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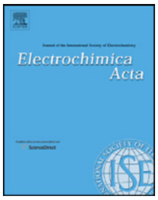

Preparation and characterization of block copolymers containing multi-sulfonated unit for proton exchange membrane fuel cell

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ABSTRACT

Multi-sulfonated block copolymers (MSBPs) with sulfonated units of 5, 9, 10, and 14 mol% were successfully synthesized for proton exchange membrane. The hydrophobic block oligomer was prepared by 4,4′-dihydroxydiphenylsulfone and 4,4′-difluorodiphenylsulfone. And also hydrophilic block oligomer was prepared by multiphenyl structured monomers of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene and 1,2-bis(4-hydroxyphenyl)-3,4,5,6-tetraphenylbenzene by varying the different mole ratio to control the degree of sulfonation. The two steps of sulfonation was carried out under chlorosulfonic acid, and then concentrated sulfuric acid separately. The sulfonation was performed selectively on hydrophilic block segment and para position of the side chain phenyl groups. MSBPs were studied by FT-IR, ^{1}H NMR spectroscopy, and thermo gravimetric analysis (TGA). Sorption experiments were conducted to observe the interaction of MSBPs with water. The wateruptakes were 9.6–42.5% at 25 °C and 14.7–90.8% at 80 °C. The resulted ion exchange capacities (IEC) were 0.79–1.87 (mmol g^{-1}) and proton conductivities were evaluated as increasing IEC.

1. Introduction

There have been great developments in proton exchange membrane fuel cell (PEMFC) since they play an important role as the power source for vehicles and portable devices. For decades the perfluororinated sulfuric acid membranes (Nafion and Aciplex) have been used because they exhibit a unique combination of properties, including excellent chemical and high ionic conductivity with selectivity, and super acid strength [1,2]. Recently many research groups have studied how to overcome the drawbacks of Nafion membranes [3–12].

Especially thermally stable hydrocarbon PEMFC is emerging as candidate membranes to be used at elevated temperatures of greater than 100 °C. Poly(ethersulfone)s and poly(etherketone)s are primarily chosen because they have achieved an excellent position among other thermoplastic polymers by virtue of their superior properties such as thermal stability, high heat distortion temperature, chemical inertness, electrical performance, and flame retardancy [13–20].

The researchers have effort the studies of the modification of the monomer structures and polymer matrix. The resulting hydrocarbon PEMFCs were classified fifth generations which are linear, block, grafting, crosslinked/branched, and inorganic/organic composite polymer membranes. Despite this superiority and the considerable research undertaken, the hierarchical structure of the membrane and the mechanism of cation exchange remain poorly understood and those hydrocarbon PEMFCs did not show sufficient results replace to Nafion. To improve proton conductivity, introducing a high content of sulfonation on polymer backbone is necessary but it has a disadvantage of swelling effect that reduces mechanical properties [21–24].

To improve the proton conductivity and cell power, Hay and co-workers also investigated the effect of the different sized hydrophilic block segments in the main chain on the morphology of membranes as well as the relationship between the morphology. Polymer membranes are randomly distributed nanoclusters of 6 or 12 sulfonic acids derived from hexaphenyl-bisphenol monomer with better hydrophilic/hydrophobic microphase separation, exhibiting much better single fuel cell performance [25]. Ueda also reported the sulfonated poly(ether sulfone)s with highly sulfonated units, which has excellent hydrophilic/hydrophobic microphase separation, show higher water uptake and proton conductivity. McGrath reported block copolymers which are formed better hydrophobic/hydrophilic phase separation, and have better performance than random copolymers at low hydration levels [26,27]. We have previously reported thermally and hydrolytically stable sulfonated poly(arylene ether ketone sulfone)s containing four sulfonic acid groups on pendant phenyl groups [24]. These

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results encouraged us to further investigate the effect of the morphology of sulfonated block copolymer membranes on properties including water uptake, proton conductivity, and cell performance.

