



Polymer actuators of fluorene derivatives with enhanced inner channels and mechanical performance

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ARTICLE INFO

Article history:

Received 28 April 2017

Received in revised form 28 July 2017

Accepted 14 August 2017

Available online 19 August 2017

Keywords:

Ionic exchange polymer metal composite (IPMC)

Electromechanical response

Fluorene blocked polysulfone

Yield modulus

Phase separation

ABSTRACT

A novel ion-exchange polymer-metal composite (IPMC) actuator is fabricated by sandwiching sulfonated fluorene blocked polysulfone (SDPF-*b*-PSU) between two Pt nanograin sheets. With increased concentration of chlorosulfonic acid, the SDPF-*b*-PSU film with more sulfonic groups exhibits strong ion exchange capacity, high Li⁺ ion conductivity, and ordered phase separation, which may contain an increased number of cations and possess larger and better interconnected inner channels for ion migration, thus providing the power to produce large force and power outputs. The SDPF-*b*-PSU film also exhibits enhanced mechanical performance and water uptake when compared to the pure Nafion film, providing a strong, hydrated matrix to support IPMC functions. At the driving voltage of 4 V, the SDPF-*b*-PSU actuator exhibits a strong force output which is 11 folds higher than that of the pure Nafion actuator.

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1. Introduction

Electro-active polymer (EAP) systems are considered as promising candidates for robotic actuators, artificial muscle, and dynamic sensors [1,2]. A promising ion-type EAP, the ion-exchange polymer-metal composite (IPMC) actuator has a wide range of applications because it is capable of producing a large displacement output under a very low driving voltage [3–7]. However, a small power output and a short stable actuation time limit its applications [8].

For conventional IPMC actuators, an ion exchange film is sandwiched by two inert metal sheets as working electrodes. The displacement and force are likely generated via the migration of hydrated cations along the inner channels [2]. DuPont perfluorinated acid (Nafion) is a commonly used ion exchange resin [9]. Its main chain is a linear hydrophobic structure, which crystallizes into a non-ionic phase; conversely, the branch chains of sulfonic groups are hydrophilic, and form an ionic phase with adsorbed water molecules. Ionic domains aggregate to form inner channels, allowing hydrated cations to migrate. Thus, it is expected that the

ion exchange film containing more hydrophilic groups such as sulfonic groups can increase the number of hydrated cations, the size or density of the inner channels, all of which improve IPMC performances. Meanwhile, during actuation of IPMC, water molecules are carried by hydrated cations moving between the electrodes, resulting in high rates of evaporation and electrolysis [1,2]. Thus, increased water uptake (WU) might improve IPMC actuation stability. Additionally, force and power outputs require appropriate mechanical properties to support the actuator, requiring optimization of the rigid hydrophobic crystalline segments [10–12].

Improvement of IPMC electromechanical performance has been an important topic over the past 10 years. Zhang et al. made an IPMC actuator with a fast, anisotropic electromechanical response by using vertically aligned carbon nanotubes, with doped Nafion as electrodes [13]. Chen et al. improved its electrochemical stability by using graphene stabilized silver nanoparticles or graphitic carbon nitride nanosheets as the electrode [14–16]. Oh et al. made graphene mediated electrodes to fabricate biocompatible IPMC actuators for bioengineering applications [17,18]. Yoo et al. made a IPMC actuator with high force and displacement outputs by doping montmorillonite inside Nafion [19,20]. Bennett et al. and other groups made IPMC actuators using ionic liquid as the electrolyte instead of water, with resultant IPMC actuators exhibiting long and stable actuations in the air, under low actuation frequencies [21,22].

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Additionally, our previous studies focused on improving film structure and mechanical performance for longer and more powerful actuation [23–25]. To further increase electromechanical performances, a novel direction is to create new ion exchange film, which counters Nafion drawbacks, such as fast back relaxation, early water loss, and high cost [26,27]. Aromatic hydrocarbon polymers with acidic function groups were previously shown as possible candidates [28]. The most widely reported aromatic hydrocarbon polymers include sulfonated derivatives of poly(phenylene)s [29–31], poly(arylene ether sulfone)s [32], polyetherimide [33], and poly(arylene sulfide sulfone)s [34–36]. These polymers form flexible films with high chemical and thermal stabilities [37–39].

Compared to phenyl-based polysulfone derivatives, fluorene-based polysulfones always have a larger amount of sulfonation and stronger mechanical properties. This is due to: a) the fluorene ring has more conjugated π electrons for the electrophilic reaction of chlorosulfonic acid, and thus facilitates binding sulfonic groups [40]; b) fluorene derivatives always have more active sites to bind sulfonic groups, and thus more sulfonic groups present on their skeletons [28]; c) two benzene rings of the fluorene molecule are nearly coplanar with the central carbon, thus making the fluorene derivatives stiffer [40]. Therefore, some fluorene derivatives with high ion exchange capacity (IEC), WU, proton conductivity, methanol permeability, and better phase separation were reported for making fuel cells instead of Nafion [41–44]. However, to the best of our knowledge, no studies have used fluorene derivatives for an IPMC actuator.

