



Enhanced proton conductivity of sulfonated poly(*p*-phenylene-co-aryl ether ketone) proton exchange membranes with controlled microblock structure



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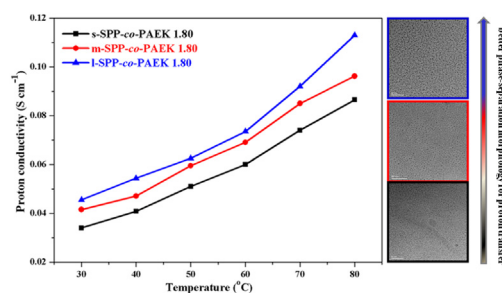
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HIGHLIGHTS

- SPP-co-PAEK polymers with controlled microstructure were prepared as PEM materials.
- They displayed well phase-separation structure and reasonable size of ion channels.
- Proton conductivity of PEMs was enhanced by tuning polymer hydrophobic segments.
- I-SPP-co-PAEK 1.80 membrane exhibited better cell performance than Nafion[®] 117.

GRAPHICAL ABSTRACT



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ABSTRACT

A new series of sulfonated poly(*p*-phenylene-co-aryl ether ketone)s (s, m, l-SPP-co-PAEKs) microblock polymers containing different hydrophobic units with precisely defined lengths have been prepared via the nickel (0) catalyzed coupling copolymerization and characterized to act as proton exchange membranes. By controlling the length and chemical structure of the hydrophobic units in the copolymers, these novel microblock polymers can exhibit well-developed nanophase morphologies and large length-scale of the ionic channels, resulting in the improvement of the proton conductivity in both the wet and dry state. Moreover, the membrane l-SPP-co-PAEK 1.80 with the largest hydrophobic micro-block length shows high proton conductivity, excellent dimensional stability, low glass-transition temperature (*T*_g), good oxidative stability and superior cell performance.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been intensively developed during the past decades as clean and high-efficiency energy conversion devices. [1] Proton exchange membranes (PEMs) are one of the key components of the PEMFCs for

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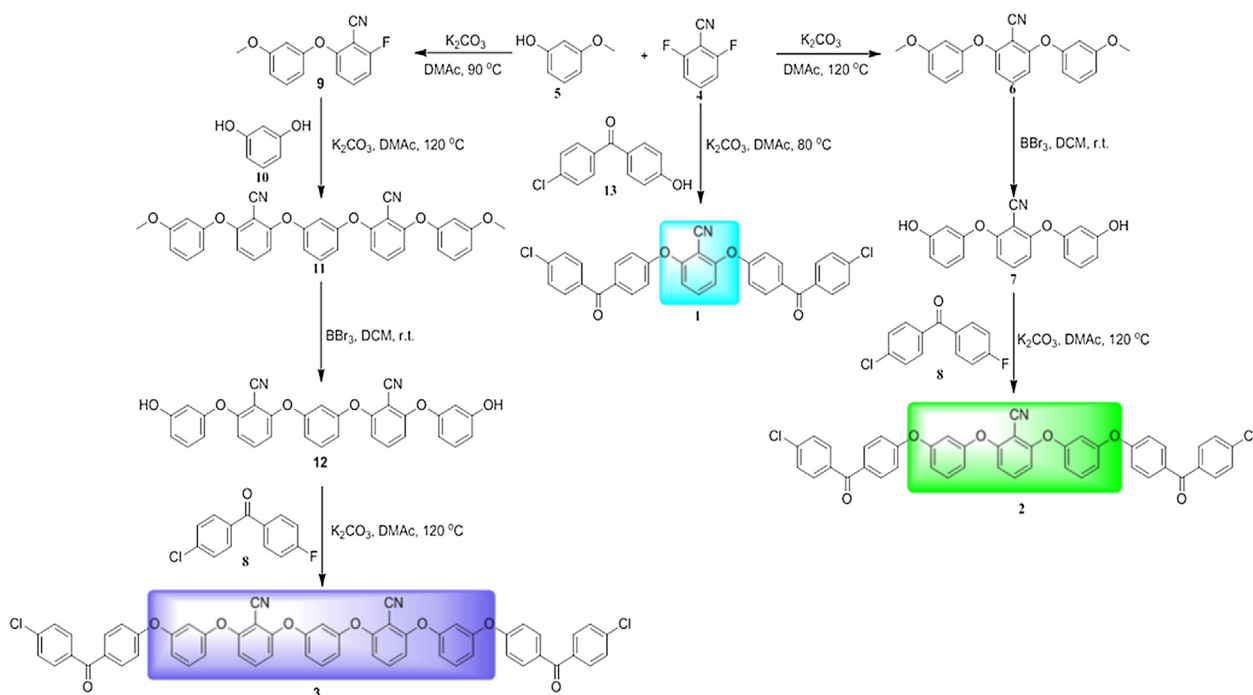
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separating the electrodes and conducting protons from the anode to cathode. [2,3] The majority of current research on PEMs is based on non-perfluorosulfonated aromatic polymers, including sulfonated poly(arylene ether sulfone)s (SPESs), [4–6] sulfonated poly(arylene ether ketone)s (SPEEKs), [7–9] sulfonated polyimides (SPIs), [10,11] sulfonated polyphenylenes and their derivatives (SPPs), [12–15] because of their high thermal and chemical stabilities, as well as excellent mechanical properties of the parent polymers. In particular, SPPs and their derivatives have many advantages, such as excellent oxidative stabilities and easy synthesis via the nickel (0) catalyzed coupling copolymerization. [16–19] Moreover, the chemical structure and feed ratio of the monomer can be adjusted by a reasonable change in the molecular design to obtain novel SPPs with expected properties. For example, the introduction of naphthalimide segments results in high proton conductivity and glass-transition temperature (T_g). [17] The ether linkage and perfluoroisopropyl group in polymer chains enhances the solubility of the polymer in organic solvents [20] and the longer alkyl side chain can facilitate the development of a microscopic structure. [18] The introduction of meta ether linkages and cyano groups in the polymer backbone maintains the oxidative stability of the polymer and the materials thus obtained exhibits preferable cell compatibility (the capability to be assembled into a membrane electrode assembly (MEA)). [21].

