

Preparation of carboxylated/sulfonated poly(arylene ether ketone)s for fuel cell applications

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Fuel cell has been greatly developed during the past decade with the growing demand for efficient, reliable and environmentally friendly energy sources. As the key components of proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), proton exchange membranes are required to have combined electrochemical stability, workability, high ionic conductivity, low permeation of the reactants, and mechanical integrity^[1-3].

Here we report a new series of novel poly(arylene ether ketone)s with simultaneously sulfonic and carboxyl groups^[4]. The resulting polymers exhibit excellent thermal and mechanical properties, low methanol permeability and appropriate conductivity.

1. Experimental part

1.1 Synthesis of the starting polymers

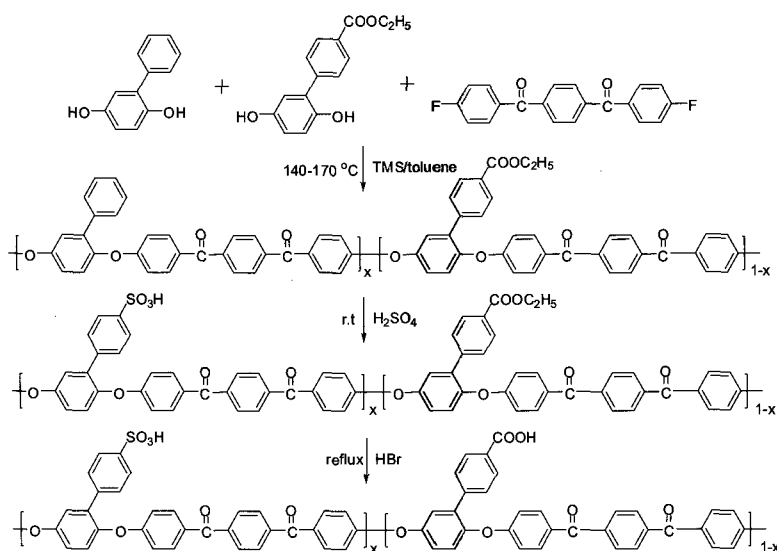
The starting polymers, PEEKK-X, were prepared through the route shown in **Scheme 1**, and X refers to the molar ratio of 4-ethylcarboxylphenylhydroquinone / (4-ethylcarboxylphenylhydroquinone + phenylhydroquinone). For example, 4-ethylcarboxylphenylhydroquinone (5.0 mmol), phenylhydroquinone (5.0 mmol), 1,4-bis(4-fluorobenzoyl) benzene (10.0 mmol) and K₂CO₃ (10.5 mmol) were added into a three-necked flask with a Dean-Stark trap, a condenser, a mechanical stirrer and a nitrogen inlet and outlet. Tetramethylene sulfone (25 mL) and toluene (10 mL) were used as solvent and azeotropic reagent, respectively. The reaction mixture was refluxed at 140 °C for 2 h to dehydrate the system. After dehydration and removal of toluene, the reaction temperature was increased to 170 °C and then held at this temperature for another 6 h. The fibrous precipitate was filtered off and purified by washing with boiling deionized water and ethanol, and dried in vacuum oven at 80 °C overnight. All the other polymers were prepared and purified using the same procedure (Scheme 1).

1.2 Sulfonation of the starting polymers

To a 100 mL of flask, 1 g of polymer and 20 mL of concentrated sulfuric acid (95-98%) were added. After stirring at room temperature for 12 h, the homogeneous viscous solution was poured into deionized water to get a silklike solid. The solid was washed with deionized water until the water reached neutral. The sulfonated polymer was dried in a vacuum oven at 100 °C for 24 h.

1.3 Hydrolysis of the polymers

We treated the sulfonated polymer with hydrobromic acid (≥40%) at a refluxing temperature for 12 h (Scheme 1), and then washed with deionized water for several times to get the polymer containing both -COOH and -SO₃H groups.



Scheme 1. Synthesis of the polymers containing both $-\text{COOH}$ and $-\text{SO}_3\text{H}$ groups.

2 · Results and discussion

2.1 Synthesis and characterization of the polymers

Due to the deactivation of $-\text{COOEt}$, there were no sulfonation reaction occurred on the 4-ethyl carboxylphenyl pendants, which could be confirmed by the ^1H NMR spectroscopy. And then, after treating the sulfonated polymers in hydrobromic acid for 12 h at the refluxing temperature, the sulfonated/carboxylated ones were obtained. The structure was confirmed by ^1H NMR spectroscopy.

