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Communications to the Editor

Ionomers for Proton Exchange Membrane Fuel Cells with Sulfonic Acid Groups on the End Groups: Novel Linear Aromatic Poly(sulfide−ketone)s

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Fuel cells, electrochemical devices converting chemical energy efficiently into electrical energy via redox reactions, are expected to be one of the clean future power sources.[1,2] Proton exchange membranes (PEM), which act as an electrolyte to transport protons from the anode to the cathode, are the key component of PEM fuel cell systems. Perfluorosulfonic acid membranes such as Nafion are the current choice for PEMs because of their superior chemical and electrochemical stability, in addition to high proton conductivity with relatively low ion exchange capacity (IEC). However, their critical drawbacks of high cost, high methanol crossover, and low proton conductivity as well as poor mechanical stability at elevated temperatures ($T > 80$ °C) have led researchers to investigate promising alternatives.[2,3] There has been considerable effort on PEMs based on sulfonated polystyrenes and their derivatives,[4,5] acid complexes of basic polymers,[6,7] and organic−inorganic hybrids.[8,9] However, the majority of current research on PEMs is based on sulfonated high-performance aromatic polymers because of the high thermal and chemical stabilities as well as excellent mechanical properties of the parent polymers.[10,11] Two general approaches are available for the synthesis of sulfonated high-performance aromatic polymers: (1) post-sulfonation of existing aromatic polymers usually leading to random functionalization along polymer main chain;[12] (2) direct copolymerization of sulfonated monomers to afford random copolymers. However, sulfonated random copolymers prepared by these approaches can generally achieve conductivities comparable to that of Nafion only with high IECs, resulting in high water uptake (WU) and loss of mechanical properties. For example, randomly sulfonated poly(ether−ether−ketone), one of the membranes studied extensively for PEMs, required an IEC of 1.52 mequiv/g to attain conductivity of 0.4 mS/cm[13] and an IEC of 2.45 mequiv/g for a conductivity of 51 mS/cm.[14] It is widely recognized that the superior proton conductivity of Nafion is attributed to the extensive nanoscale phase separation of ionic and nonionic domains.[15−18] The model suggested by Kreuer[16] for a sulfonated poly(ether−ketone) shows less pronounced ionic/nonionic separation than that of Nafion, i.e., a morphology with narrower channels than those in Nafion but with highly branched channels and many dead-end channels. A few recent reports on sulfonated aromatic multiblock copolymers are of interest because they showed higher conductivities than the corresponding random copolymers,[19−22] probably due to better phase separation. However, the research on this class of copolymers is still in the initial stage, and the precise control of nanoscale morphology of multiblock copolymers may be restricted due to the polydispersity of each block.[18]

Herein, we report the first examples of aromatic polymers bearing sulfonic acid groups only on the end groups as ionic clusters. We believed that this architectonically novel class of polymers would be capable of better microphase separation of the nonpolar and ionic moieties to enhance proton conductivity than that of random copolymers or polydisperse multiblock copolymers. Phase separation of the backbone polymer in the end-capped polymers should be greatly facilitated since there would be few small incompatible segments. We have previously reported regioselective post-sulfonation of pendant phenyl rings along a main chain.[23,24] Therefore, we designed a novel end group with a number of pendant phenyl rings providing selective sulfonation sites and soluble, non-fluorinated, chemically stable, and wholly aromatic poly(sulfide−ketone)s (PSKs) as main chains. While the design of a non-fluorinated main chain is essential in terms of cost and methanol permeability, the introduction of the ketone group as a strong electron-withdrawing group promises good stability for post-sulfonation and good solubility for efficient post-sulfonation.

The key end group with pendant phenyl groups as selective post-sulfonation sites, 1-(4-hydroxyphenyl)-2,3,4,5,6-pentaphenylbenzene (**1**), was successfully synthesized via Diels−Alder reaction of 1-methoxy-4-(2-phenylethynyl)benzene and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one, followed by the deprotection of methoxy group by use of boron tribromide. Pure **1** was obtained in high yield by either recrystallization from acetone or washing with hot acetone using a Soxhlet extractor (Scheme 1).

