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PAPER

Novel polyaromatic ionomers with large hydrophilic domain and long hydrophobic chain targeting at highly proton conductive and stable membranes

Dongyang Chen,[a] Shuanjin Wang,*[a] Min Xiao,[a] Yuezhong Meng*[a] and Allan S. Hay[b]

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A novel dihydroxyl monomer bearing 18 electron rich phenyl rings were synthesized and polymerized with other monomers bearing electron deficient phenyl rings to give dense and selective sites in macromolecules for post-sulfonation, which was successfully conducted in $ClSO_3H/CH_2Cl_2$ solution at room temperature in a subsequential step. The chemical structures were confirmed by ^1H NMR and FT-IR spectra. The ionic exchange capacity (IEC) was controlled to be from 0.65 to 1.21 mequiv g^{-1} to afford considerable proton conductivity. Distinct phase separation was observed in the resulting membranes from SAXS profiles. The SPAEK-5 with an IEC of 1.21 mequiv g^{-1} gave better proton conductivity than Nafion 117 at all tested temperatures under 100% relative humidity. The membranes exhibited an exceeding stability when immersing in Fenton's reagent (3 wt.% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C. These properties make them promising candidates for electrochemical applications.

Introduction

Sulfonated polymeric ionomers, as one of the most distinguished functional polymeric materials, have attracted extensive interest for a variety of applications such as polymer electrolyte membrane fuel cell, actuator, vanadium redox flow battery, electrolyzer, nanofiltration, chlor-alkali industry and so on.[1,2] Among all the properties proton conduction is the basic functionality, whereas the mechanical strength should be satisfied for assembly and the thermal and chemical stability should be filled for device operation. The perfluorosulfonic acid ionomers which integrate a hydrophobic Telfon-like backbone with hydrophilic ionic side chain possess excellent proton conductivity at low temperatures, which provides valuable models of efficient proton conduction for the design of alternative candidates for different purposes. Since these perfluorosulfonic acid ionomers possess low ion selectivity, high electrolyte permeability, are environmentally unfriendly andhave high cost, numerous works have been done on the development of high performance proton exchange membranes for electrochemical applications.[3–5] The high oxidative stability of perfluorosulfonic acid ionomers is attributed to the great hydrophobicity of the fluorine atom, which is not accepted to be environmentally benign. However, the excellent proton conductivity is attributed to their phase separations where the hydrophobic phase imparts mechanical support and the hydrophilic phase forms proton conducting channels.[6,7]

Sulfonated aromatic polymers have attracted lots of attention owning to their high thermal and chemical stability, excellent mechanical strength and easy manufacturing. The introduction of the sulfonic acid group is approachable through copolymerization with sulfonated monomer or post-sulfonation of parent polymers bearing sulfonation sites. However, it is envisaged that the proton conductivities of randomly sulfonated ionomers are too low as compared with NafionTM (Dupont) at the same ionic exchange capacity (IEC) level. Redesign of the polymer chemical structure is demanded for the development of high proton conductive ionomers.[8,9] Hay *et al.* have advanced several linear or branched end-capped ionomers exhibiting defined phase separation, however, the IEC of those ionomers is limited by the balance between the amount of end group and the molecular weight of the ionomers.[10–12] Ueda *et al.* have developed locally and densely sulfonated ionomers possessing improved proton conductivity due to the formation of a well-connected proton path. They have demonstrated that the ionomer with an IEC of 2.38 mequiv g^{-1} has comparable proton conductivity with Nafion even at 30% relative humidity.[13,14] Miyatake *et al.* have presented aromatic ionomers containing highly sulfonated block with proton conductivity comparable to (<40% RH) or higher than (>40% RH) that of Nafion membranes although still with higher IEC.[15] They also have exploited the influence of acidity on the proton conductivity, and achieved better performance than the common sulfonated poly(fluorenyl ether sulfone)s.[16]

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[a] *State Key Laboratory of Optoelectronic Materials and Technologies, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-Sen University, Guangzhou, 510275, (China). E-mail: mengyzh@mail.sysu.edu.cn; wangshj@mail.sysu.edu.cn*
[b] *Department of Chemistry, McGill University, 801 Sherbrooke West, Montreal, Quebec, H3A 2K6, Canada*

We have previously investigated many ionomers with sulfonic acid group on the main chain or pendent, randomly or multiblock distributed.[17–20] It is demonstrated that the aggregation and the mobility of sulfonic acid group are of primary importance for proton conduction. Herein, we report the design of novel ionomers bearing highly centralized and flexible sulfonic acid groups with the aim to construct unhindered proton conducting channels. The long hydrophobic chain is expected to impact mechanical support even after the degradation of hydrophilic segments, so as to avoid the direct contact of cathode and anode in the corresponding cell.

Experimental

Materials

4, 4′-Difluorobenzophenone and decafluorobiphenyl were purchased from Aldrich Chemical Co. and the former was recrystallized from ethanol. Bis(4-hydroxylphenyl)sulfone (99.9% purity), 4-phenylphenol, 4-methoxylphenol, boron tribromide were bought from Aladdin reagent Co., China. *N*,*N*′-Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), toluene, $CHCl_3$, CH_2Cl_2, methanol, ethanol, concentrated H_2SO_4 (95–98%), $ClSO_3H$, HCl, NaOH, *tert*-butylamine, anhydrous K_2CO_3 and aqueous H_2O_2 (30%) were obtained from commercial sources. DMAc and toluene were dried with 4 Å molecule sieves prior to use. Potassium carbonate was dried at 130 °C for 10 h prior to use.

