Proton conducting graft copolymers with tunable length and density of phosphonated side chains for fuel cell membranes

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ABSTRACT

Polysulfones functionalized with highly phosphonated poly(pentafluorostyrene) side chains of different lengths were synthesized applying controlled polymerization and modification methods. The graft copolymers' thermal properties were evaluated by differential scanning calorimetry and thermal gravimetrical analyses. The proton conductivity of membrane prepared from the graft copolymer with the shortest phosphonated side chains was 134 mS cm^{-1} at 100 °C under fully immersed conditions. The graft copolymer TEM image shows a nanophase separation of ion-rich segments within the polysulfone matrix. Increasing the ionic groups content in the graft copolymers led to extensive membrane swelling. To improve the dimensional stability the graft copolymers were blended with pyridine-modified polysulfone. The blend membranes were transparent with formation of nano-phase domains as revealed from TEM images. The acid–base blend membranes exhibited a slightly higher thermal stability but lower proton conductivity compared to the membranes formed from pure graft copolymers.

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1. Introduction

Proton conducting polymer electrolyte membranes (PEMs) are one of the key components that determine the cost and performance of polymer electrolyte membrane fuel cells (PEMFCs). In recent years, there has been increased interest in the design and development of novel proton conducting PEMs able to operate at high temperatures (> 100 °C) under low humidification conditions [1,2]. Higher operation temperatures result in faster electrode kinetics, reduced risk of catalyst poisoning, smaller heat exchanger and easier water/thermal management [3,4]. The most widely used commercially available PEMs are based on perfluorosulfonic acid (PFSA) ionomers, such as Nafion®, produced by DuPont. Despite their good thermal and mechanical properties, the PFSA-based ionomers have several disadvantages including the high cost, decreased performance and dehydration at temperatures above 90 °C [5]. The evaluation of three model compounds containing different protogenic functionalities: sulfonic acid, phosphonic acid and imidazole, for high temperature and low humidity operation has shown that only the phosphonic acid-based system exhibits high conductivity in the temperature range 100–200 °C [6]. The significant strength of the carbon–phosphorus bond makes

the polymers bearing covalently attached phosphonic acid groups attractive for high temperature operation. Moreover, due to the amphoteric nature of phosphonic acid, the membranes are able to conduct protons by diffusion at low humidity, while the proton conductivity is facilitated by the dynamics of the water under immersed conditions. In terms of the copolymer architecture, the ion-containing block and graft copolymers are of significant interest due to their ability to self-assemble in ordered nanostructures that facilitate proton/water transport over a wide range of conditions [7,8]. A number of block and graft copolymers containing phosphonic acid groups have been reported and some of them have also been evaluated for potential fuel cell applications [9–13].

Generally, the proton conductivity and the water retention capacity of the membranes are enhanced when the content of ionic groups is increased [14]. However, upon reaching a certain level, the membranes become highly swollen and even soluble in water. A way to overcome this problem is to cross-link the polymer [15]. The process of cross-linking might be chemical [16–18] or physical [19–21]. The influence of tuning the ionic content of membranes by blending, as opposed to varying the degree of sulfonation, has been evaluated by blending highly sulfonated graft copolymers with fluorous homopolymers [22]. Most often the physical cross-linking is achieved via acid–base interactions between the proton conducting acidic polymer and a suitable basic polymer [23].

Very recently, we introduced a multistep synthetic strategy for the preparation of novel graft copolymers with a polysulfone (PSU)

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backbone and highly phosphonated poly(pentafluorostyrene) (PFS) side chains [24]. The controlled polymerization and modification steps involved allow straightforward tuning of graft copolymer architecture in terms of length and density of the phosphonated side chains. The initial evaluation of copolymer membrane proton conductivity and thermal stability showed promising results. In the present work, we have extended the variety of phosphonated graft copolymers in the search for an optimal balance between high proton conductivity and membrane dimensional stability. We tuned the copolymer architecture to obtain a twice as high grafting degree as that achieved previously. The length of the side chains was also varied in a controlled manner. Furthermore, to improve the membrane dimensional stability, acid–base polymer blends were prepared from the phosphonated graft copolymers and a polysulfone bearing pyridine side groups. The membranes formed from the pure graft copolymers and from the acid–base blends were evaluated for their thermal properties, water uptake and proton conductivity.

2. Experimental

2.1. Materials

Graft copolymers with PSU backbone and highly phosphonated PFS side chains of different lengths (PSU-g-PhPFS) were synthesized as previously described [24]. Briefly, PSU (Udel® P-3500 LCD MB8, $M_n = 40,000$ g mol^{-1}, PDI: 1.95, Solvay Advanced Polymes) was lithiated with n-butyllithium in tetrahydrofuran (THF), followed by the addition of (chloromethyl)benzoyl chloride. The targeted degree of functionalization (DS = 0.14, i.e., 14 substitutions per 100 PSU repeating units) was achieved and confirmed by ^{1}H NMR spectroscopy. The benzyl chloride-containing PSU was converted into a multiazide-functionalized polymer (PSU-N) through reaction with sodium azide. Alkyne end-functionalized PFSs (PFS-A) of three different number-average molar masses ($M_n = 3700$, 7600 and 10,500 Da) were synthesized by atom transfer radical polymerization (ATRP) and "clicked" onto the PSU-backbone via copper catalyzed azide-alkyne 1,3-cycloaddition (CuAAC). Finally, the grafts were phosphonated through reaction with tris(trimethylsilyl) phosphite as described by Atanasov and Kerres [25].