Model reactions for end-capping of the main chain were performed by two methods: (1) synthesis of a block bearing both fluoride end groups, followed by the end-capping reaction with a large excess of **1**; (2) one-pot polycondensation of monomers in the presence of **1**. While the former resulted in the chain cleavage of the block, the latter afforded cleanly end-capped polymer. The end-capped structure and M_n were confirmed by its ^{1}H NMR spectrum.[25]

We employed both aromatic dihalides (**2**) and aromatic dithiols (**3**) bearing at least one ketone group on each phenyl ring as monomers to ensure the stability of the main chain toward sulfonation. At first uncapped **PSK**s (**4**s) were synthesized by the polycondensation of **2** and **3** in the absence of **1** (Scheme 2). The polycondensation of **2a** and **3a** in sulfolane at

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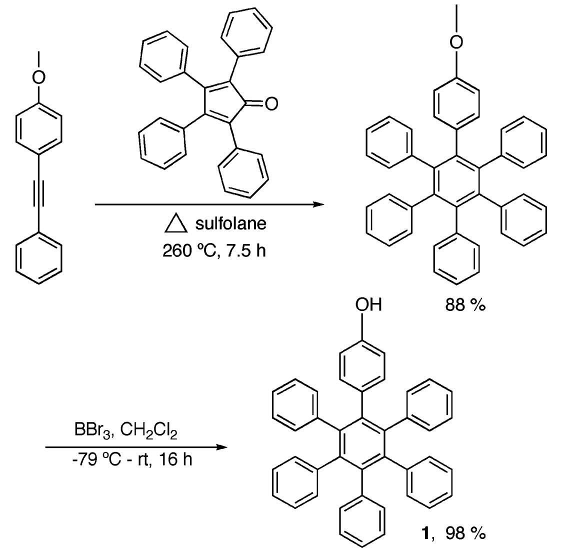
Scheme 1. Synthesis of End Group 1



215 °C in the presence of potassium carbonate afforded **4a**, which was insoluble in any organic solvent due to its rigid and regular structure. High molecular weight **4b** was obtained under highly concentrated conditions (initially 41% w/w, followed by dilution to 32% w/w with the increase in viscosity of the reaction system) at 150 °C in 1-methyl-2-pyrrolidinone (NMP), to minimize the formation of macrocyclic oligomers. In contrast to **4a**, **4b** showed remarkably good solubility in various organic solvents such as dichloromethane due to its lower stereoregularity resulting from the introduction of the ortho-substituted phenyl ring. **4c** was readily synthesized by the same procedure and showed good solubility due to the introduction of four bulky methyl groups. End-capped **PSK**s (**5b** (M_n 24 000 from the ^{1}H NMR spectrum, M_n 13 000, M_w 76 000, and MWD 6.0, by GPC) and **5c** (M_n 25 000 from the ^{1}H NMR spectrum, M_n 15 000, M_w 79 000, and MWD 5.2, by GPC)) were synthesized by the same procedure described for the model reaction of end-capping, method 2.

In order to investigate the stability of the main chains under sulfonation conditions, control experiments for sulfonation were performed using **4b** and **4c**. No difference was observed in their ^{1}H NMR and IR spectra and GPC profiles before and after the treatment under sulfonation conditions for **4b** and **4c**, indicating their excellent stabilities, i.e., neither sulfonation nor chain cleavage occurred.[25]

To sulfonate the end groups, **5b** was allowed to react with a large excess of chlorosulfonic acid in dichloromethane at room temperature. Then sulfonyl chloride intermediate (**6b-SO$_2$Cl**) was hydrolyzed by 3% KOH aqueous solution, followed by acidification by concentrated HCl aqueous solution (Scheme 3). The number of sulfonic acid groups introduced on each end-capped polymer chain was calculated using M_n of **5b** from the ^{1}H NMR spectrum and IEC of **6b-SO$_3$H** from titration and back-titration measurements. After 2 h reaction with chlorosulfonic acid, 6.0 sulfonic acid groups were introduced on each end-capped polymer chain, and reaction for prolonged times up to 19 h introduced 12 sulfonic acid groups on each end-capped polymer chain, i.e., 6 sulfonic acid groups were introduced on each end group. This result indicates that selective and quantitative sulfonation occurred exclusively only on the end groups in **5b**. It has been reported that regioselective chlorosulfonation at all para positions of the pendant phenyl rings for hexaphenylbenzene takes place under similar conditions.[26,27] By analogy, although there is no direct evidence for the regioselectivity, we presume that sulfonation occurred principally at the para positions of the five pendant phenyl rings and at the position ortho to the ether group on the end group. **6c-SO$_3$H** was readily synthesized by the same procedure used for **6b-SO$_3$H**, except that NMP was used as solvent instead of dimethyl sulfoxide (DMSO) for the hydrolysis step due to the insolubility of **6c-SO$_2$Cl** in DMSO. A characteristic IR absorption $\nu_{S=O}$ of the sulfonic acid group was observed at 1034 cm^{-1} for **6-SO$_3$H**s. The TGA curve of **6-SO$_3$H**s showed weight loss starting near 230 °C, a typical decomposition temperature of sulfonic acid groups.