In this article, we report on the propeller-like non-planar building unit containing poly(aryl ether ketone)s, which has eight sulfonic acids per hydrophilic unit on the side chain phenyl groups, not main chain. The characteristics of this work were to provide high proton conductivity, excellent mechanical strength and high thermal stability with less water uptake phenomena. The chemical structure of synthesized polymers was investigated, and the synthesized copolymers were characterized by FT-IR, ^{1}H NMR spectroscopy, thermogravimetric analysis (TGA), the proton conductivities, water uptake, and ion exchange capacity (IEC), and also studied cell performance. The propeller-like non-planar phenyl rings on side chain of the MBP were selectively sulfonated, but phenyl rings beside sulfone groups on main chain are deactivated toward sulfonation by strong electron-withdrawing groups. The sulfonic acid on side chain would be provided better clustering effect and hydrophilic/hydrophobic separation, improving cell performance. The results suggest potential applications of the synthesized polymer as proton exchange membrane fuel cell.

2. Experimental

2.1. Materials

1,2-Bis(difluorobenzoy1)-3,4,5,6-tetraphenylbenzene was synthesized as described previously [28]. Zinc powder, $TiCl_4$, pyridine, 4-methoxy benzaldehyde, bromine, triethylamine, potassium carbonate, tetraphenylcyclopentadienone, boron tribromide, sodium chloride, sodium sulfate, 4,4′-difluorophenylsulfone (DFPS), bis(4-hydroxyphenyl)sulfone (BHPS), chlorosulfonic acid, concentrated sulfuric acid, sodium hydroxide, and hydrochloric acid were purchased from Aldrich Chemical and used as received. Commercial grade sulfolane and chlorobenzene were dried overnight over calcium hydride and distilled prior to use. Other commercially solvents, such as DMSO, tetrahydrofuran, dichloromethane, hexane, methanol, acetone, toluene, ethylacetate, ethanol, and distilled water were used without further purification.

2.2. Synthesis of 1,2-bis(difluorobenzoy1)-3,4,5,6-tetraphenylbenzene, (BFBTPB)

1,2-Bis(4-fluorobenzoyl)acetylene (18.6 mmol, 5.0 g) and tetraphenylcyclopentadienone (18.6 mmol, 7.15 g) in sulfolane (70 mL) were refluxed for 2 h under nitrogen atmosphere. The reaction mixture was cooled and poured into a large volume (300 mL) of methanol to give yellow power. The crude product was dissolved in toluene and refluxed with charcoal. The solution was crystallized in toluene to give a white crystalline compound with yielded 75%. ^{1}H NMR (400 MHz, DMSO-d_6, δ=ppm): 6.78–6.89 (m, 24 H, 4 C_6H_5 and 2 ortho C_6H_2F), 7.57–7.62 (d, 4 H, 2 ortho C_6H_2CO), mp 318–320 °C.

2.3. Synthesis of 1,2-bis(4-hydroxybenzene)-3,4,5,6-tetraphenylbenzene, (BHPTPB)

Under an N_2 atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with 1,2-bis(4-dimethoxybenzene)acetylene (18.6 mmol, 4.43 g) and tetraphenylcyclopentadienone (18.6 mmol, 7.15 g) in sulfolane (70 mL) were refluxed for 2 h under an atmosphere of nitrogen. The reaction mixture was cooled and poured into a large volume (300 mL) of methanol and refluxed in toluene/charcoal to give a white crystalline compound, 1,2-bis(4-dimethoxybenzene)-3,4,5,6-tetraphenylbenzene. A three-necked flask equipped with a magnetic stirrer was charged with the obtained 1,2-bis(4-dimethoxybenzene)-3,4,5,6-tetraphenylbenzene (18.6 mmol, 11.06 g) in dichloromethane (50 mL) was added BBr_3 (44.64 mmol, 4.23 mL) in dichloromethane (10 mL) at 0 °C under nitrogen atmosphere. The solution was allowed to warm to room temperature and stirred overnight. The solution was cooled in an ice bath, quenched with water, and partitioned between ethylacetate and 1 M hydrochloric acid. The aqueous layer was extracted with ethylacetate. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. In some cases, a basic workup was used: The quenched reaction was diluted with dichloromethane and extracted with 1 N NaOH twice. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ethylacetate twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated with yielded 65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ=ppm): 5.08 (s, 2 H, OH), 6.85–7.45 (m, 28 H, ArH).

