

Side-chain-acid poly(aryl ether)s for fuel cell applications

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Abstract: Sulfonated Ph-PES (Ph-SPES) bearing acid groups on pendant phenyl groups and backbones and sulfonated DiPh-PES (DiPh-SPES) bearing acid groups only on pendant phenyl groups could be prepared using a mild postsulfonation method. Both of two of polymers had excellent mechanical properties, such as high glass transition temperatures, good thermal and oxidative stability, as well as good dimensional stability in hot water. It was interesting to note that side-chain-acid DiPh-SPES copolymers obviously possessed better thermal and oxidative stability than that of corresponding side-chain-acid/main-chain-acid Ph-SPES copolymers. The methanol permeability values of Ph-SPES and DiPh-SPES membranes at room temperature were in the range of 7.0×10^{-7} -- 9.4×10^{-8} cm²/s at 30 °C, which is several times lower than Nafion 117. DiPh-SPES-50 and Ph-SPES-40 also exhibited high proton conductivity of about 0.13 S/cm at 100 °C, which is comparative to Nafion 117. The above results showed these copolymers are possible candidate materials for proton exchange membranes (PEM) in fuel cell applications.

Introduction

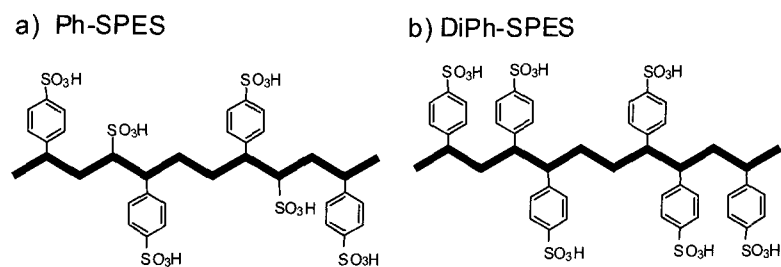
Fuel cells known for transforming chemical energy directly into electricity with high efficiency are one of the promising clean future power sources. Lots of efforts are being made to develop proton conductive membranes for using in proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) systems.^{1,2} One challenge is to find high-performance proton conductive membranes as an alternative to Nafion[®]. Hydrocarbon polymers with sulfonic acid groups are being investigated as an attempt to overcome the difficulties of high cost, low operation temperature (≤ 80 °C), high methanol crossover, and environmental recycling uncertainties.³

Since their outstanding thermal and chemical stability, sulfonated derivatives of polyarylether-type polymers, such as polyethersulfone (SPES), polyetherketone (SPEK), polyarylether (SPAE) and polyethernitrile (SPEN) are being investigated as potential PEMs.⁴ Although lots of above polymers have been successfully made, there are still some challenges, such as the optimization and simplification of sulfonation reactions, stereo controllable chemical structures including easily-controllable degree of sulfonation (DS) and sulfonation sites, and performance enhancement and microstructure improvement of PEMs by reasonable design of chemical structures.⁵

Most of polyarylether-type sulfonated membranes were developed based on post-sulfonated existing polymers or on copolymers produced from sulfonated monomers.³ The post-sulfonation approach is well known as simple reaction procedure and scalable up process. However, difficulties may exist in the precise control of the sulfonation sites and the degree of sulfonation (DS). In addition, rigorous reaction conditions, such as high temperature and strongly acidic sulfonating agent, may lead to the occurrence of side reactions and degradation of the polymer backbone. The copolymerization of sulfonated monomer with other nonsulfonated monomers has the potential for synthesizing random copolymers with a better control of sulfonation content (SC) and more defined chain structures in comparison with the copolymers by post-sulfonation method. However, the limited number of

sulfonated monomers is available and the preparation of the sulfonated monomers is sometimes tedious and difficult.⁶ Therefore, it is of interest to prepare sulfonated polymers via the post-sulfonation method whereby they have controllable sulfonation sites and DS in a similar way to polymers prepared by the direct copolymerization method.

In this study, the PES copolymers consisting of segments: those that are readily sulfonated and those that are not were synthesized. Aimed at preparation of sulfonated polymers with stereo controllability of sulfonation sites via a post-sulfonation method under mild reaction conditions, the sulfonation behaviors of both phenylated and diphenylated PES polymers were investigated. The target side-chain-acid polymers were successfully prepared, and the properties related to PEM materials for FC applications were also evaluated.



Scheme 1. Representations of: a) main-chain-acid/side-chain-acid Ph-SPES polymers; b) side-chain-acid DiPh-SPES polymers.

