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# Novel Synthesis of Sulfonated Poly(phthalazinone ether ketone) Used as a Proton Exchange Membrane via N−C Coupling Reaction

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Nafion perfluorinated resins[1,2] that contain perfluorosulfonic acid groups have outstanding properties as membranes in polymer electrolyte membrane fuel cells when used up to about 80 °C. At the higher temperatures dehydration of the membrane occurs with concomitant loss of conductivity. The Nafion membranes are expensive, and there is a need for resins that can operate at the higher temperatures. Many unsuccessful attempts have been made to replace Nafion with other sulfonated polymers that can meet the rigorous conditions required for use as proton exchange membranes in fuel cells. Most of the known high-performance polymers have been converted to ionomers containing sulfonic acid groups, and this subject has been extensively reviewed.[3−6] There is very little in the literature on the long-term stability of these materials in fuel cells. In this paper, we report a new approach to the preparation of ionomers from poly(phthalazinone ketone)s that have been recently synthesized by a N−C coupling reaction.

Poly(aryl ether)s (PAE) are engineering polymers that possess good mechanical properties and excellent thermal, oxidative, and chemical stability, and they have been extensively studied as a base for new ionomeric materials.[3,4] Most of the effort until recently involved postsulfonation of the PAEs. It had been demonstrated some time ago that polymers containing sulfonic acid groups could be prepared by direct reaction of sulfonated monomers in which the sulfonic acid group was on the biphenol[7] or the dihalo compound.[8] The latter reaction has recently been studied extensively for the synthesis of ionomeric PAEs.[3]

Several years ago we found that 4-(4-hydroxyphenyl)-phalazin-1-one (**1**) behaved like a bisphenol and that under conventional conditions used to form poly(aryl ether)s the phthalazine structure **3** was formed by reaction, e.g., with bis(4-fluorophenyl) sulfone (**2**).[9−11] These polymers have very high glass transition temperatures and are thermoxidatively stable. The phthalazinone polymers have been converted to ionomers by sulfonation[12,13] and by direct polymerization,[12,14] and these polymers have shown excellent properties as membranes. The phthalazinone-based proton exchange membrane also appears to have lower crossover of methanol in a direct methanol fuel cell (DMFC).[15]

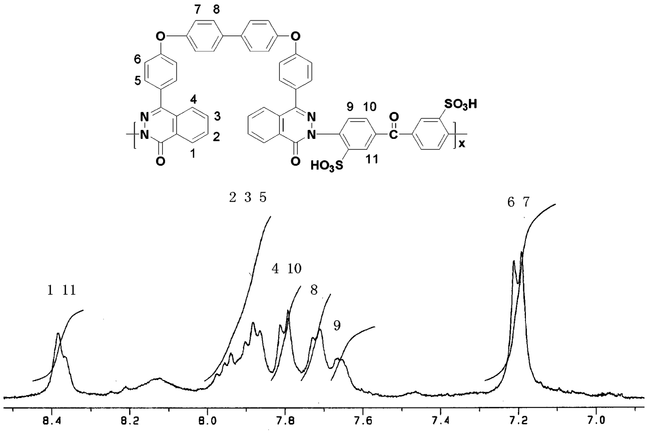

**Figure 1.** $^1$H NMR spectrum of sulfonated poly(phthalazinone ether ketone), **6**.

More recently, we found that bisphthalazinone monomers can readily react with activated dihalides to give high-molecular-weight polymers via a N−C coupling reaction.[16−18] In this work, the bisphthalazinone monomer **4** was polymerized with sulfonated 4,4′-difluorobenzophenone (**5**) to give sulfonated poly(phthalazinone ether ketone) (**6**), as depicted in Scheme 1,[25] in a yield of 93%. Figure 1 shows the $^1$H NMR spectrum of polymer **6**. A high inherent viscosity ($\eta_{\mathrm{inh}}$) of 1.02 dL/g for polymer **6** was obtained. This polymer was unlike other sulfonated polymers reported in the literature,[19−21] which normally dissolve in water at high degree of sulfonation. This means that the sulfonated poly(phthalazinone ether keton)s can have higher proton conductivity by increasing their sulfonation degree or decreasing their EW values due to the fact that water serves as carrier for proton transportation. The sulfonated polymer **6** was insoluble in water but soluble in dipolar aprotic solvents such as *N,N′*-dimethylacetimide (DMAc), dimethyl sulfoxide (DMSO), *N,N′*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidinone (NMP) at room temperature, and it could be readily cast into a tough and smooth film from solution. After immersion in 80 °C water for 24 h, the water uptake of the membrane was determined to be 46% by measuring the weight change after being dried.