PSU grafted with 40 mol% of basic pyridine side groups (PSU-Py) was synthesized as previously described [26].

2.2. Membrane preparation

The pure graft copolymers (1–2 wt%) were suspended in N-methylpyrrolidone (NMP) at 80 °C. The temperature was increased to 150 °C and the mixtures were stirred overnight until the polymers dissolved. The membranes were cast at 80 °C during 4 days under nitrogen onto glass plates. In the case of the acid–base blend membranes, a solution of PSU-Py in NMP (2 wt%) was prepared separately at 80 °C. Then, it was slowly added to the copolymer solutions. The resulting mixtures were spread onto glass plates and the membranes were cast in the oven at 150 °C during 8 h. All membranes were detached from the glass plates after immersion in deionized water, followed by repeated rinsing and washing with deionized water.

2.3. Characterization

^{1}H NMR spectra were recorded in CDCl$_3$ or DMSO-d_6 on a Bruker Avance 300 MHz spectrometer. Size-exclusion chromatography (SEC) was carried out with a Viscotek GPCmax VE-2001 equipped with Viscotek TriSEC Model 302 triple detector array (refractive index detector, viscometer detector, laser light scattering detector with the

light wavelength of 670 nm and measuring angles of 90° and 7°), and a Knauer K-2501 UV detector using two PLgel mixed-D columns from Polymer Laboratories. The samples were run in THF at 30 °C (1 mL min^{-1}). The molar-mass characteristics were calculated using polystyrene standards. Thermal analyses were carried out on a differential scanning calorimeter DSC Q1000 (TA Instruments) in a temperature range of 25–400 °C at a heating and cooling rate of 10 °C min^{-1} under nitrogen. The glass transition temperatures (T_g) were determined during the second heating cycle at the inflection point of the thermal transition. Thermogravimetric analysis (TGA) was performed on a TGA Q500 instrument from 50 to 600 °C with a heating rate of 20 °C min^{-1} under nitrogen flow.

The ion exchange capacity (IEC, meq. g^{-1}) was calculated assuming 100% efficiency of the "click" grafting, 90% phosphonation of the grafts and considering both protons of each phosphonic acid group. The water uptake (WU) was measured from the weight increase of membranes after soaking them in deionized water at temperatures between 20 and 100 °C by increments of 20 °C to investigate the temperature dependence. It was calculated as: WU (wt%) = (W_{wet} − W_{dry}) × W_{dry}^{-1} × 100, where W_{wet} and W_{dry} are the membrane weights under hydrated and dry condition respectively. The number of water molecules per H$^+$ in the phosphonic acid group (λ) was calculated as: $\lambda = 1000 \times (W_{wet} - W_{dry}) \times W_{dry}^{-1} \times (IEC \times 18)^{-1}$. The proton conductivity (S cm^{-1}) of fully immersed membranes was measured in a sealed cell between −20 and 120 °C, using a Novocontrol high resolution dielectric analyzer V 1.01S in the frequency range 10–10^7 Hz at 50 mV voltage amplitude in a two-probe method. The humidity dependence of the proton conductivity from 30% to 90% relative humidity (RH) was investigated at 80 °C by a four-probe method with a Gamry potentiostat/galvanostat/ZRA in the frequency range 10^{-1}–10^5 Hz and a Fumatech MK3 conductivity cell, where the humidity was equilibrated by deionized water in a closed system. The samples for transmission electron microscopy (TEM) were stained with lead acetate and microtomed as previously described [22]. Electron micrographs were obtained with a Tecnai T20 G^2 instrument operated at an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Synthesis and characterization of the graft copolymers

The synthetic sequence of efficient and controlled polymerization and modification steps allows us to finely tune the copolymer composition in the search for an optimal balance between proton conductivity and mechanical properties of PEMs. We decided to explore the influence of the grafting density as well as of the length of the phosphonated side chains on the copolymer membranes properties. The grafting sites on the PSU backbone were doubled as compared to those obtained in our first work and were set to 14 mol%. Separately, three alkyne end functionalized PFSs (PFS-A) of different lengths were synthesized and grafted onto the PSU backbone through copper catalyzed azide–alkyne 1,3-cycloaddition. The final reaction step was the phosphonation of the PFS side chains. The intermediate and final products were analyzed and characterized as previously described [24]. The precursor and copolymer characteristics are summarized in Table 1. The previously obtained copolymer compositions comprising the PSU backbone grafted with two different lengths of phosphonated PFS side chains are also added for comparison. By doubling the grafting sites, and further varying the length of the phosphonated side chains, our aim was to adjust the optimal composition for that copolymer architecture in order to achieve maximum proton conductivity without scarifying the polymer membrane mechanical properties.