Results and Discussion

Most recently, we have found that phenylated PAEKs could be sulfonated on the pendant groups in 95-98% concentrated sulfuric acid at room temperature within 3 h to obtain their side-group-acid analogues.⁷ However, it had a risk that sulfonation reaction occurred on the benzenes connected with activated ether linkages and phenyl groups if the longer time or stronger sulfonation reagents were adopted. To further optimize the chemical structures to make exact side-chain-acid aromatic polymers, which could be prepared via the postsulfonation of existing polymers, we designed and prepared a new series of diphenylated aromatic poly(ether sulfone)s. The starting copolymers were composed of sulfonatable segments (activated by diphenylated moieties) and unsulfonated segments (deactivated by sulfonyl groups). Meanwhile, monophenylated ones were prepared as an attempt of making direct comparisons of sulfonation reaction and properties between monophenylated and diphenylated analogues.

In the present study, a simple and mild sulfonation reaction condition of room temperature sulfuric acid was applied to investigate the sulfonation of the polymers. After stirring polymer solution in 95-98% H_2SO_4 at a concentration of 5 g/100 ml at room temperature for one week, double-acid substitution polymers could be obtained. It was noted that the sulfonation reaction rate was faster than that of Victrex PEEK. At the same sulfonation conditions, about 31 days was needed for PEEK to get full sulfonation (DS~1).⁸ Both of monophenylated and diphenylated PAES polymers also showed good controllability of reaction sites. The results of NMR spectra and titration test showed the DS values for these polymers could reach 2.0 under this reaction conditions. Differed from the sulfonation of phenylated PAES polymers, which led to side-chain-acid/main-chain-acid polymers, the sulfonation of diphenylated polymers could exactly form side-chain-acid polymers. Two substitution sites on pendant phenyl groups were unambiguously confirmed by NMR and titration test. Their schematic representations are shown in Scheme 1.

Glass transition temperature (T_g) is one of important criteria for applications of amorphous polymers. High T_g s is usually required for PEM materials to operate at higher temperature. Only one transition temperature was found in the DSC curve before decomposition temperature for all the samples, which indicated their amorphous nature. For unsulfonated starting polymers, high T_g values ranged from 190 °C to 228 °C were mainly caused by rigid sulfonyl-containing backbones. In general, polymers have higher T_g values after sulfonation because of the introduction of polar sulfonic acid groups, which may enhance the interaction of molecular chains. The T_g values of Ph-SPES and DiPh-SPES were as high as 263~285 °C.

Judged from TGA curves, all the starting materials possessed excellent thermal stability due to their fully aromatic chemical structure. There were no any weight loss below 400 °C and the temperatures at 5% weight loss were above 505 °C in air. After sulfonation, the thermal decomposition temperatures went down to around 334~354 °C because of the introduction of sulfonic acid groups. It was very interesting to note that DiPh-SPES series all had better thermal stability than that of Ph-SPES ones. An obvious difference of 14~17 °C between DiPh-SPES and Ph-SPES copolymers could be observed in Figure 1. To our knowledge, it might be the first time to give a direct proof that side-chain-acid polymers had much better thermal stability than that of main-chain-acid (or a mixture of main-chain-acid/side-chain-acid analogues). It was also observed these sulfonated polymers even showed improved thermal stability than Nafion under the exact same testing conditions.

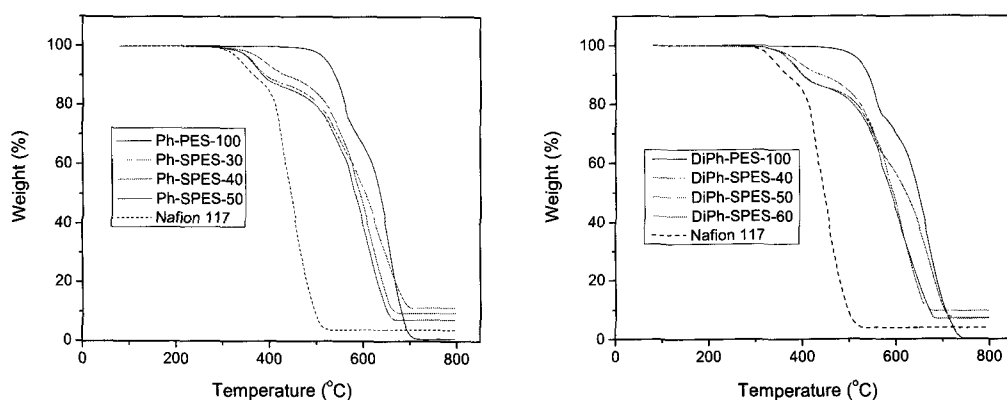


Fig.1. TGA curves of the polymers in air.

One of key requirements for PEMs to apply in the fuel cell operating conditions is good oxidative-hydrolytic stability.³ Side-chain-acid polymers, whose sulfonic acid groups attached to the pendant groups of polymer chains, are expected to have improved oxidative resistance over main-chain-acid ones. Generally, the polymers bearing less $-\text{SO}_3\text{H}$ groups always had better oxidative stability. It was interesting to note that the diphenylated series exhibited improved oxidative resistance over the phenylated ones at the similar level of $-\text{SO}_3\text{H}$ content. For example, DiPh-SPES-50 (IEC~1.70 meq/g) well maintained shapes after 3h treatment in Fenton's reagent. However, Ph-SPES-40 (IEC~1.60 meq/g) already dissolved into Fenton's reagent after 2.5h treatment. Especially, DiPh-SPES-40 (IEC~1.50 meq/g) could keep integrity after 4h treatment, which suggested its excellent oxidative resistance.