The equivalent weight (EW) of polymer **6** was calculated to be a considerably smaller than Nafions at 482 g/mequiv and was confirmed by elemental analysis. The ion exchange capacity (IEC) of polymer **6** was determined by titration,[2] and the value was 2.04 mequiv/g (calcd 2.07 mequiv/g). Proton conductivity measurements were conducted on hydrated film samples using a Solartron 1255B frequency response analyzer functioning with an oscillating voltage of 10 mV and using two probes with frequencies between 1 MHz and 5 kHz. The measurements were performed at 20 °C and 100% relative humidity, and the cell assembly was similar to that used in the literature.[22] Prior to examination, the membrane were hydrated in cold water for 24 h. The proton conductivity of polymer **6** was 1.06 × $10^{-2}$ S cm$^{-1}$, while that of Nafion 117 was 2.03 × $10^{-2}$ S cm$^{-1}$

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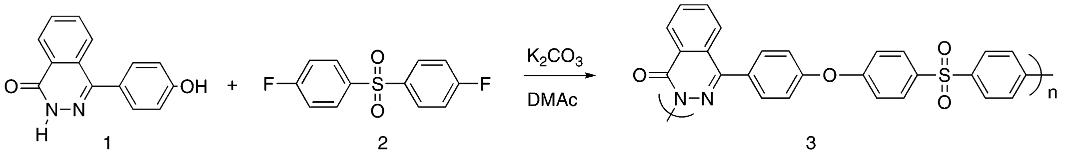
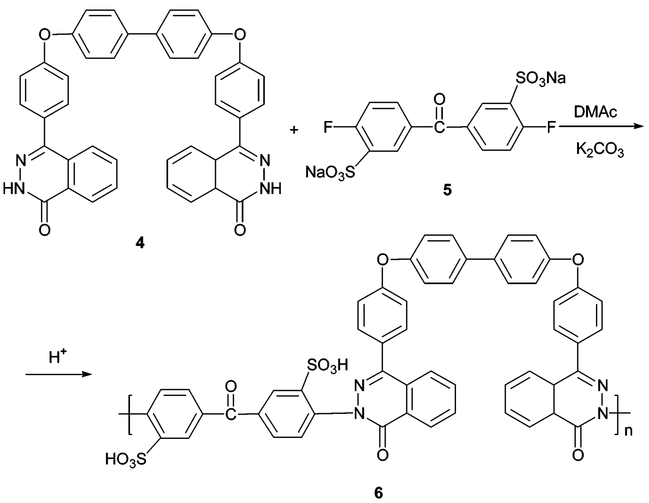
**Scheme 1. Polymerization of 4-(4-Hydroxyphenyl)phalazin-1-one with Bis(4-phenyl sulfone)**



**Scheme 2. Synthesis of Sulfonated Poly(phthalazinone ether ketone), 6**



under the same conditions, indicating that polymer **6** exhibits a proton conducting ability comparable to Nafion 117.

The stability of the proton exchange membrane against oxidation was investigated by soaking the film in Fenton's reagent (30 ppm $FeSO_4$ in 30% $H_2O_2$) at 30 °C. It took 28 h before the film started to break into pieces and 40 h before it disappeared into solution. The results indicated that the membrane shows improved property of resistance to oxidation compared with other sulfonated polymers.[22,23] It is the aromatic nature and the heterocyclic N−C bond *ortho* to the sulfonic acid group, instead of the arylene ether bond, that the sulfonated polymer is expected to have excellent thermal and chemical stability as well as resistance to oxidation and hydrolysis. As confirmed by oxidative and hydrolytic investigations, the membrane after immersing in 100 °C water for about 100 h showed no change in its appearance and strength.

