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Properties, degradation and high temperature fuel cell test of different types of PBI and PBI blend membranes

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ABSTRACT

Polybenzimidazoles (PBIs) with synthetically modified structures and their blends with a partially fluorinated sulfonated aromatic polyether have been prepared and characterized for high temperature proton exchange membrane fuel cells. Significant improvement in the polymer chemical stability in terms of the oxidative weight loss, molecular weight decrease and onset temperatures for the thermal SO_2 and CO splitting-off was achieved with the electron-deficient polybenzimidazoles containing $-S(O)_2-$ and $-C(CF_3)_2-$ bridging groups. Ionical cross-linking in the form of acid–base blends was found to further improve the polymer stability and assist maintaining the membrane integrity. Upon acid doping the membrane swelling was reduced for the modified PBI and their blend membranes, which, in turn, results in enhancement of the mechanical strength, proton conductivity and high temperature fuel cell performance.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) operating at temperatures above 100 °C have in recent years been recognized as a promising solution to meet the technical challenges of the technology [1–3]. The most successful example of such cells utilizes phosphoric acid doped polybenzimidazole membranes [4–7], typically based on poly[2,2′-*m*-(phenylene)-5,5′-bibenzimidazole] (PBI or *m*-PBI, Scheme 1a), as recently reviewed [8].

More efforts have recently been made to explore the chemistry of the polymers and possibilities of improving the membranes for fuel cells. Most of these efforts are focused on achieving higher molecular weight polymers and improved solubility and processibility, which are of significance for mechanical stability and functionalization processing of PBI membranes. Another important goal is the synthesis of polymers with tailored bacisities, which makes it possible to optimize the acid–base properties of the membranes. These modifications can be accomplished in two ways, either by synthetically modifying the monomers prior to polymerization or by the post-polymerization substitution of the polymer at the reactive benzimidazole N–H sites.

As a synthetically modified polymer, poly(2,5-polybenzimidazole) (ABPBI, Scheme 1b) has a simpler structure than PBI without the connecting phenyl rings and therefore a high concentration of the basic sites in the structure [4,9]. While PBI is synthesized from 3,3′-diaminobenzidine and phthalic acid, ABPBI is polymerized from a single monomer (3,4-diaminobenzoic acid, DABA), which is less expensive and commercially available. Poly[2,2′-*p*-(phenylene)-5,5′-bibenzimidazole] (*p*-PBI, Scheme 1c) has been synthesized by using *para*-terephthalic acid (TPA) and recently received more attention because the *para* structure of the polymer has shown superior tensile strength and stiffness [10–13]. Pyridine dicarboxylic acids such as 2,4-, 2,5-, 2,6-, and 3,5-pyridine dicarboxylic acids have been used to prepare pyridine PBI (PyPBI, e.g. Scheme 1d) with improved solubility [13,14]. The incorporation of an extra nitrogen atom in the PBI main chain also increases the base content of the polymer, thereby enhancing the acid doping and proton conductivity, while retaining the inherently high thermo-oxidative stability of the polymer. It was reported that both the acid doping level and the proton conduc-

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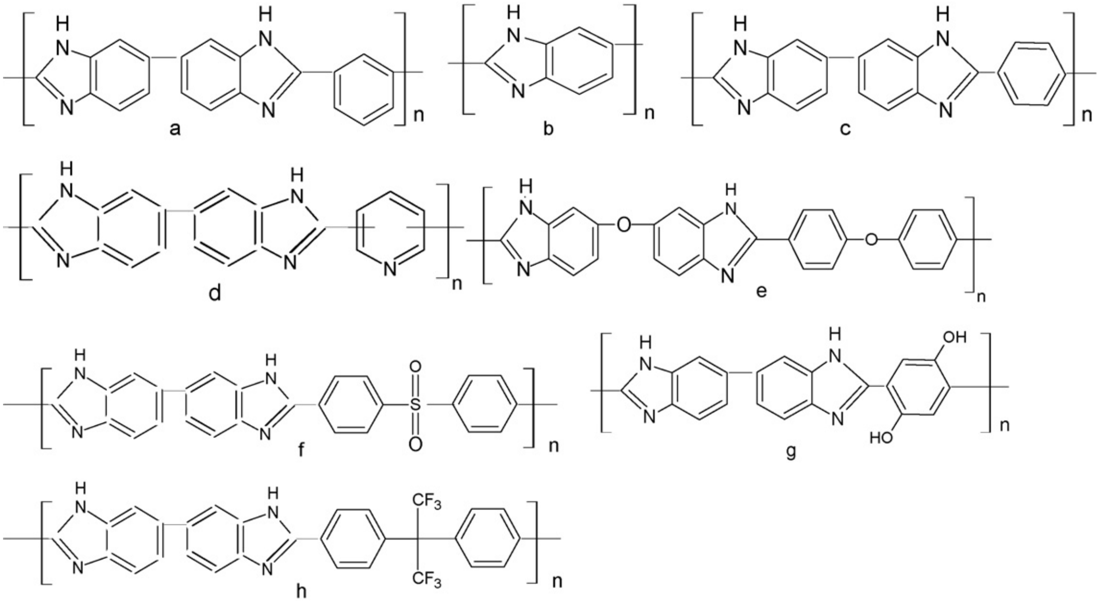