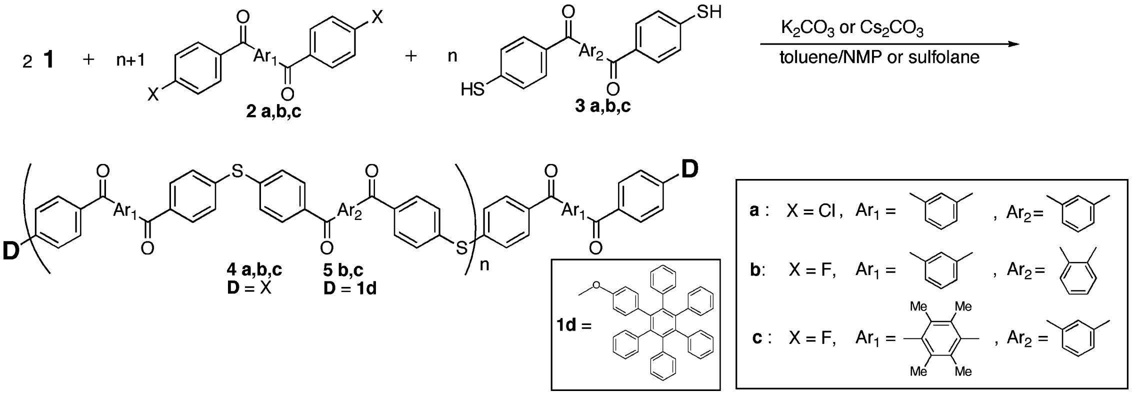
Strong membranes of **6-SO$_3$H**s were prepared by casting in sulfonic acid form from the DMSO or NMP solution. Nafion membrane is usually prepared by extrusion in the sulfonyl fluoride form, followed by hydrolysis by immersion of the film in basic aqueous solution and then acidification in aqueous acid solution.[28] Solution-cast Nafion membrane, when dissolved and cast in the acid form, can show 10^4 times lower conductivity than that of as-received membrane.[17] Therefore, casting membranes in sulfonyl chloride form would be of interest. To our knowledge, there are no reports on the comparison of conductivities of membranes cast in sulfonyl chloride form with those cast in sulfonic acid form, although there is a patent[29] that reported casting membranes in soluble sulfonyl chloride form due to the insolubility of the acid form. A DMSO solution of **6b-SO$_2$Cl** was directly cast onto a glass plate. After drying in vacuo at 60 °C for 3 days, the sulfonyl chloride group in the membrane was hydrolyzed by immersion in 1 M NaOH aqueous solution at room temperature for 48 h, followed by acidification in boiling 0.5 M H_2SO_4 aqueous solution for 2 h.

Table 1 summarizes the properties of the membranes. The T_g of **6b-SO$_3$H** and **6c-SO$_3$H** was higher than that of **5b** and **5c**, respectively, due to the introduction of the polar sulfonic acid groups. The measured IECs of **6b-SO$_3$H** and **6c-SO$_3$H** agreed well with the calculated IECs. **6b-SO$_3$H** and **6c-SO$_3$H** showed similar WU and hydration number (λ), as expected from their similar IECs. In contrast to sulfonated random aromatic polymers reported in the literature, both **6-SO$_3$H**s achieved relatively high proton conductivities (6.9 or 3.7 mS/cm) with very low IECs (0.48 or 0.47 mequiv/g). For example, the proton conductivity (6.9 mS/cm) of **6b-SO$_3$H** with much lower IEC (0.48 mequiv/g) was 1 order of magnitude higher than that (0.4 mS/cm) of the above-mentioned sulfonated poly(ether−ether−ketone) with IEC of 1.52 mequiv/g.[13] These results could be accounted for by significant phase separation of **6-SO$_3$H**s. A low IEC membrane could have the advantage of low WU and hence good mechanical properties in its hydrated state. Although the proton conductivity of the **6-SO$_3$H**s was still much lower than that of Nafion, it has encouraged us to study the properties of this class of polymers with higher IECs because the proton conductivity generally depends on the IEC.

