

Novel iodo-containing poly(arylene ether ketone)s as intermediates for grafting perfluoroalkyl sulfonic acid groups



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ABSTRACT

A synthetic approach to poly(arylene ether ketone)s grafted with super-acidic perfluoroalkyl-sulfonic-acids is reported. A series of iodo-containing poly(arylene ether ketone)s derived from a 4-iodophenylated hydroquinone monomer were synthesized by aromatic nucleophilic substitution (SNAr). The iodo-containing polymers were functionalized via the Ullmann reaction to give poly(arylene ether ketone)s grafted with perfluoroalkyl-sulfonic-acid. The perfluoroalkyl-sulfonic-acid functionalized aromatic polymers were investigated as proton exchange membranes (PEM). The membranes had good overall properties of thermal-oxidative stability, mechanical strength, methanol permeability and proton conductivity. A membrane with IEC ~ 1.37 meq g^{-1} had a proton conductivity of 0.088 S cm^{-1} at 100 °C, which was higher than many sulfonated hydrocarbon PEMs with similar IEC values.

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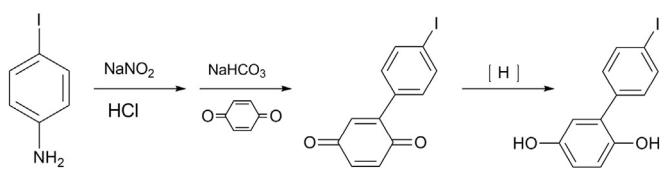
1. Introduction

Poly(arylene ether ketone)s (PAEKs) are a family of high-performance engineering thermoplastics, known for their excellent thermal, mechanical, and electrical properties. These advanced materials have been successfully applied to aerospace, automobile, nuclear power, and many other high-technology fields [1,2]. PAEKs and their chemically modified structures are receiving considerable attention for applications, including low- k dielectrics, high-efficiency separation membranes, optical waveguide films and proton exchange membranes, through rational structural and chemical modifications [3,4]. The incorporation of halogens into polymers imparts functionality, reactivity, and some attractive properties. For example, fluorinated polyarylethers have higher gas permeability, lower dielectric constants, higher transparency and lower refractive indices in comparison with non-fluorinated analogues [5]. Among reported halogen-substituted PAEKs, only fluorinated PAEKs have been synthesized and investigated widely. That is, the synthesis and properties of PAEKs containing halogens other than -F, particularly those containing -I, have seldom been investigated. So far, only several iodo-containing polyarylether-type polymers, e.g. polysulfones and polyarylethers have been prepared via the post-functionalization of the polymeric precursors or the

polymerization of the iodo-containing monomers [6–8]. For example, Guiver reported an iodo-containing polysulfone obtained by a lithiation reaction of polysulfone [6]. Watanabe and Miyatake reported the iodo-containing polyarylether-type polymers derived from an iodo-containing hydroquinone monomer, which was synthesized via a two-step reaction procedure [8]. It should be pointed out that reactive iodo-containing monomers and high-molecular-weight iodo-containing polyarylethers are usually difficult to prepare, due to possible crosslinking or reactivity of the iodine atoms. Thus, the development of simple and mild routes to iodo-containing monomers and polymers is especially attractive.

Proton exchange membrane fuel cells (PEMFC) have received much attention in the last two decades as clean and efficient power devices. The proton exchange membrane (PEM), a key component of PEMFCs, requires high ionic conductivity, low fuel permeability, good thermal and hydrolytic stability, excellent mechanical properties in the dry and hydrated states, moderate water absorption, and good dimensional stability under the operating environment of the fuel cells [9,10]. Nafion®-type PEMs with the chemical structure of perfluoroalkyl sulfonic acids have been widely used in fuel cells and gained commercial success, because of their high proton conductivity and high stability [11,12]. These properties are due in part to the super-acidic fluorosulfonic acid side-chain, which also drives phase separation between the hydrophobic main chain and the hydrophilic side chain. Their well-known limitations of high cost, high fuel permeability and limited operation temperature,

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Scheme 1. Synthesis route of IPHQ monomer.

have led to the search for alternative membranes [4]. To overcome the shortcomings of the widely used Nafion membranes, sulfonated aromatic polymers have been investigated for their low fabrication cost, higher thermal stability, and a wide variety of polymer architecture [12–16].

In typical backbone-sulfonated aromatic PEMs, the aryl sulfonic acid group is much less acidic than the super-acidic fluorosulfonic acid side-chain found in Nafion, and thus it imparts lower proton conductivity.