Proton conductivity, which directly correlates to the corresponding cell performance, could be the most significant characteristic of PEMs for PEMFC applications. [22] PEMs with high proton conductivities have been reported to show attractive fuel cell performance. Control of polymer morphologies and ionic nanostructures is effective to obtain PEMs with high proton conductivities. Several efficient methods that exploit this strategy have been developed, such as the development of phase separation with block copolymers, [23–26] modification of PEMs with pendant or branched sulfonic acid groups, [27,28] and controlling the position of the sulfonic acid group position and their concentration. [29,30] However, the precise control of nanoscale

morphology of random polymers to improve proton conductivity is still a challenge and is an area of active research. More recently, novel microblock copolymers have been prepared and studied, in which densely sulfonated moieties are regularly spaced by monodispersed nonsulfonated segments. [31–33] These microblock copolymers show attractive properties, including well-developed hydrophilic/hydrophobic phase separation, reasonable water uptake, high proton conductivity, and excellent oxidative and dimensional stability. Therefore, it provides a new pathway for the control of random polymer morphologies to prepare new PEMs with high proton conductivity.

The design and synthesis of the monomers is the significant step for the synthesis of the microblock copolymers, because the hydrophobic units in the copolymers essentially determine the sequence distribution of the sulfonic acid groups of their corresponding membranes. Herein we report a novel approach to develop the microblock SPPs with high proton conductivity, reasonable T_g value and good cell performance by controlling the phase-segregated morphology with the sequence distribution of sulfonic acid groups. By careful design, three bischloride monomers (1–3) containing different hydrophobic units with precisely defined lengths were synthesized, as shown in Scheme 1, in which the content and distribution of the meta ether linkages and cyano groups are different. Then, three new microblock SPPs with good phase-segregated morphology were prepared by employing the nickel (0) catalyzed coupling copolymerization of 2, 5-dichloro-3-sulfobenzophenone (SBJT) and (1–3). Due to the simple control of the length and chemical structure of the hydrophobic units, these new SPP-co-PAEKs exhibit good phase-segregated morphology, which results in a significant enhancement of proton conductivity at elevated temperature and over a wide range of humidity. Moreover, it has been shown that the T_g values of polymers can be adjusted to improve the adhesivity of PEMs for fuel cell application by tuning the length of the hydrophobic units. These ionomers have been characterized as PEMs and subjected to electrochemical investigations in fuel cells. Herein, the design and synthesis of SPP-



Scheme 1. Synthesis of the bischloride monomers.

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