Synthesis

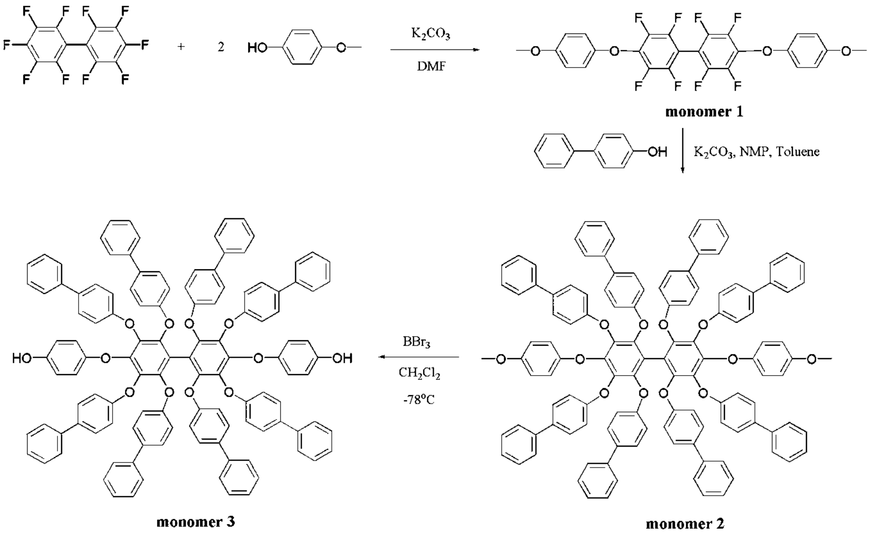
The synthetic processes of monomers and polymers are depicted in Scheme 1 and Scheme 2 respectively.

Synthesis of monomer 1. To a 25 mL three-neck round bottom flask equipped with a N_2 inlet, a Dean–Stark trap and a magnetic stirrer, 0.2482 g (2 mmol) 4-methoxylphenol were charged with 0.4170 g (3 mmol) K_2CO_3, 10 mL DMF as solvent and 5 mL toluene as azeotropic agent. The mixture was heated at 145–150 °C for 3 h to eliminate the produced water and then cooled down to 90 °C. 0.3341 g (1 mmol) decafluorobiphenyl was added and the reaction was continued for another 2 h. Finally the mixture was cooled down and precipitated out at water. Crude product was collected by filtration and recrystallized from ethanol/chloroform twice. Pure crystals were obtained with 83% yield (0.4502 g). m.p.: 97 °C. ^{1}H NMR (400 MHz, CDCl3, δ): 3.83 (s, 6H, CH_3), 6.88–6.94 (d, 4H, Ar H), 7.02–7.08 (d, 4H, Ar H).

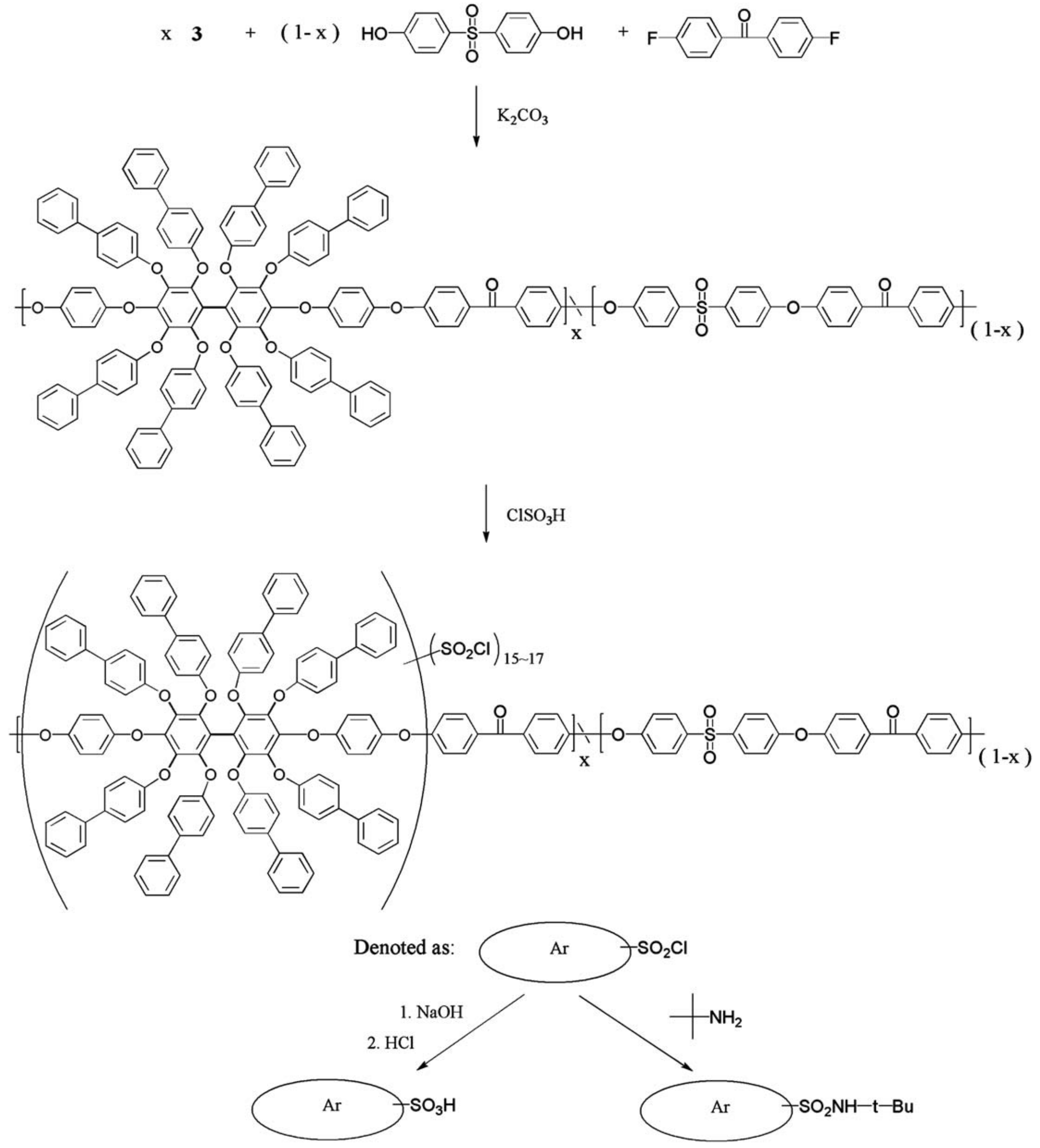
Synthesis of monomer 2. To a 25 mL three-neck round bottom flask equipped with a N_2 inlet, a Dean–Stark trap and a magnetic stirrer, 0.5424 g (1 mmol) monomer **1** and 1.3616g (8 mmol) 4-phenylphenol were charged with 1.3900 g (10 mmol) K_2CO_3, 10 mL NMP as solvent and 5 mL toluene azeotropic agent. The mixture was heated at 145–150 °C for 3 h to eliminate the produced water then the reaction temperature was increased to 190 °C and hold for 20 h. The mixture was cooled down and poured into water. The precipitate was collected by filtration and purified by column chromatography on a silica gel (dichloromethane: hexane = 1 : 1). Yield: 71% (1.2382 g). m.p.: 123–125 °C. ^{1}H NMR (500MHz, CDCl3, δ): 3.66 (s, 6H, CH_3), 6.42–7.55 (m, 80H, Ar H).