Herein, we synthesized a series of sulfonated diphenyl fluorene blocked polysulfones (SDPF-*b*-PSUs) by varying sulfonic concentration via block copolycondensation reaction between dichlorodiphenyl sulfone (DCDPS) and Bis(4-hydroxyphenyl) fluorene (BHPF) (Fig. 1). The resultant SDPF-*b*-PSUs exhibit high WU, IEC, and Li^+ ion conductivity, as well as well-ordered phase separation and moderate yield modulus in the wet state. Therefore, SDPF-*b*-PSUs were demonstrated to be viable ion exchange films for the fabrication of high-performance and cost-effective IPMC actuators, which could be used as artificial muscle for flexible actuators or displacement/vibration sensors.

2. Experiments

2.1. Materials

Nafion-115 (~5%) was obtained from Dupont Company (Wilmington, DE, USA). $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, bis(4-hydroxyphenyl) fluorene (BHPF), and dichlorodiphenyl sulfone (DCDPS) were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). Chlorosulfonic acid, 1,2-dichloroethane (DCE), dimethyl sulphoxide (DMSO), NaBH_4 , and other reagents were reagent grade and used without further purification.

2.2. Syntheses and characterizations of SDPF-*b*-PSUs

2.2.1. Synthesis of DPF-*b*-PSU

Steps to synthesize DPF-*b*-PSU were followed as previously reported [28]. Briefly, 25.0 g of DCDPS (87 mMol) and 13.8 g of K_2CO_3 were mixed in a round bottom flask containing 100 mL dry DMSO and 30 mL dry toluene, stirring for 30 min at room temperature for complete dissolution. Next, 30.5 g of BHPF (87 mMol) was added into the mixture, and subsequently refluxed with a condebelt separator tube under Nitrogen gas. This course occurred over 5 h at 150 °C for complete removal of water. The condebelt separator tube was removed, and the mixture continually reacted overnight at 180 °C. Resulting pale brown mixture was placed into supermassive methanol solution, producing white precipitate of DPF-*b*-PSU.

DPF-*b*-PSU precipitate was dissolved in 10 mL DCE, and refined in methanol. After drying, the yield of 34.17 g was around 87%.

2.3. Synthesis of SDPF-*b*-PSUs

10.0 g of DPF-*b*-PSU was dissolved in a round bottom flask containing 80 mL DCE solution. 0.5 mL chlorosulfonic acid (11.6 mMol) dispersed in 20 mL DCE solution was slowly added into the resulting solution over 2 h, and the mixture was permitted to react another 2 h. The mixture was dropped into methanol, generating precipitate of SDPF-*b*-PSU. Resulting precipitate was washed by KOH (3%), and subsequently by HCl (5%). The product was pale yellow in color, denoted SDPF-*b*-PSU-1, with a yield of 93%. To increase the degree of sulfonation, the content of chlorosulfonic acid was increased to 1.0 mL and 1.5 mL. Repeating the sulfonation reaction, obtained products of SDPF-*b*-PSU-2 and SDPF-*b*-PSU-3, respectively.

2.4. Characterizations

Polymers were characterized by vacuum Fourier transform infrared spectroscopy (ν -FTIR) with a Bruker IFS66/S spectrometer, gel permeation chromatography (GPC, Waters2695) with a UV detector using pure *N,N*-dimethylformamide as the eluent and calibrated with linear polystyrene standards, and nuclear magnetic resonance (^1H NMR) with a Bruker Advance III 600 spectrometer (deuterium dimethyl sulphoxide was used as the solvent). ^1H NMR (500 MHz, δ , ppm): 7.06, 7.12, 7.13, 7.24, 7.35, 7.43, 7.53, 7.68, 7.73, 7.90, 8.21. Samples were heated from the room temperature to 800 °C at a heating rate of 10 °C/min under N_2 for thermogravimetric analysis (TG, SDTQ600). Thermal properties were analyzed by using a thermal analyzer (Q100).

2.5. Fabrications and characterizations of ion exchange films

2.5.1. Fabrications of ion exchange films

DPF-*b*-PSU and SDPF-*b*-PSUs of 0.5 g were completely dissolved into 15 mL DMSO solution, the solutions were respectively poured into four self-made poly(dimethylsiloxane) (PDMS) containers with dimensions of $30 \times 40 \times 50 \text{ mm}^3$, and put into a vacuum oven under 90 °C for continual removal of solvent. The films were annealed at 150 °C for 5 min, and then boiled in deionized water to remove DMSO residues. The resulting thicknesses are 212, 214, 221, and 227 μm , respectively. For control, 12 mL of Nafion (5%) was poured into the former container, forming a film with thickness of 225 μm .

2.6. Detections of WUs

Films were soaked in deionized water at room temperature overnight and subsequently weighed, to obtain wet mass (m_{wet}). Samples were then dried in a vacuum oven at the temperature of 80 °C for 24 h. The dry mass (m_{dry}) was obtained. WU is calculated using the following equation:

$$\text{WU} = (m_{\text{wet}} - m_{\text{dry}}) / m_{\text{dry}} \times 100\% \quad (1)$$

2.7. Detections of IECs

The films were put in the HCl solution (0.0374 Mol/L), and boiled for 30 min. Films were then cleaned in deionized water with methyl orange, until the solution color did not change. Samples were incubated in NaOH (0.0390 Mol/L) solution, and titrated with the HCl solution by using an indicator of tricyclohexyltin hydride. IEC is calculated with the following equation:

$$\text{IEC} = (C_{\text{NaOH}}V_{\text{NaOH}} - C_{\text{HCl}}V_{\text{HCl}}) / m \quad (2)$$

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