Good mechanical properties are another important factor for PEMs applications. The tensile properties of these novel membranes and Nafion 117 in their wet state were tested. In comparison

with Nafion 117, most of new membranes possessed higher tensile strength and Young's module. The samples had tensile strength of 21.6~40.9 MPa and Young's module of 0.36~1.00 GPa. Their elongations at break were up to 52~139 %, which suggested they were flexible materials.

To maintain high proton conductivity, sufficient amount of water molecules within the membrane is indispensable. However, more sulfonic acid groups are also necessary for highly conductive membranes. As an unfavorable side effect, high sulfonation content always results in much water absorption, and the excessive water uptakes would lead to unacceptable dimensional change or loss of dimensional shape.³ The preparation of alternative PEMs with high content of $-SO_3H$ groups and small dimensional change is one of important topics. At room temperature, all the membranes exhibited ideal water absorption and swelling ratio (swelling ratio $\leq 17\%$). At 80 °C, Ph-SPES-50 and DiPh-SPES-60 having high IEC values lost their dimensional shapes. DiPh-SPES-50, DiPh-SPES-40 and Ph-SPES-30 had acceptable dimensional change (swelling ratio $\leq 30\%$) even at high evaluated temperature.

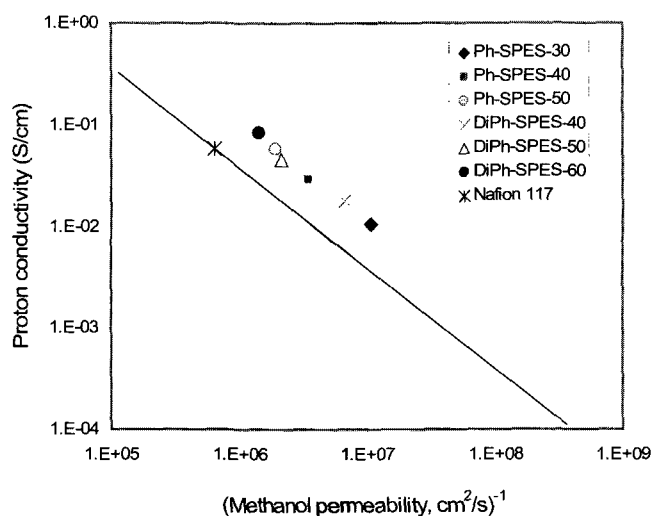


Fig. 2. Methanol permeability vs. proton conductivities of the membranes and Nafion 117.

Generally, the conductivities of all the samples increase with temperature in the range of evaluated temperature. All the membranes possessed room temperature conductivities higher than 1.0×10^{-2} S/cm, which is conventionally regarded as the minimum value required for PEM practical application in FC. DiPh-SPES-60 exhibited higher proton conductivities than that of Nafion 117 from 30 °C to 70 °C, although it lost shape at higher evaluated temperature. At 100 °C, proton conductivities of DiPh-SPES-50 and Ph-SPES-40 were as high as 0.130 and 0.117 S/cm, which were comparable to 0.138 of Nafion 117.

One significant drawback for Nafion's DMFC application is its high methanol crossover. This limitation may be associated with the microstructure of Nafion, where interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion. The methanol permeability values of the membranes were ranged from 7.0×10^{-7} -- 9.4×10^{-8} cm²/s at 30 °C, which is many times lower than the value of Nafion 117 of 1.55×10^{-6} cm²/s. The membranes having high proton conductivity and low methanol crossover are being pursued for DMFC system. It is facile to evaluate the membranes through drawing a plot containing both methanol permeability and proton conductivity.⁹ As shown in Figure 2, and all the points appeared on

the right top corner of the plot.

Conclusions

Ph-SPES bearing acid groups on pendant phenyl groups and backbones and DiPh-SPES bearing acid groups only on pendant phenyl groups were successfully prepared using a mild postsulfonation method. Side-chain-acid polymers (DiPh-SPES) had obviously better thermal stability and oxidative stability than the other Ph-SPES series. In comparison with Nafion 117, these new membranes possessed low methanol permeability in the range of 7.0×10^{-7} -- 9.4×10^{-8} cm²/s at 30 °C. DiPh-SPES-50 and Ph-SPES-40 with suitable IEC values also exhibited high proton conductivity of about 0.13 S/cm at 100 °C, which is comparative to Nafion 117. Combined with their good mechanical property and low dimensional change in hot water, several of them are promising PEM materials for PEMFC and DMFC applications.

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