Several approaches to circumvent the lower proton conductivity brought about by aryl- or alkylsulfonic acid PEMs include stabilized, crosslinked or network PEMs with high ion exchange capacity (IEC) values, blends, or the development of nanophase-separated morphology that leads to the formation of conducting channels [17–19].

In the present study, we prepared a poly(aryl ether ketone) with pendant perfluoroalkyl sulfonic acid groups by the aromatic nucleophilic substitution reactions of 4,4-difluorobenzophenone and 4-iodophenylhydroquinone (IPHQ), or 4,4-difluorobenzophenone and 4-iodophenylhydroquinone/4,4'-(hexafluoroisopropylidene)diphenol (6FBPA) to form iodine-substituted polymers. The resulting iodine-substituted polymer was reacted with potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (PFS-I) through Ullman coupling, successfully introducing the strongly acidic perfluorosulfonic side chain into the polymer. Selected properties of relevance to PEM, such as thermal stability, oxidative stability, water uptake and proton conductivity, were investigated in detail. The

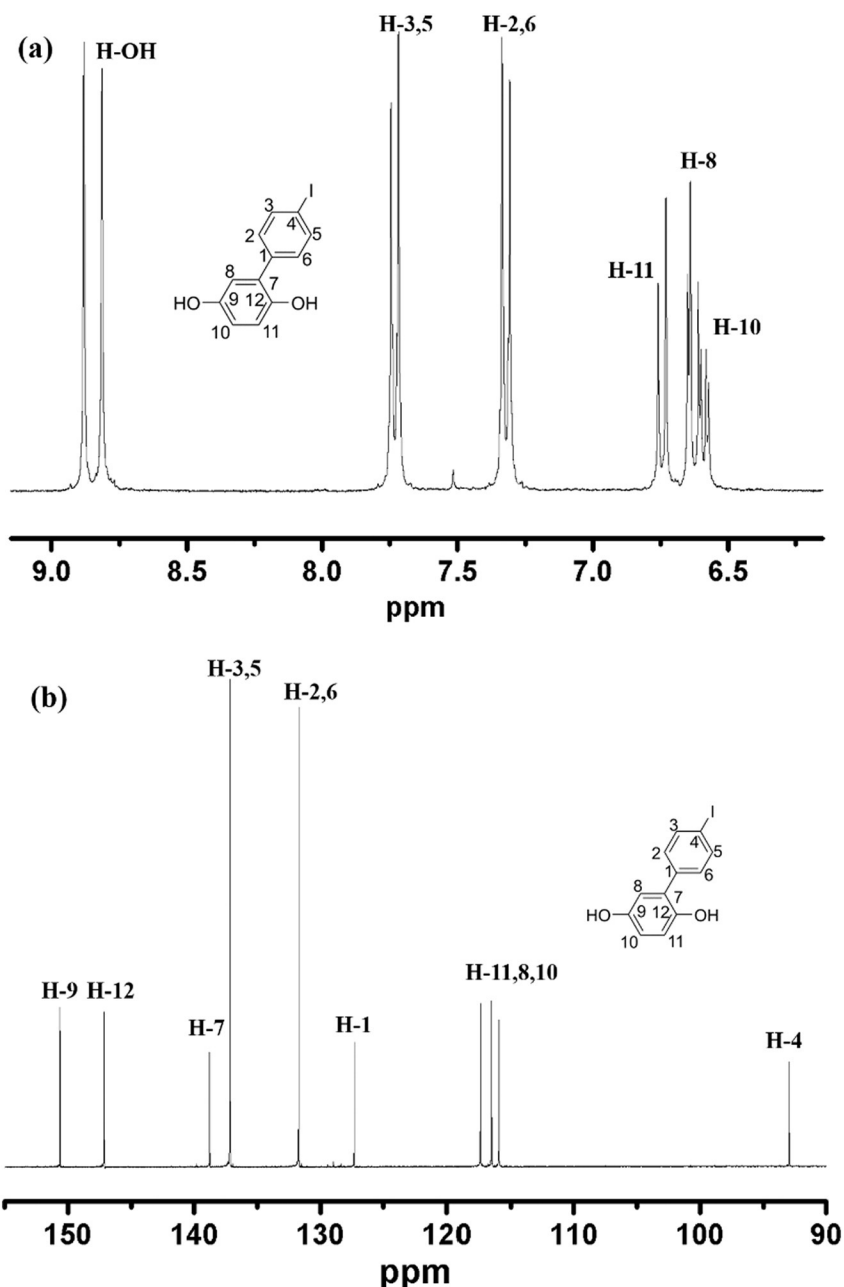


Fig. 1. (a) ^1H (500 M, $\text{DMSO-}d_6$) and (b) ^{13}C NMR (150 M, $\text{DMSO-}d_6$) spectra of the monomer.

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