2.4. Preparation of multi block copolymer, (MBP 10)

2.4.1. Synthesis of hydrophilicblock 1

1,2-bis(4-hydroxybenzene)-3,4,5,6-tetraphenylbenzene (BHPTPB, 0.566 g, 1.00 mmol), 1,2-bis(difluorobenzoy1)-3,4,5,6-tetraphenylbenzene (BFBTPB, 0.626 g, 1.00 mmol), potassiumcarbonate (0.165 g, 1.20 mmol), sulfolane (4.7 mL), and chlorobenzene (5 mL) were placed in a 50 mL round bottomed flask, and the reaction mixture was heated with a Dean–Stark trap at 160 °C for 2 h, and then at 180 °C for 30 min. The temperature was then decreased to room temperature and the resulting slightly viscous mixture was diluted with sulfolane (5 mL).

2.4.2. Synthesis of hydrophobic block 2

4,4′-difluorophenylsulfone (DFPS, 2.375 g, 9.00 mmol), bis(4-hydroxyphenyl)sulfone (BHPS, 2.298 g, 9.00 mmol), potassium carbonate (1.492 g, 10.80 mmol), sulfolane (18 mL), and chlorobenzene (18 mL) were placed in a 100 mL round bottomed flask, and the reaction mixture was heated with a Dean–Stark trap at 160 °C for 2 h, and then at 180 °C for 30 min. The resulting mixture was slightly viscous. The temperature was then decreased to room temperature.

2.4.3. Block copolymerization

The hydrophilic block 1 solution was added into hydrophobic block 2 solution for block copolymerization (Scheme 1). The mixture of hydrophilic block and hydrophobic block (1 and 2) mixture solution was refluxed for 3 h at 160–180 °C. After the produced water was azeotroped off with chlorobenzene, the mixture was heated at 210 °C for about 1 h until high viscosity solution was obtained. The resulting mixture was cooled, diluted with sulfolane, and then poured into a mixture of methanol (100 mL)/water (100 mL) to precipitate a white fibrous polymer. The precipitated fiber was stirred in diluted hydrochloric acid, collected by filtration and washed with water. The crude polymer was purified by reprecipitation from dichloromethane solution into methanol, and the polymer collected by filtration was dried in vacuum at 80 °C for 24 h. ^{1}H NMR (400 MHz, DMSO-d_6, δ=ppm): 7.75–8.22 (d, 8 H, 2 ortho $C_6H_2SO_2C_6H_2$), 7.40–7.61 (d, 4 H, ortho C_6H_2CO), 7.12–7.40, 6.35–7.12 (d, 8 H, 2 meta $C_6H_2SO_2C_6H_2$), 6.35–7.12 (m, 52 H, 8 C_6H_5, 2 C_6H_4O and 4 H, meta C_6H_2CO), FT-IR: 1249 cm^{-1}, 1026 cm^{-1}, 690 cm^{-1} (stretching (O—S—O), 1710 cm^{-1} (stretching (C═O)).

2.5. Preparation of multi-sulfonated block copolymer, (MSBP)

A typical sulfonation procedure follows (Scheme 1). To a solution of block copolymer (MBP, 1.25 g, 2.345 mmol) in dichloromethane (35 mL) was dropwised chlorosulfonic acid (1.6 mL, 0.023 mmol) in dichloromethane (10 mL) at 0 °C for 30 min.