Synthesis of monomer 3. To a solution of monomer **2** (1.7440 g, 1 mmol) in dichloromethane (20 mL) was added 3 mL BBr_3 dropwise at −78 °C. The mixture was stirred at −78 °C for 1 h. Then the reaction temperature was elevated to room temperature and the reaction continued for 10 h, the mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$ and concentrated in vacuum. High purity product was obtained by column chromatography purification (dichloromethane) on a silica gel. Yield: 75% (1.2863 g). m.p.: 140–142 °C. ^{1}H NMR (500MHz, CDCl3, δ): 5.29 (s, 2H, OH), 6.42–7.55 (m, 80H, Ar H).

Copolymerization of poly(arylene ether ketone)s (PAEK)s (typical procedure, PAEK-1). To a 25 mL three neck flask equipped with a magnetic stirrer, a N_2 inlet, a Dean–Stark trap



Scheme 1 Synthesis of monomers.



Scheme 2 Copolymerization of PEAKs and sulfonation of SPEAKs and *t*-Bu-PAEKs.

and a condenser, monomer **3** (0.0343 g, 0.02 mmol), Bis(4-hydroxylphenyl)sulfone (0.0245 g, 0.98 mmol), potassium carbonate (0.0209 g, 1.5 mmol), 4, 4′-Difluorobenzophenone (0.0218 g, 1 mmol), toluene (2 mL) and DMSO (3 mL) were charged. The mixture was first heated at 145–150 °C for 3 h to eliminate the produced water, then the toluene evaporated out and brought up to 175 °C, and reacted at that temperature for another 3 h. After cooling down, the viscous mixture was poured into ethanol to precipitate out the polymer which was collected by filtration. The polymer was purified by redissolving it in $CHCl_3$ and precipitated out three times. The product was dried at 120 °C in vacuum for 24 h.

Synthesis of sulfonated poly(arylene ether ketone)s (SPAEKs). To a 150 mL round bottom flask, 75 mL dichloromethane and 0.4573 g (1 mmol) PAEK were introduced. After PAEK was dissolved completely, 3.6 mL of 1 M solution of HCl (3.6 mmol) in CH_2Cl_2 was added dropwise under 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. 90 wt.% of the solid was dissolved in 20 mL DMAc. To the solution 20 mL of 3 wt.% NaOH aqueous solution was added to react for 5 h, then the reaction mixture was acidified with 50 mL of 5 vol.% HCl 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.

Synthesis of t-Bu-PAEKs (typical procedure). The remaining 10 wt.% polymer from the above sulfonation procedure was dissolved in 5 mL NMP, then an 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. Then the solid was dried in vacuum at 100 °C for 3 h.

Membrane preparation. The synthesized ionomers were dissolved in DMAc and cast onto glass plates. Membranes with thickness between 100–200 μm were obtained after being dried at 80 °C for 24 h at atmosphere then 120 °C for 6 h in vacuum. Followed by release from the glass plates, membranes were immersed in 1 M H_2SO_4 solution at 80 °C for 2 h and boiling deionized water for 3 h with changing the water at least three times. Membranes were kept in deionized water until use.

Characterization

Instrumental

Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in a Bruker DRX NMR instrument and the chemical shifts were listed in 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. HPLC analysis was performed on SHIMADZU HPLC instrument equipped with LC-20AT pump and SPD-20A detector. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 Fourier transform spectrometer with membrane samples. Inherent viscosity of ionomers was determined using an Ubbelohde viscometer in DMAc at 20 °C. Melting point was taken on a SGW X-4 melting point apparatus. Thermal stability was analyzed using a PerkinElmer Pyris Diamond TG/DTA analyzer. The temperature was increased from 50 °C to 600 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere. The proton conductivity was 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 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). Samples were cut into dumbbell shape and immersed in deionized water prior to testing. Matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass spectra were recorded on a BRUKER DAL TONICS Ultraflex #xX_CYR_HEX_428; with the instrument set in the positive reflection mode. Lithium bromide and dithranol were used as cationization reagent and matrix respectively. Small Angle X-Ray Scattering (SAXS) spectrum was determined on Bruker D8 Advance X-Ray Diffractometer. Samples were conditioned at atmosphere overnight and irradiated by X-ray (Cu-Kα, λ = 1.5406 Å) at 40 kV and 30 mA.