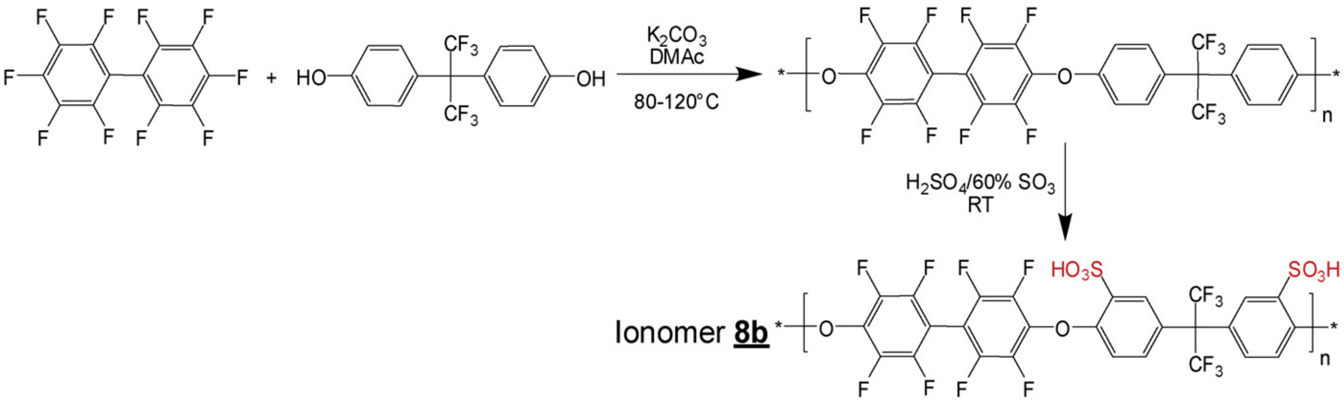
Scheme 1. Various structures of synthetically modified PBI. (a) *meta*-PBI; (b) ABPBI; (c) *para*-PBI; (d) PyPBI; (e) OOPBI; (f) SO_2PBI; (g) 2OHPBI; (h) F_6PBI.

tivity increased remarkably with the membrane basicity, which depends on the amount of NH-groups as well as their position in the polymer backbone [14].

Another example is poly-[(1-(4,4′-diphenylether)-5-oxybenzimidazole)-benzimidazole] (OOPBI, Scheme 1e) [15], where the ether linkages activate both the hydroquinone and the benzimidazole segment of the polymer chain for post-synthesis modification such as direct sulfonation. Similarly Qing et al. [16] prepared sulfone-containing PBI (SO_2PBI, Scheme 1f) by using 4,4′-sulfonyldibenzoic acid. By using a variety of diacids, more synthesis has been made of PBI with modified structures. Dihydroxy-PBI (2OHPBI, Scheme 1g) was synthesized [17], from which membranes were prepared by direct casting the polymer solution in polyphosphoric acid. The membranes showed higher conductivity than the corresponding *para*-PBI membranes. And hexafluoro PBI (F_6PBI, Scheme 1h) has been prepared using 4,4-(hexafluoroisopropylidene) bis(benzoic acid) [18,19]. In general the polymers containing heterogroups have lower thermo-oxidative stability but increased solubility and flexibility, which allow further processing, modification (cross-linking, sulfonation to high ion exchange capacity (IEC)) and production of films with good mechanical properties.

The NH-groups in the imidazole rings are chemically reactive. N-substituted PBI can be prepared by post-polymerization substitution of PBI, an interesting way to prepare sulfonated PBI [20–22]. Another way of post-polymerization modification of PBI is cross-linking, either ionically [6,23,24] or covalently [25,26]. Flexible ionomer networks can be prepared from acid–base polymers by ionical cross-linking of polymeric acids and polymeric bases [27–31], as developed and recently reviewed by Kerres [6]. Generally speaking, acid-excess ionically cross-linked membranes can show insufficient dimensional stability (too strong swelling in liquid water at temperatures above 100 °C and elevated pressures) if the ionical cross-linking degree and/or the basicity of the basic blend component is too low, leading to mechanical instability [6]. On the other hand, covalently cross-linked membranes tend to become brittle if the cross-linking density is too high as they dry out. Kerres et al. [32,33] recently introduced a covalent cross-linker (1,4-diiodobutane, DIB) into an ionically cross-linked blend to avoid the disadvantages of solely covalently or ionically cross-linked ionomer membranes.

Further doping of PBI-based acid–base blend membranes comprising an excess of basic moieties with phosphoric acid yields a ternary blend membrane [34,35]. Compared with H_3PO_4-doped



Scheme 2. Synthesis of the partially fluorinated polyether **8b**.