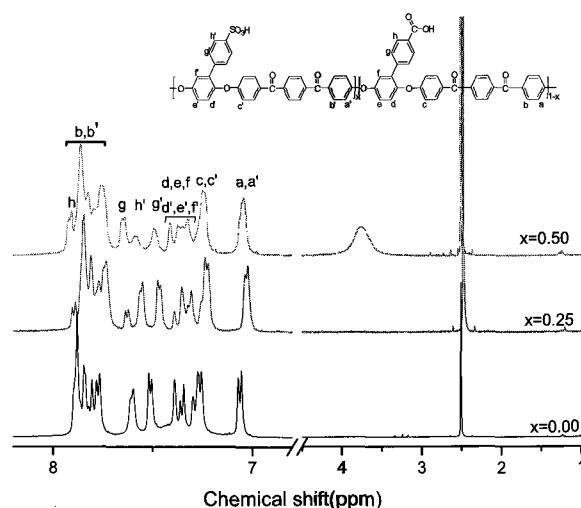


Fig.1 ^1H NMR spectra of HBr-S-X% ($X=0.00$, 0.25 and 0.50).

2.2 Thermal and mechanical properties

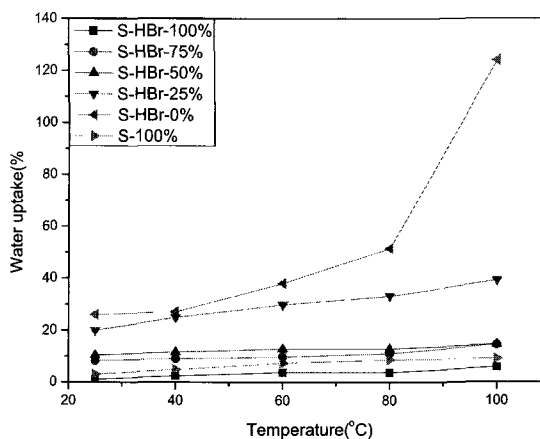
All the polymers showed good thermal stability and mechanical properties within the range of fuel cell application although slightly decreased compared with their corresponding polymer form evaluated by TGA curves as shown in Table.1.

Table.1 Thermal properties and mechanical properties of the resulting polymers

Polymer	T_g (°C)	$T_{d5\%}$ (°C)	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)		Methanol diffusion ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)
			Dry	Wet	Dry	Wet	Dry	Wet	
HBr-S-100 %	208	248	84	70	1.4	0.02	6	12	0.02
HBr-S-75%	229	464	79	59	1.4	0.06	22	50	0.06
HBr-S-50%	233	383	65	57	1.2	0.28	10	27	0.28
HBr-S-25%	237	366	63	54	1.4	0.81	49	102	0.81
HBr-S-0%	231	377	62	57	1.8	3.07	25	99	3.07

2.3 Water uptake, proton conductivity and methanol crossover

Water uptake is highly relative to the comprehensive performance of the membranes, such as proton conductivity and mechanical property. Moderate water uptake is greatly helpful for the stability of the membranes. The water uptake results are shown in Fig. 2. Proton conductivity is a key parameter for the membrane to be used in fuel cells. The proton conductivities of the membranes under 100% relative humidity are shown in Fig. 3. Also, the membranes showed lower methanol permeability than that of Nafion, as shown in Table 1.

**Fig. 2** Water uptake of the membranes.

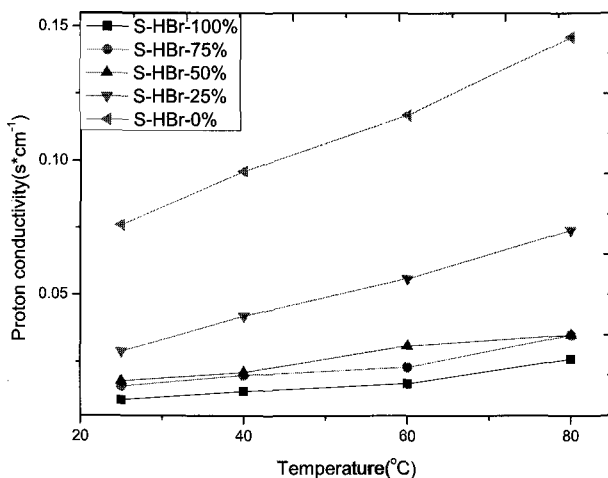


Fig. 3 Proton conductivities of the membranes.

3. Conclusions

A novel series of poly(arylene ether ketone)s containing carboxyl/sulfonic acid groups were successfully synthesized through a sulfonation reaction and then a hydrolysis reaction based on well-designed starting polymers. The properties including thermal, water absorption, mechanical properties, proton conductivity and methanol crossover of sulfonated/carboxylated polymers were well investigated. It was found that all the membranes exhibited good thermal, dimensional stability and mechanical properties.

References

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(continuing from p280)The 21% strain is a great improvement compared to the previously reported 4.9% of high strength polyimide nanofiber mats. The excellent mechanical properties of copolyimide nanofiber belt are probably attributed to those flexible and rigid microblock regions uniformly distributed in the nanofibers at a level of supermolecular structure.

Reference

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