Ion exchange capacity (IEC)

Calculated by the integral ratio of all aromatic protons and protons in methyl group in ^{1}H-NMR of the corresponding *t*-butyl bearing polymers.

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.

Oxidative stabilities

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 160 μm were immersed in Fenton's reagent and conditioned at 80 °C Water Bath Shaker.

Proton conductivity

Measured by electrochemical impedance spectroscopy.[21] Samples were cut into circles with diameter of 1 cm and soaked in deionized water for 20 h prior to test. Proton conductivity (σ) of the membranes in the transverse direction was determined by measuring the impedance spectrum of a cell with the given membrane sample sandwiched between two gold electrodes.

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

Where S and d are the face area and thickness of the membrane, and R is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the $Re(Z')$ axis.

Results and discussion

Synthesis of monomers and polymers

Decafluorobiphenyl was used to synthesize linear polymers owning to the different activity of two end fluorine atoms from the other eight fluorine atoms.[22,23] From this point, we designed a novel difluoro monomer (monomer **3**) from decafluorobiphenyl through three reaction steps as illustrated in Scheme 1. It can provide 18 sulfonation sites closely connected to the central biphenyl through 10 flexible ether bonds, which is expected to modulate the hydrophilic phase toward larger channels as compared to tranditional copolymers or block architectures. The ^{1}H NMR spectrum of monomer **3** is shown in Fig. 1. The presence of the strong singlet at δ = 5.29 ppm validates the successful transformation from methoxyl to hydroxyl. However, the peaks from 6.42 ppm to 7.55 ppm are indistinguishable or overlapped, in which a same phenomenon was reported on the monomer with similar complex structure in literature.[24] Sample purity was higher than 99% according to HPLC results. The molecular weights measured by MALDI-TOF for monomer **2** and monomer **3** are 1742.5 and 1714.5 respectively.

High molecular weight poly(arylene ether ketone)s (PAEKs) were synthesized *via* one-pot copolymerization of monomer **3**, bis(4-hydroxylphenyl)sulfone and 4,4′-difluorobenzophenone through nucleophilic substitution reaction. As shown in Table 1, the PAEKs containing varying amounts of monomer **3** were obtained in high yields. The number-average molecular weights of all samples were higher than 23 kDa, implying the high purity of monomer **3**. It is found that only the electron rich phenyl rings of poly(aryl ether)s could be sulfonated in the presence of large excess of $ClSO_3H$ in CH_2Cl_2 solution at room temperature.[10] The

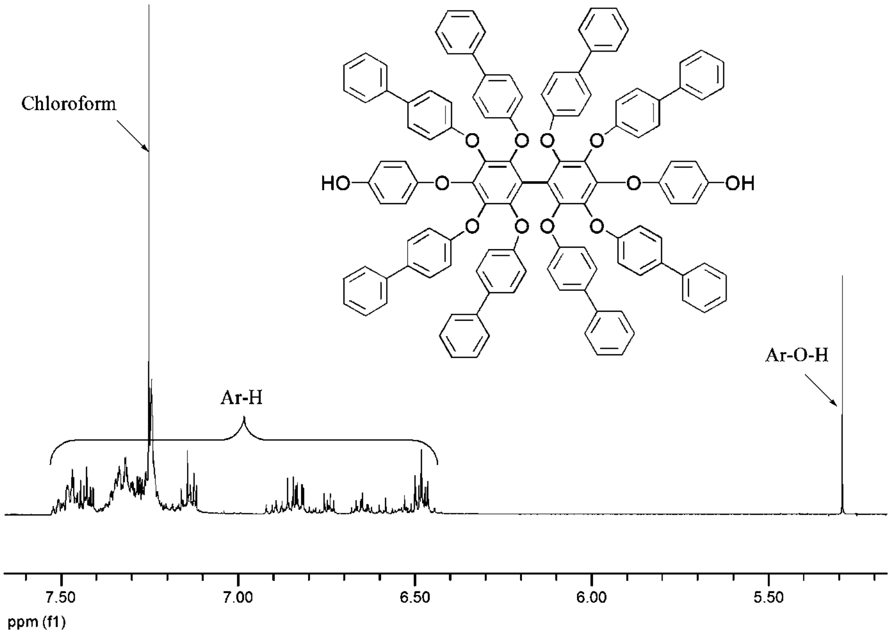


Fig. 1 ^{1}H NMR spectrum of monomer **3**.

Table 1 Basic properties of PAEKs

Sample	Monomer **3** content (%)[a]	Yield (%)	$\overline{Mn}$ (kDa)	$\overline{Mw}$ (kDa)	T_g (°C)	$T_{d\text{-}5\%}$/°C[b]	$T_{d\text{-max}}$/°C[c]
PAEK-1	2.0	>95	26	46	195.7	498.5	569.4
PAEK-2	2.3		24	42	191.7	479.2	573.3
PAEK-3	2.8		24	38	194.8	478.0	574.7
PAEK-4	3.5		23	39	192.2	471.1	568.8
PAEK-5	4.6		24	34	187.7	468.1	570.7

[a] Molar ratio of Monomer 3 in the hydroxyl groups containing monomers; [b] The 5% weight loss temperature; [c] The maximum weight loss temperature.

