

## Short communication

## Ladder-type aromatic block copolymers containing sulfonated triphenylphosphine oxide moieties as proton conductive membranes

Yaojian Zhang <sup>a</sup>, Junpei Miyake <sup>b</sup>, Ryo Akiyama <sup>c</sup>, Kenji Miyatake <sup>b, c, \*</sup><sup>a</sup> Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan<sup>b</sup> Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan<sup>c</sup> Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae, Kofu, Yamanashi 400-0021, Japan

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## ABSTRACT

The synthesis and characterization of ladder-type aromatic block copolymers containing sulfonated triphenylphosphine oxide moieties (**LadP-SPE**) are reported. Through aromatic nucleophilic substitution polycondensation and Pd-catalyzed intrapolymer Heck reaction, the target copolymers **LadP-SPE** with high molecular weight ( $M_n = 47\text{--}50$  kDa,  $M_w = 289\text{--}579$  kDa) and different ion exchange capacity (IEC) values (1.04, 1.84 and 2.22 meq g<sup>-1</sup>, by titration) were prepared. By solution casting method, all the copolymers gave transparent and bendable membranes. The membrane with IEC = 2.22 meq g<sup>-1</sup> exhibited high proton conductivity in wide range of relative humidity (RH) at 80 °C (ca. 1.6 mS cm<sup>-1</sup> at 20% RH and 351.2 mS cm<sup>-1</sup> at 95% RH). Moreover, the stiff ladder structure strengthened the molecular chain which contributed to the membrane with high IEC value and water uptake to have desirable mechanical stability up to 90% RH at 80 °C.

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## 1. Introduction

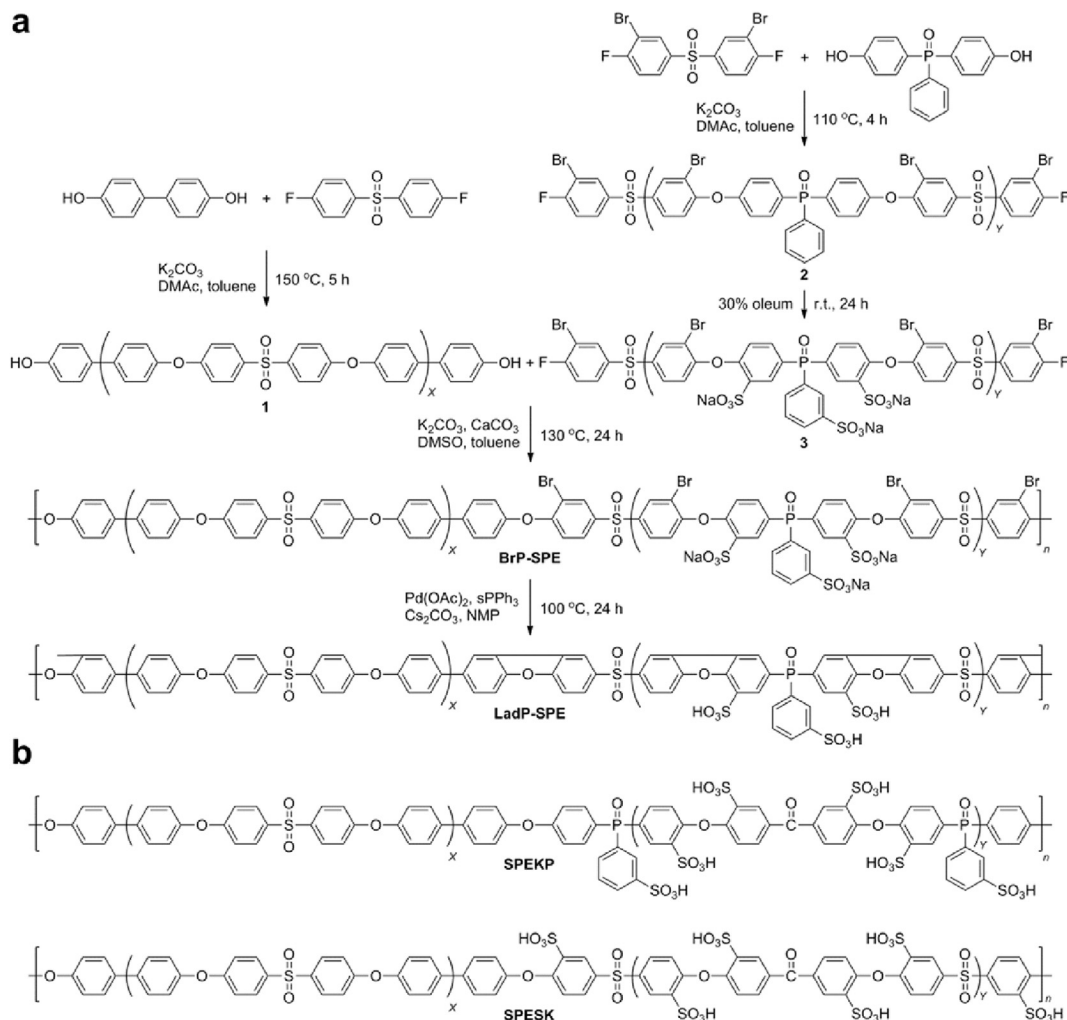
Polymer electrolyte membranes (PEMs) have gained extensive attention for full cell applications. While perfluorinated ionomers such as Nafion (du Pont) have been most used as state-of-the-art PEM, fluorine-free aromatic PEMs have been developed extensively as alternative PEMs in terms of better environmental compatibility and lower cost [1–7]. It has been demonstrated that multiblock copolymers containing sulfonated hydrophilic segments and unsulfonated hydrophobic segments show improved properties (e.g., higher proton conductivity than that of the random copolymer equivalent) due to the well-developed hydrophilic-hydrophobic phase-separated morphology with interconnected ionic channels [8–17]. Recently, our group has developed multiblock copolymers containing sulfonated triphenylphosphine oxide moiety in the hydrophilic segments (**SPEKP**, Scheme 1b) [18]. The **SPEKP** membrane exhibited high proton conductivity (216 mS cm<sup>-1</sup>) despite its low ion exchange capacity (IEC) value (1.09 meq g<sup>-1</sup>) at 80 °C and 95% relative humidity (RH), which is 1.3