Surprisingly, the **6b-SO$_2$Cl** membrane showed twice the WU and λ of the **6b-SO$_3$H** membrane. Probably because **6b-SO$_2$Cl** membrane can provide more carrier ions than **6b-SO$_3$H** membrane, **6b-SO$_2$Cl** membrane showed twice the proton conductivity of the **6b-SO$_3$H** membrane. Moreover, **6b-SO$_2$Cl** showed a small increase in T_g compared with **6b-SO$_3$H**. Therefore, it is possible that **6b-SO$_2$Cl** membrane had different morphology from the **6b-SO$_3$H** membrane.

In conclusion, we have described the successful synthesis of the first examples of **PSK**s bearing a cluster of sulfonic acid groups on the end groups. The proton conductivity of these sulfonated **PSK**s was remarkably high for membranes with such low IECs. Further investigations including the synthesis of this

Scheme 2. Synthesis of PSKs



Scheme 3. Sulfonation of End-Capped PSKs

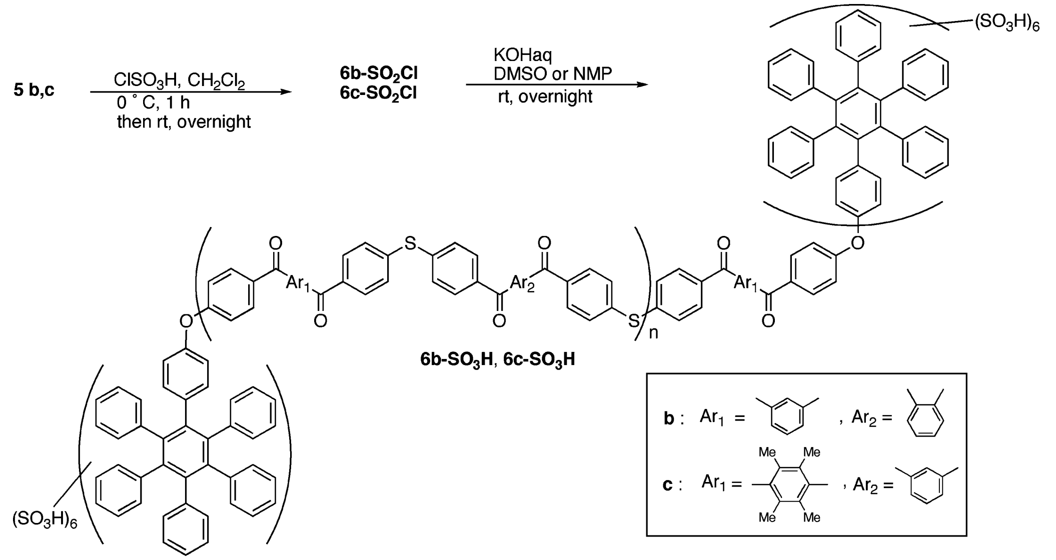


Table 1. Properties of PSKs

membrane	M_n[a]	measd[b] (calcd[c]) IEC (mequiv/g)	T_{d5}[d] (°C)	T_g[e] (°C)	T_g[f] (°C)	WU[g] (%)	λ[h] (H_2O/SO_3H)	σ[i] (mS/cm)
6b-SO$_3$H	24 000	0.48 (0.48)	461	167	161	8.3	9.7	6.9
6b-SO$_2$Cl[j]			484	172		17	20.2	16
6c-SO$_3$H	25 000	0.47 (0.45)	395	214	208	7.8	9.3	3.7
Nafion$_{N-117}$		0.91[k]				33[l]	20.2[l]	98

[a] M_n of pre-sulfonated **PSK** (**5**), calculated by ^1H NMR spectrum. [b] Ion exchange capacity, measured by titration and back-titration. [c] IEC, calculated using M_n of pre-sulfonated **PSK** (**5**) from the ^1H NMR spectrum for the introduction of 12 SO_3H group on each end-capped polymer chain. [d] 5% weight loss temperature. [e] T_g of sulfonated **PSK** (**6**). [f] T_g of pre-sulfonated **PSK** (**5**). [g] Water uptake at rt after 1 w for **6-SO$_3$H**s and 2 d for **6b-SO$_2$Cl**. [h] Hydration number. [i] Proton conductivity at rt with 100% RH. [j] Cast in SO_2Cl form, hydrolyzed, and then acidified in SO_3H form. [k] Reported value. [l] Obtained from ref 30.

class of polymers with higher IECs are ongoing in our laboratory.

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Supporting Information Available: Additional discussion on model reactions for end-capping, detailed experimental procedures, and characterization of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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