introduction of sulfone and ketone groups as strong electron withdrawing groups promises good stability of the adjacent phenyl rings in the sulfonation process and good solubility of the built polymer for efficient post-reaction. Selective sulfonation was successfully carried out in CH_2Cl_2 using $ClSO_3H$ as sulfonation agent. Sulfonated poly(arylene ether ketone)s (SPAEKs) were obtained with high inherent viscosities as shown in Table 2. The ionic exchange capacity (IEC) can be calculated from the integral area ratio of all aromatic protons to protons in the methyl group in the ^{1}H NMR spectrum. Every t-butyl group represents one sulfonic acid group in the polymer. The IEC measured in this way is demonstrated to be in good accordance with the titrated IEC value.[10] The representative ^{1}H NMR spectrum of t-butyl bearing polymers (*t*-Bu-PAEK-4) is shown in Fig. 5 (see later). An obvious resonance peak at 1.25 ppm is observed, which is assigned to the resonance of protons in methyl group. The resonance peaks from 6.70 ppm to 8.20 ppm are assigned to the signal of aromatic protons. From the integral area ratio of these two kinds of peaks, the t-butyl group content in the polymer can be calculated and translated to the sulfonic acid group content (the IEC value of the polymer). By controlling the feed ratio of monomer **3**, ionomers with different IECs can be readily synthesized. As shown in Table 2, five samples with the IEC varied from 0.65 to 1.21 mequiv g^{-1} were obtained ($IEC_{Nafion117}$ = 0.91 mequiv g^{-1}). The sulfonation degrees were calculated to be larger than 80%. Good solubility in *N*,*N*′-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP) was found for SPAEKs, while PAEKs only showed good solubility in $CHCl_3$ and CH_2Cl_2.

The chemical structures of PAEKs were examined by ^{1}H NMR and FT-IR techniques, which are shown in Fig. 2 and Fig. 3 respectively. After the introduction of sulfonic acid groups, a resonance peak of sulfonic acid group is observed as a single and broad peak in ^{1}H NMR spectrum (Fig. 4), which is a typical resonance peak of active proton. In FT-IR spectrum, the

Table 2 Basic properties of SPAEKs

Ionomers	IEC/ mequiv. g^{-1}	Solubility	Inherent viscosity/dL g^{-1}	T_g/°C	$T_{d\text{-}5\%}$/°C
SPAEK-1	0.65	DMF	0.41	192	355
SPAEK-2	0.82	DMAc	0.44	188	346
SPAEK-3	0.98	DMSO	0.48	194	345
SPAEK-4	1.07	NMP	0.53	201	337
SPAEK-5	1.21		0.44	195	336

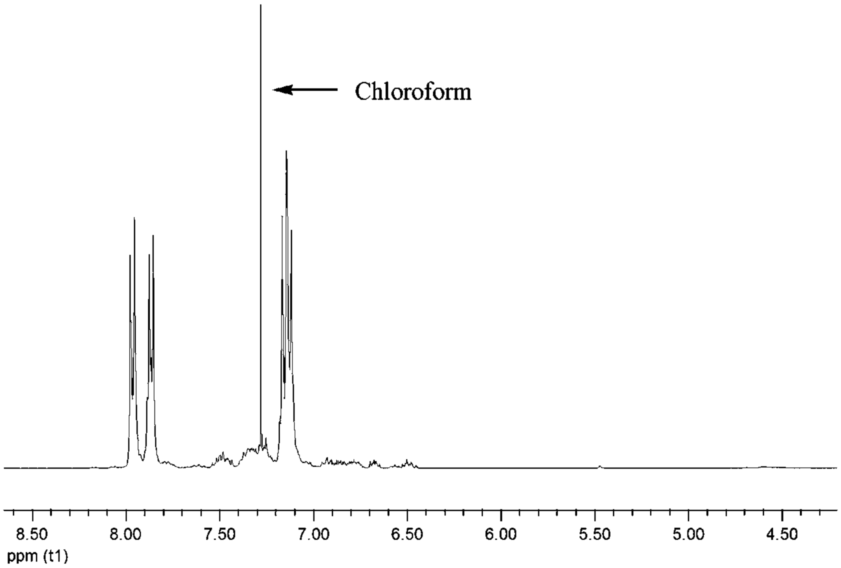


Fig. 2 ^{1}H NMR spectrum of PAEK-5.

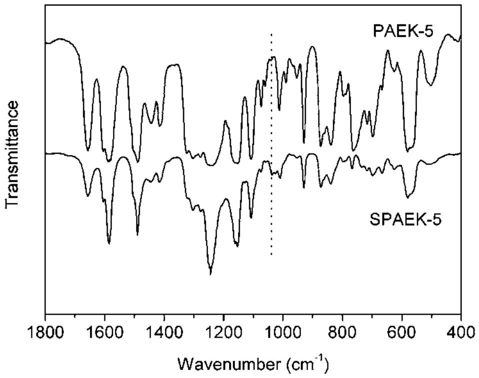


Fig. 3 Normalized FT-IR spectra of PAEK-5 and SPAEK-5.

absorption peak at 1032 cm^{-1} of SPAEK-5 is assigned to the asymmetric vibration of O=S=O in sulfonic acid group, which is absent in the FT-IR spectrum of PAEK-5. Both ^{1}H NMR and FT-IR results indicate the successful introduction of sulfonic acid groups.

