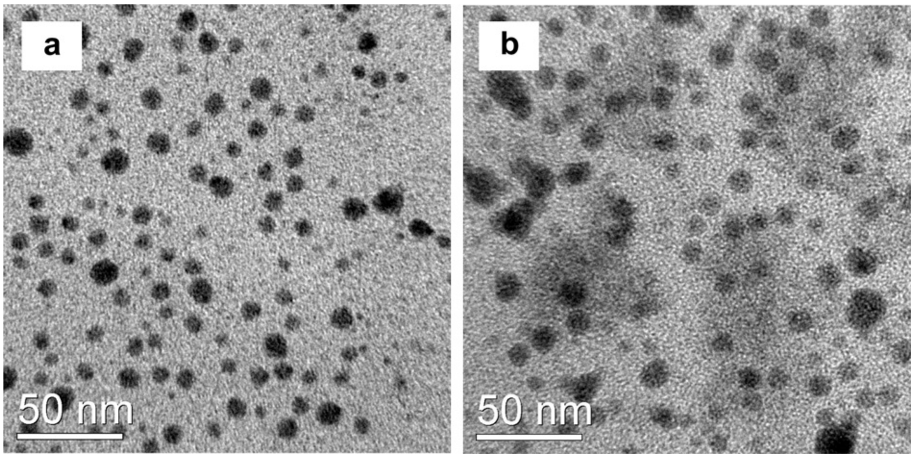


Fig. 7. TEM images of (a) SPFETK-2 and (b) SPFETK-3.

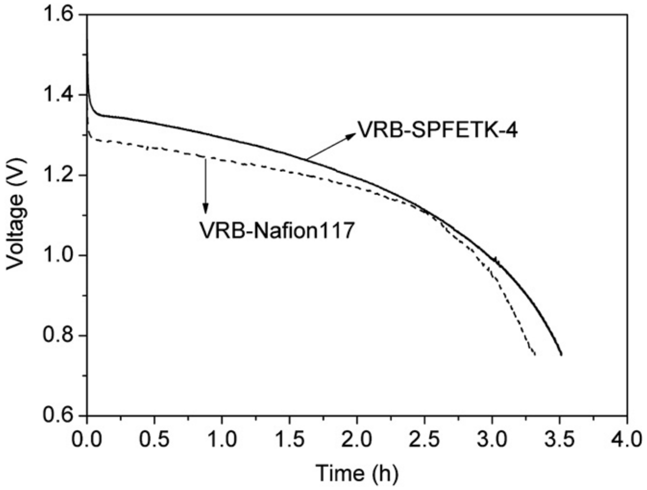


Fig. 8. Discharge characteristics of VRBs assembled with SPFETK-4 and Nafion117 at the current density of 50 mA cm^{-2}.

3.6. Cell performance

The discharge characteristics of VRBs assembled with SPFETK-4 and Nafion117 (denoted as VRB-SPFETK-4 and VRB-Nafion117 respectively) at a current density of 50 mA cm^{-2} are shown in Fig. 8. The thickness of SPFETK-4 used here is 170 μm, equivalent to that of Nafion117. It can be seen that VRB-SPFETK-4 had higher discharge voltage and longer discharge time than VRB-Nafion117. The higher discharge voltage is attributed to the lower resistance of SPFETK-4 while the longer discharge time is due to the lower electrolyte permeation of SPFETK-4 as discussed above. The columbic efficiency of VRB-SPFETK-4 is 84.2%, significantly higher than that of VRB-Nafion117 of 75.1%.

4. Conclusions

Bulky-block poly(fluorenyl ether thiother ketone)s can be readily synthesized by a two-step one-pot protocol, followed by the sulfonation using $ClSO_3H$ as sulfonating agent to obtain sulfonated block poly(fluorenyl ether thiother ketone)s (SPFETKs) for vanadium redox flow battery (VRB) application. The sulfonic acid groups are introduced on to both the main chain and side chain phenyl rings. The ionic exchange capacity (IEC) of SPFETKs can be controlled by adjusting the content of biphenyl fluorene segment in the parent polymers. All the SPFETKs show improved proton conductivity as compared to our precious reported random copolymers with similar structure at equivalent IEC value. The SPFETK-4 with an IEC value of 1.95 mequiv. g^{-1} exhibits about 40% higher proton conductivity and 10% lower VO^{2+} permeability than Nafion117. As expected, the VRB-SPFETK-4 has higher discharge voltage and longer discharge time than VRB-Nafion117.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.09.021.

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