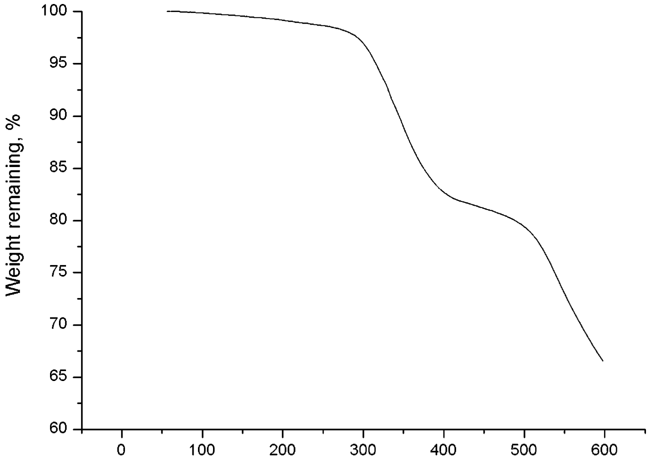


**Figure 2.** TGA trace of sulfonated poly(phthalazinone ether ketone), **6**.

The thermal stability of polymer **6** was determined by TGA and DSC. A two-step degradation profile was observed, as shown in Figure 2. The first weight loss (about 20 wt %) at about 300 °C was attributed to the elimination of sulfonic acid groups and a small amount of absorbed water, whereas the second weight loss peak at about 450 °C was due to the degradation of the main chain. It should be noted that in order to minimize the effect of absorbed water, we have first dried the polymeric films at 200 °C for 10 min, followed by cooling to about 70 °C and performing the TGA measurements. No glass transition temperature was observed for polymer **6** in the temperature range 30−250 °C.

In conclusion, high-molecular-weight sulfonated poly(phthalazinone ether ketone) (**6**) can be prepared through direct polymerization via a N−C coupling reaction. The as-made polymer was thermally and oxidatively stable. The high degree of sulfonation and reasonable water uptake endowed a good proton conductivity and made it a promising proton exchange membrane for fuel cell application.

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(25) Reaction procedure: Bis(phthalazinone) monomer **4** was prepared according to the literature.[17] Sulfonated ketone **5** was prepared according to the literature.[24] Preparation of sulfonated polymer **6**: To a 25 mL three-necked round-bottomed fitted with a Dean−Stark trap, a condenser, a nitrogen inlet/outlet, and a magnetic stirrer was added bis(phthalazinone) monomer **4** (0.6267 g, 1 mmol), sulfonated ketone **5** (0.4223 g, 1 mmol), anhydrous potassium carbonate (0.1935 g, 1.4 mmol), 5 mL of DMSO, and 6 mL of toluene. Nitrogen was sparged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 140 °C with stirring for 2 h. After the produced water was azeotroped off with toluene, the temperature was slowly raised to 175 °C. The temperature was maintained for 20 h, and the viscous solution was cooled to 100 °C followed by diluting with 2 mL of DMSO and, thereafter, precipitating into 100 mL of 1:1 (v/v) methanol/water. The precipitates were filtered and washed with water three times. The fibrous residue was collected and dried at 110 °C under vacuum for 24 h. A total of 0.9423 g of polymer **6** was obtained in 93% yield. The protonic form of the polymer was obtained by precipitating the 5% solution of sodium form of the polymer in DMAc into 100 mL of 10% hydrogen chloride aqueous solution, followed by keeping the mixture at 60 °C for 6 h. The precipitated polymer was dialyzed to remove inorganic salts. The final polymer was filtered and washed with water three times and then dried at 110 °C for 24 h. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.20$ (d, 8H), 7.66 (d, 2H), 7.71 (d, 4H), 7.80 (d, 4H), 7.86−7.98 (m, 8H), 8.38 (m, 4H). $(C_{53}H_{32}N_4O_{11}S_2{\cdot}6H_2O)_n$ $(1073.08)_n$: Calcd C, 59.32; H, 4.28; N, 5.22; S, 5.98. Found C, 59.25; H, 5.15; N, 6.84; S, 6.07.

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