Thermal property

One advantage of the adoption of aromatic polymers as supporting materials is their good thermal properties which are beneficial to elevate their operation temperature for potential applications. Because of the long hydrophobic chain (accounts for more than 95 mol%) of SPAEKs, the glass transition temperatures (T_g) are not obviously influenced by the introduction of sulfonic acid groups and were measured to be about

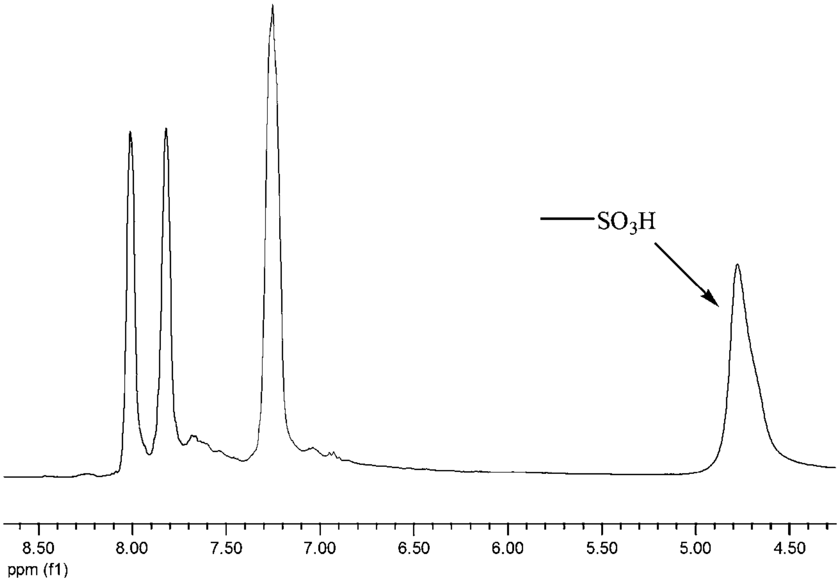


Fig. 4 ^{1}H NMR spectrum of SPAEK-5.

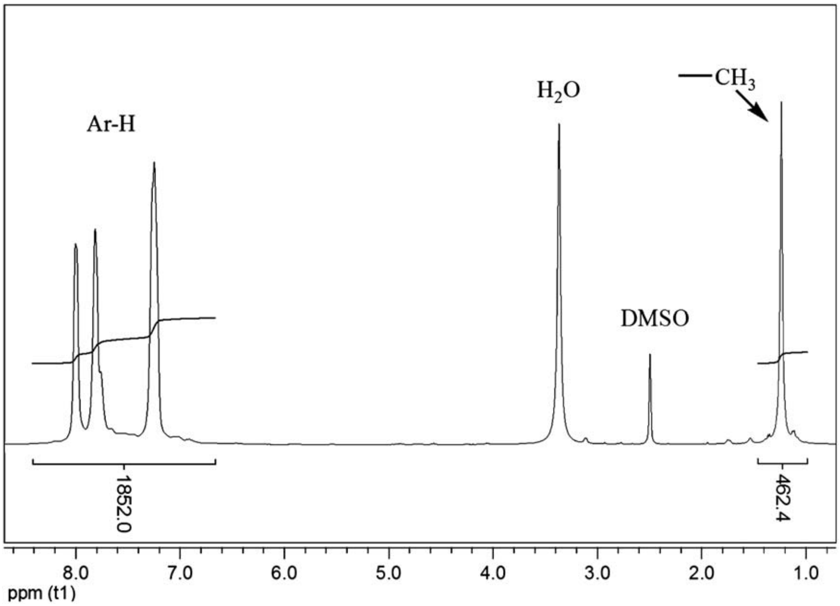


Fig. 5 ^{1}H NMR spectrum of *t*-Bu-PAEK-4.

190 °C as listed in Table 2. These results are similar to those of parent PAEKs. This is quite different from the random polymeric ionomers and those block polymeric ionomers with relative short hydrophobic chain (T_g can not be obtained before decomposition),[18] and even the block polymeric ionomers with certain length of hydrophobic chain (great increase in T_g after sulfonation).[25]

The TG curves of PAEKs and SPAEKs are shown in Fig. 6 and Fig. 7 respectively. PAEKs exhibit good thermal stability all the way up to 460 °C, while SPAEKs exhibit two steps decomposition profile (the decomposition of sulfonic acid group in the first step and the decomposition of the backbone of the polymer in the second step), the same as most of the reported sulfonated poly(arylene ether)s.[26] The 5% weight decomposition temperatures ($T_{d\text{-}5\%}$) are listed in Table 2. It can be seen that all of the $T_{d\text{-}5\%}$ are higher than 330 °C. With the decreasing in IEC, the $T_{d\text{-}5\%}$ of SPAEKs increases gradually.

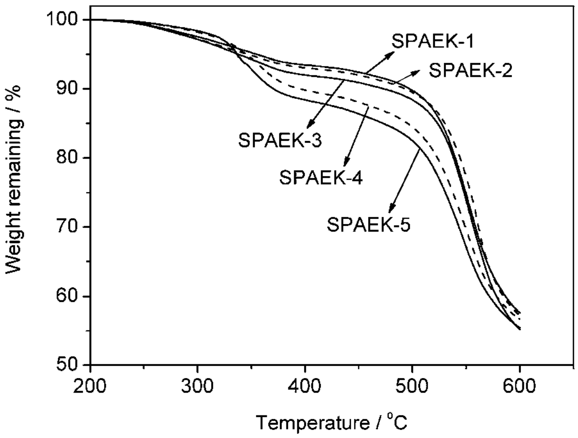


Fig. 7 TG curves of SPAKEs.

