



# Poly(arylene ether sulfone)s with different positions of pyridyl groups: Synthesis of the basic diphenyl sulfone dihalide monomers in lithiation and the optimal polymerization in condensation



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## ABSTRACT

The present study consists of three parts: 1) synthesis of diphenyl sulfone dihalide monomers with different positions of pyridyl groups; 2) fundamental understanding of polymer chain growth (*i.e.*, condensation) and scission (*i.e.*, *trans*-etherification) involving use of the novel dihalides; and 3) general properties of the basic polymers prepared. The dihalides are 4,4'-difluorodiphenyl sulfone contained with pyridyl groups where the nitrogen atom is in either *ortho*- or *para*-position to the ketone bridges, synthesized via lithiation using *n*-butyl lithium and the corresponding electrophiles. Both dihalides were found to be thermally stable up to 250 °C and their melting points were 222 and 206 °C, respectively. Their versatilities for K<sub>2</sub>CO<sub>3</sub>-mediated poly-condensation were confirmed with a careful control of reaction time, temperatures and solvents to depress *trans*-etherification and cross-linking reactions with an activation energy sufficiently for polymer chain growth. Consequently, the optimal conditions were 130 °C for 24 h in dimethylacetamide that resulted in polymer products with high molecular weights (*M<sub>w</sub>*) ranging from 40 to 200 kDa. The glass transition points of poly(arylene ether sulfone)s (PAESs) with pyridyl groups in the *para*-positions were higher than those of PAESs with pyridyl groups in the *ortho*-positions under a given *M<sub>w</sub>*, and the thermal decomposition points were higher for PAESs in the *ortho*-positions than in the *para*-positions under a given degree of pyridyl substitution. These findings would consequently open up many synthetic routes towards various kinds of monomers and polymers via metalation and condensation reaction schemes.

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## 1. Introduction

Aromatic polymers, so-called engineering polymers or plastics, have received much attentions since they have several characteristic and comparable properties to those of metal materials and components, including high thermal stability, high chemical resistance and high mechanical modulus. For example, decreasing the total weight of vehicle systems is one of important solutions for an improved fuel efficiency in the field of automotive development, where material gravimetric densities are much smaller for polymers than for metals [1,2]. Reducing the number of production process is an additional merit via material replacement of metals to polymers, by way of polymer injection/extrusion molding of vehicle parts, instead of metallic welding. Among aromatic polymers, poly(arylene sulfone)s, poly(arylene ketone)s and

poly(arylene)s are categorized as super-engineering polymers, because of their excellent thermal, chemical and mechanical stability. In particular, poly(arylene sulfone)s have been well investigated, including polysulfone (namely PSU) and poly(ether sulfone) (namely PES) [3,4]. The present study also focuses on a family of poly(arylene sulfone)s, *i.e.*, synthesis of novel monomers and characterization of the corresponding poly(arylene ether sulfone)s (PAESs).

PAESs are soluble in several organic solvents that enable film formation through solution cast methods, therefore triggering a huge interest in film applications, including humidification, reverse osmosis for desalination and ion exchange application [5–8]. The main target application behind the present study is an ion- (cation or anion) exchange membrane [9] that showed its usability in the field of zero emission fuel cell electric vehicles (FCEVs), as a promising alternative technology to internal combustion engine vehicles, and would contribute to reduction of global carbon dioxide emission. Notably, as announced in the past development of

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proton exchange membranes for FCEVs, Honda Motor successfully employed cation-exchanging aromatic copolymers, jointly developed with a Japanese chemical company, JSR whose results encourage further investigation of aromatic polymers for ion exchange applications [10]. JSR's polymers are block copolymers between PAESs and poly(phenylene)s that show very promising and attractive membrane properties and fuel cell performance. However, these polymers are very complicated due to several synthesis steps needed which cast doubt on the industrial applicability, including reproducibility and yield. Recently, we reported on a compatible acid-base blend polymer membrane, where comparable membrane properties were achieved to the state-of-the-art technologies [11]. As a result, the basicity of polymers blended in acidic polymers affected membrane properties, calling for further investigation on various kinds of basic polymers for blending with acidic polymers. In fact, a small addition of poly(benzimidazole), a relatively strong basic polymer, to an acidic polymer showed excellent film formability, however, sacrificing a decrease in membrane properties, in particular ionic conductivity [11].

Therefore, the present study is to synthesize a new series of PAESs in which relatively weak basicity is covalently incorporated in the corresponding monomers. Pyridyl-group contained PAESs were, as a matter of fact, reported using a post-modification approach on commercially available PAESs, e.g., UDEL<sup>®</sup> (by Solvay), whose basicity was calculated for the basic PAESs derived from different types of pyridyl groups [12]. Then, two cases of pyridyl groups were selected for preparation of monomers and polymers in the present study, whose *pK*s ranged from 0 to 2.5 when incorporated in PAESs. Two synthetic approaches were studied as shown in Scheme 1: (a) post-modification on existing

polymers; (b) polymerization using novel functional monomers. The detail procedure of the former approach was depicted in Scheme 2, as previously reported [12,13]. Some preliminary studies were also implemented to understand the versatility of post-modification in lab-scale, resulting in poor reproducibility and widening poly-dispersity index (PDI) in the resulting polymers as summarized in Fig. 1 (also see Supplementary Information, Fig. S1, regarding the detailed <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra of each product). In general, a post-modification involving lithiation chemistry is sensitive to several factors including, e.g., water contents, reaction temperature, solution concentration, along with cross-linking side reaction [14].