times higher than that of Nafion. However, similar to most aromatic-type PEMs, the **SPEKP** membrane suffered from mechanical instability under wet conditions. In addition, higher IEC membrane for higher proton conductivity was not available due to dissolution in water.

More recently, we have achieved a novel polymeric structural conversion (i.e., intrapolymer Heck reaction) to form ladder structure on diphenyl ether moieties in aromatic PEMs [19]. The advantage of the polymer reaction is that higher density of the ladder structure can be achieved than using the monomeric ladder compounds [20]. The dense ladder structure provided the PEM with improved mechanical stability under wet conditions, probably due to the enhancement of interpolymer interactions derived from the rigid and planar dibenzofuran (ladder) moieties and/or reduction in polarity caused by the aromatic nature of dibenzofuran moieties. The results prompted us to further examine whether the ladderization of the sulfonated triphenylphosphine oxide moieties might enable the increase in IEC, resulting in the improvement of proton conductivity without compromising the mechanical stability. In this paper, we report synthesis and properties of ladder-type aromatic multiblock copolymers containing sulfonated triphenylphosphine oxide moiety as hydrophilic segments and oligo(arylene ether) as hydrophobic segments (**LadP-SPE**, Scheme 1a).

\* Corresponding author. Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan.

E-mail address: [miyatake@yamanashi.ac.jp](mailto:miyatake@yamanashi.ac.jp) (K. Miyatake).



**Scheme 1.** (a) Synthesis of title block copolymers (**LadP-SPE**) and (b) chemical structure of reference polymers (**SPEKP** and **SPESK**).

## 2. Experimental section

Detailed experimental on the synthesis and characterization are available in the [Supporting Information](#).

## 3. Results and discussion

**Scheme 1a** shows the overall synthetic route for the title block copolymers (**LadP-SPEs**); (i) Synthesis of hydrophobic (unsulfonated) telechelic oligomers **1** and hydrophilic (sulfonated) telechelic oligomers **3**, separately, (ii) block copolymerization of the oligomers **1** and **3** to give precursor multiblock copolymers (**BrP-SPEs**), and (iii) Pd-catalyzed intrapolymer Heck reaction of **BrP-SPEs** to give the title block copolymers (**LadP-SPEs**). First of all, oligomers **1** were prepared by the typical aromatic nucleophilic substitution polycondensation of 4,4'-biphenol (BP) and bis(4-fluorophenyl)sulfone (FPS) with  $\text{K}_2\text{CO}_3$  as base and DMAc as solvent. The chain lengths ( $X$ ) and terminal groups (OH) were controlled by the feed comonomer ratios. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra ([Fig. S1 in Supporting information](#)) supported the formation of the targeted oligomers **1** with controlled  $X$  and OH-terminals ([Table S1 in Supporting information](#)). The chain lengths obtained by the  $^1\text{H}$  NMR spectra were similar to those by the feed comonomer ratios, while those by GPC were larger probably because the oligomers **1** are composed of rigid molecular structure

and eluted fast in our GPC system.

The preparation of oligomers **2** were carried out in a similar manner as described for the oligomers **1**. It should be noted that the high reactivity of FPS with Br-substituents allowed milder reaction conditions (lower reaction temperature such as  $110^\circ\text{C}$ ) for the preparation of the oligomers **2** as well as for the following the preparation of multiblock copolymers **BrP-SPEs** compared to those of the oligomers **1** [20]. The chemical structure of the oligomers **2** was characterized by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra, in which all signals were well-assigned ([Fig. S4 in Supporting information](#)). For example, in the  $^{31}\text{P}$  NMR spectra of the oligomers **2**, a singlet peak was observed at 24.8 ppm which was different from that of the BHPPO monomer (26.1 ppm), suggesting the complete consumption of the BHPPO monomer. Although the  $Y$  values obtained by  $^1\text{H}$  NMR spectra were in fair agreement with those calculated from the feed comonomer ratios, the ones obtained by GPC analyses were much lower ([Table S1 in Supporting information](#)). This result is consistent with our previous result, in which phosphine oxide-containing oligomers had some interactions with our GPC columns resulting in the underestimation of  $M_n$  (i.e., lower  $Y$  values) [18].

Oligomers **3** were prepared by sulfonation reaction of the oligomers **2** with 30% oleum at room temperature for 24 h. The chemical structure of the oligomers **3** were characterized by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra ([Fig. S5 in Supporting information](#)). The  $^{19}\text{F}$

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