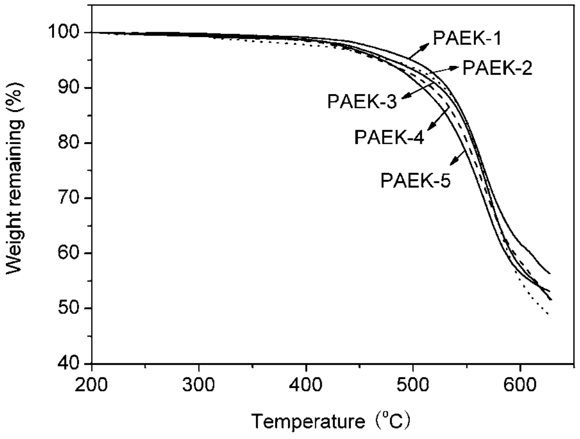


Fig. 6 TG curves of PAEKs.

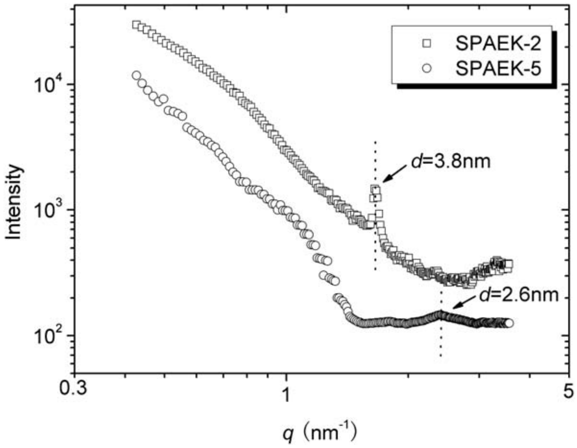


Fig. 8 SAXS profiles of SPAEK-2 and SPAEK-5.

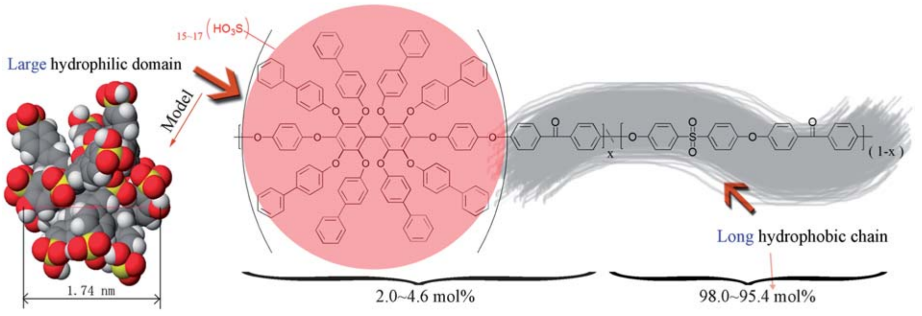


Fig. 9 Graphical illustration of the structure of SPAEKs.

Membrane morphology

The self-assembling of hydrophilic and hydrophobic phases produces an ionomer peak in small angle X-ray scattering (SAXS) which is attributed to the electron density difference of the separated phases. The scattering peak is considered to be the spacing of proton conductive channels.[27] Fig. 8 shows the SAXS profiles of SPAEK-2 and SPAEK-5 membranes. Intensive peaks are observed, indicating periodical electron density changed in distances of 3.8 nm ($d = 2\pi/q$) and 2.6 nm for SPAEK-2 and SPAEK-5 respectively. The spacing of proton conductive channels in SPAEK-5 is lower than that of SPAEK-2 because of its higher IEC value to form more hydrophilic channels. From these representative SAXS profiles it could be inferred that distinct phase separations in SPAEKs are achieved by this novel molecular design. The graphical illustration of the structure of SPAEKs is shown in Fig. 9. The hydrophilic domain is composed of sulfonated monomer[3] segments, whose single molecular length is as large as 1.74 nm (calculated using Cache software). The hydrophobic segments account for 98∼95.4 mol% of the linear ionomers. These large hydrophilic domains and long hydrophobic chains should facilitate the self-assembling of each phase during membrane preparation and account for the distinct phase separation observed above. The highly centralized sulfonic acid groups thus are more convenient to form inter-connected proton conducting channels.

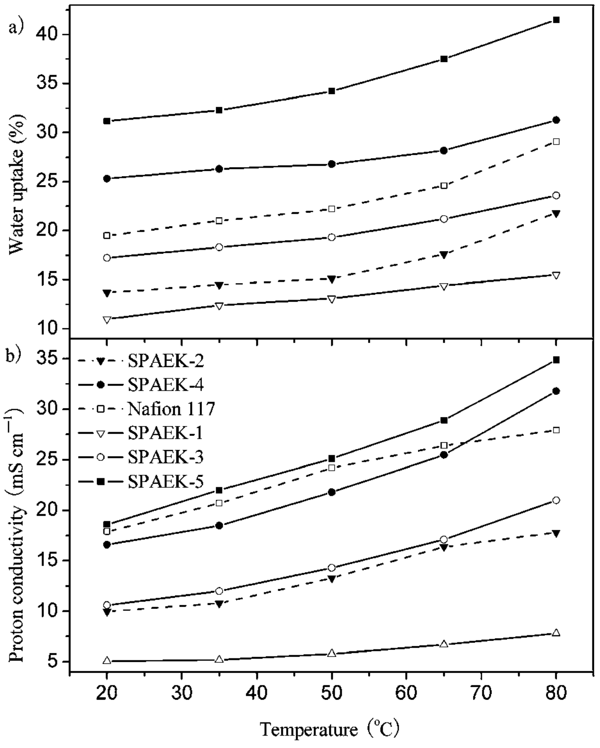


Fig. 10 Water uptake (a) and proton conductivity (b) of Nafion 117 and SPAEKs as a function of temperature at 100 RH%.