Thus, in the present study, two sorts of new pyridyl group contained diphenyl sulfone dihalides were prepared in order to attain a control of final product, as described in Scheme 3. First of all, synthesis and identification of these novel dihalides with two different positions of pyridyl groups were discussed, followed by their general characterizations. Next, their polymerizability was investigated in K<sub>2</sub>CO<sub>3</sub>-mediated poly-condensation. A conventional condition did not yield a target molecular design, and so a considerable investigation of the reaction condition was carried out, where a possible side-reaction or degradation mechanism is the most probably so called “*trans*-etherification” that very few research articles have reported on [15–19], whereas cyclization, which would more easily take place in a lower solid concentration than a conventional reaction condition, has been known as another side-reaction that would impede the chain growth [16,17]. After preparing and identifying a series of corresponding basic copolymers for each dihalide under the optimal poly-condensation, general properties of the resulted polymers were evaluated, including glass transition points, thermal decomposition temperatures and molecular weights, while a future publication will report on fuel cell membrane properties and performance.

## 2. Experimental section

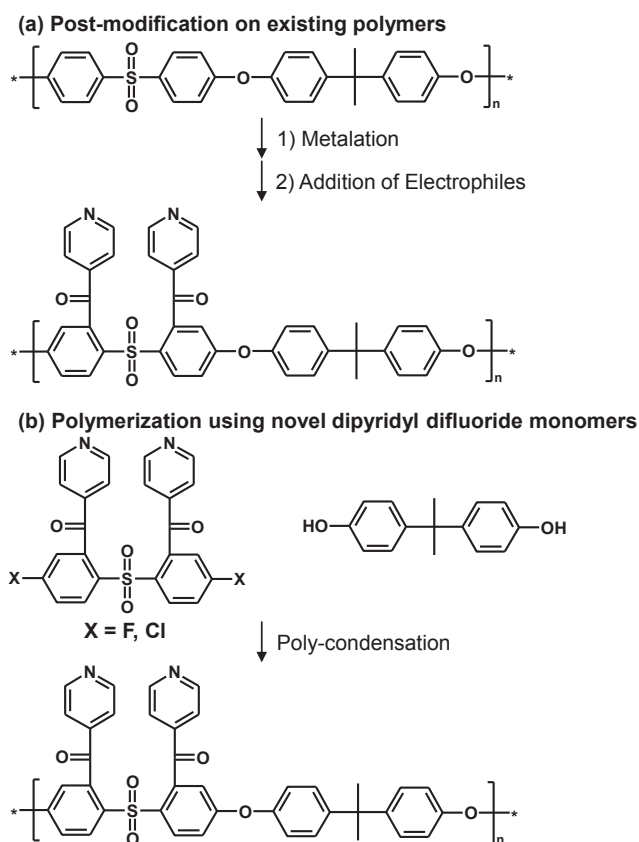
### 2.1. Material

All the reagents and solvents in this study were used with no further purification, as follows. 4,4'-difluorodiphenyl sulfone (DFDPS, 99%, Fumatech); 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, >99%, Sigma-Aldrich); ethyl isonicotinate (EIN, 98%, Sigma-Aldrich); ethyl 2-picolinate (E2P, 99%, Sigma-Aldrich); *n*-butyllithium (*n*-BuLi, 1.6 M in hexanes, Sigma-Aldrich); potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, >99.0%, Sigma-Aldrich); 1-methyl-2-pyrrolidinone (NMP, >99.9%, Sigma-Aldrich); dimethylacetamide (DMAc, 99.5%, Acros); dimethylsulfoxide (DMSO, >99.9%, Sigma-Aldrich); dimethylformamide (DMF, ACS reagent, >99.8%, Sigma-Aldrich); toluene (ACS reagent, >99.7%, Sigma-Aldrich); cyclohexane (HPLC grade, VWR); 2-propanol (ACS reagent, >99.8%, Sigma-Aldrich); methanol (HPLC grade, VWR); tetrahydrofuran (THF, Inhibitor-free, HPLC grade, >99.9%, Sigma-Aldrich). The potential basic ion-exchange capacity (*IEC*<sub>b</sub>, meq. g<sup>-1</sup>) of the copolymers prepared was calculated on an assumption that one unit of pyridyl group would play a role as one mole basicity.

### 2.2. Monomer, polymer and membrane preparation

#### 2.2.1. Pyridine-modified difluoro-diphenylsulfone monomer

Two types of novel dihalide monomers including a pyridine moiety were prepared via lithiation. An example of the synthetic procedure for *dp*DFDPSp (DFDPS with dipyridyl groups in the *para*-positions to the ketone linkages) is described as below. DFDPS (20.0 g, 78.7 mmol) was introduced to a 1 L round flask equipped with a magnetic stirrer, a septum and an inlet/outlet for gas-



**Scheme 1.** Two synthetic pathways to prepare pyridyl-group contained PAESs: (a) post-modification on existing polymers; (b) polymerization using novel pyridyl groups contained difluoride monomers.

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