Proton conductivity and water uptake

The dependence of water uptake and proton conductivity on temperature at 100% relative humidity is shown in Fig. 10. Both properties increase with increasing temperature for SPAEKs and Nafion 117. Furthermore, the higher IEC of SPAEKs resulted in the higher water uptake and proton conductivity. SPAEK-2, which has slightly lower IEC compared to Nafion 117, exhibits about half the proton conductivity of Nafion 117. This behavior is not often reported in literatures. In case of only increasing the IEC to 1.21 mequiv g^{-1} (SPAEK-5), the proton conductivity becomes higher than that of Nafion 117 at all the tested temperatures. The dramatically improvement is considered to be the result of distinct phase separation originated from the novel structure as illustrated above. It should be mentioned that, according to the results obtained in our measurements, the proton conductivities of Nafion 117 are slightly lower than that reported in literatures.

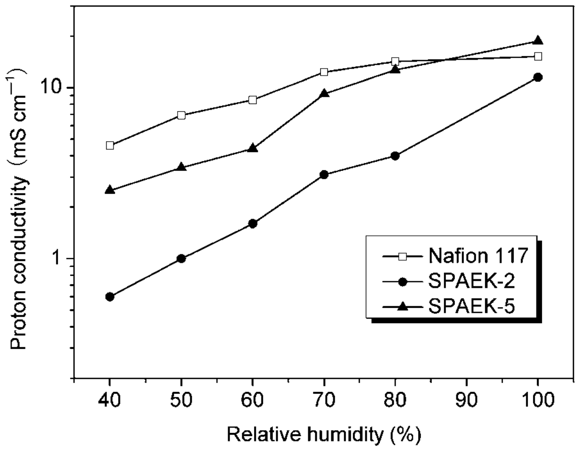


Fig. 11 The dependence of proton conductivity on relative humidity at 90 °C.

Table 3 Mechanical properties of SPAEKs

Sample	Tensile strength/Mpa	Elongation at break (%)
SPAEK-1	22.6 ± 2%	26.1 ± 5%
SPAEK-2	19.3 ± 1%	28.8 ± 2%
SPAEK-3	18.1 ± 2%	33.4 ± 3%
SPAEK-4	16.5 ± 4%	38.9 ± 4%
SPAEK-5	15.3 ± 3%	44.0 ± 2%

Fig. 11 shows the dependence of proton conductivity on relative humidity at 90 °C. It is well accepted that the efficient transportation of proton needs the assistance of water.[1] With increase in relative humidity, the proton conductivity shows an obvious increase. SPAEK-5 exhibits comparable proton conductivity with Nafion 117 under low relative humidity, which validates the construction of well-connected proton conductive channels. The higher proton conductivity of Nafion 117 here should not only be ascribed to the pronounced phase separation of hydrophilic and hydrophobic domains but also the shape of the hydrophilic channels (cylindrical[28]). The hydrophobic phase of Nafion 117 consists of crystalline domains and amorphous domains. However, the hydrophobic phase of SPAEKs is totally amorphous according to the DSC characterization. This intrinsic difference leads to the different interaction between hydrophilic and hydrophobic phases, so as to the different shape of the hydrophilic channels. Therefore, it is of great challenge to modulate the proton conductive channels not only from the viewpoint of phase separation but also the interaction between hydrophilic and hydrophobic phases. This provides a new way to design the molecular structure of sulfonated polymeric ionomers.

Mechanical property and oxidative stability

From Table 3 it can be seen that all of the samples possess relative high tensile strength (higher or comparable to the tensile strength of Nafion[29]). The tensile strength of SPAEKs decreases with increasing IEC value while the elongation at break gives a reverse trend. This is because the higher IEC value should result in higher water uptake (Fig. 10), leading to more swelling of the membrane and lower cohesion of polymer molecules.

It is well accepted that the oxidative stability decreases with increasing IEC value and water uptake.[20] The oxidative stability of SPAEKs is supposed to be similar to other aromatic polymeric ionomers with the same IEC value and water uptake due to the same degradation mechanism involved. However, an abnormal phenomenon was observed. The samples of SPAEKs did not break into pieces in a Water Bath Shaker for more than 24 h. By comparing with our previous similar systems under the same testing conditions, the oxidative stability of SPAEK-5 exhibited a dramatic improvement as shown in Table 4. During the accelerated test, samples underwent decomposition at the hydrophilic domains which leads to break up of the polymeric main chain and results in loss of mechanical strength. The SPAEKs can maintain their physical appearances for a much longer durability with very slight changes on the surface. This is attributed to the long hydrophobic chain which impacted the mechanical strength after the decomposition of the hydrophilic domains. The anti-oxidative and hydrolysis durability can endow the membrane as a stable separator to avoid short circuit of the electrochemical devices.

Table 4 Oxidative stability comparison of SPAEK-5 with our previous systems

Sample	IEC/mequiv g^{-1}	Oxidative stability/min
SPAEK-5	1.21	>1440
SPTK[20]	1.29	89
SPFEK[30]	1.92	85
2a-1[31]	0.97	85
6b[32]	1.18	130
7c[33]	1.20	150

Conclusions

Novel aromatic ionomers with large hydrophilic domain and long hydrophobic chain structure were synthesized and characterized for proton exchange membrane application. Selective sulfonation was achieved through rational molecular design, which was to control the electron density of corresponding phenyl rings of the polymers. The resulting membranes exhibited distinct phase separation and modulated proton conductive channels. The ionomer with IEC as low as 0.82 mequiv g^{-1} showed about half proton conductivity of Nafion 117 under 100% relative humidity. The SPAEK-5 with an IEC of 1.21 mequiv g^{-1} gave better proton conductivity than Nafion 117 at all tested temperatures under 100% relative humidity. These specially designed ionomers exhibit highly thermal and oxidative stability. They are promising candidates for electrochemical applications.

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