# Synthesis and Characterization of Phenol-Based Biaryl Proton Conducting Polymers

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**ABSTRACT:** Biaryl hydroxy polymers with orthogonal disposition of proton transporting –OH moieties have been synthesized via conventional free radical polymerization. The polymers are characterized for their thermal stability and proton conductivity, and the results are compared with the corresponding styrenic hydroxy polymers. The orthogonal disposition of –OH moieties in biaryl polymers does result in

**INTRODUCTION** Proton transporting polymers that can selectively and efficiently transfer protons play a pivotal role in the overall operation of a hydrogen fuel cell. Polymers that can conduct protons under anhydrous conditions are particularly interesting for applications as proton exchange membranes in high temperature hydrogen fuel cells. Polymers based on N-heterocycles such as imidazole, triazole and benzimidazole have been widely studied to develop efficient anhydrous proton conducting polymers.<sup>1-9</sup> In the case of Nheterocyclic polymers, the reorientation step in Grotthuss proton transport (PT) is well recognized to be energetically demanding, thereby adversely affecting the overall  $\ensuremath{\text{PT}}\xspace{.}^{10-12}$ We have recently introduced a new class of functional groups, phenols, for anhydrous PT and have shown that polymers based on phenols allow for facile reorientational dynamics.<sup>13</sup> It has also been shown, with the help of theoretical modeling, that the pentamers of polystyrene (tri OH) (Fig. 1) can form extended intrachain hydrogen bond network.<sup>13</sup> Both intrachain and interchain proton transfer events are important for long range PT. We hypothesized that a molecular architecture that presents PT moieties in orthogonal planes would be interesting as it would allow for greater interchain hydrogen bonding interactions along with intrachain interactions among PT moieties, thereby enhancing the overall PT (Fig. 1).

# MOLECULAR DESIGN

We envisaged that biaryl would be an interesting scaffold for the proposed molecular design because (i) the steric interactions between the ortho hydrogen atoms is well known to lower  $E_a$  for proton transport. However, the lower  $E_a$  values in biaryl polymers did not translate into a net increase in proton conductivity. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1187–1196, 2012

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lead to a twist in the phenyl rings,<sup>14,15</sup> thereby inducing the orthogonality at the molecular level, (ii) both the phenyl rings of the biaryl scaffold can be functionalized with PT moieties, thus providing an interesting spatial disposition of the PT moieties in orthogonal planes, and (iii) a polymerizable double bond can be easily introduced onto one of the phenyl rings to generate a biaryl monomer, which could be conveniently polymerized similar to that of styrene. We chose to introduce phenols as the PT moieties on the biaryl architecture. A space-filling model of a pentahydroxy biaryl compound, energy minimized using MM2 calculations, supports the presumed orthogonal spatial disposition of the PT -OH moieties (Fig. 1). The dihedral angle between the phenyl rings was found to be 55°. In this work, we report the synthesis and characterization, thermal properties, and proton conductivity of biaryl phenolic polymers (see Chart 1). To further investigate if the biaryl architecture provides any advantage over the linear styrenic architecture, the proton conductivities of the biaryl and styrenic hydroxy polymers shown in Chart 1 are compared.

# EXPERIMENTAL

# General Procedures for the Synthesis of Biaryl Monomers

# Procedure 1 for Deprotection of -OMe Group Using BBr<sub>3</sub>

A solution of the appropriate methoxy benzene (1.0 equiv) in dichloromethane (DCM) at room temperature (RT) under argon was cooled to -78 °C for 30 min, and boron tribromide (1.5 equiv per methoxy group) was added at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and

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a)





Extended intra-chain hydrogen bond network in the protonated pentamer of polystyrene (tri OH)



Disposition of PT -OH moieties in orthogonal planes

FIGURE 1 (a) Proton wire of polystyrene (tri OH) pentamer; (b) illustration of the spatial disposition of proton transporting –OH moieties in orthogonal planes.

was slowly warmed to RT and continued to stir at RT for overnight. The reaction mixture was then cooled to -78 °C and the excess BBr<sub>3</sub> was quenched with saturated NH<sub>4</sub>Cl solution. The precipitate was filtered and washed twice with excess DCM. The DCM and aqueous layers were separated, and the DCM layer was concentrated. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the crude was purified by column chromatography (SiO<sub>2</sub>).

# Procedure 2 for protection of phenolic hydroxyl group as methoxymethyl ether (MOM)

A solution of the appropriate hydroxy benzene (1.0 equiv) in dry tetrahydrofuran (THF) under argon was cooled to 0 °C. N,N-diisopropylethylamine (DIPEA) (1.5 equiv per hydroxyl group) and chloromethyl methyl ether (MOMCl) (1.5 equiv per hydroxyl group) were added and the reaction was slowly warmed to RT and continued to stir at RT. The progress of the reaction was monitored using thin layer chromatography (TLC). The reaction is usually complete in about 12 h. After



CHART 1 Structures of biaryl and styrenic hydroxy polymers.

complete disappearance of the starting material, the reaction was cooled to 0  $^{\circ}$ C and quenched with saturated NH<sub>4</sub>Cl. The organic and aqueous layers were separated and the organic layer was concentrated. The aqueous layer was extracted thrice with ethyl acetate and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the crude mixture was purified by column chromatography (SiO<sub>2</sub>).

# Procedure 3 for Conversion of Bromobenzene to the Aromatic Tributyltin

A solution of the appropriate bromobenzene (1.0 equiv) in dry THF at RT under argon was cooled to -78 °C for 30 min, and *n*-BuLi (2.0 equiv) was added. The mixture was stirred at -78 °C for 1 h and tributyltin chloride (1.5 equiv) was added. The reaction was slowly warmed to RT and stirred for overnight. The reaction mixture was then cooled to 0 °C and quenched with saturated NH<sub>4</sub>Cl solution. The organic and aqueous layers were separated and the organic layer was concentrated. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the crude mixture was purified by column chromatography (SiO<sub>2</sub>).

### **Procedure 4 for Stille Coupling Reaction**

The appropriate tributyltin (1.0 equiv), bromobenzene (1.2 equiv), and  $PdCl_2(PPh_3)_2$  (0.05 equiv) were dissolved in toluene under argon at RT. The reaction mixture was degassed for 1 h with an argon inlet/outlet and the reaction mixture was then refluxed for 48 h. After evaporating the solvent, the resultant mixture was extracted twice with ethyl acetate and water. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the crude mixture was purified by column chromatography (SiO<sub>2</sub>).

# Procedure 5 for the Reduction of Ester with LiAlH<sub>4</sub>

A solution of LiAlH<sub>4</sub> (2.0 equiv) in dry THF at RT under argon was cooled to 0 °C. The appropriate biaryl ester compound (1.0 equiv) in dry THF was then added, and the reaction mixture was slowly warmed to RT and stirred for about 12 h. The progress of the reaction was monitored using TLC. After complete disappearance of the biaryl ester compound, the reaction was cooled to 0 °C and quenched with saturated NH<sub>4</sub>Cl solution. The precipitate was filtered and washed with ethyl acetate. The filtrate was concentrated and extracted thrice with ethyl acetate and water. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the crude mixture was purified by column chromatography (SiO<sub>2</sub>).

# Procedure 6 for the Oxidation of Benzyl Alcohol to Aldehyde Using Pyridiniumchlorochromate

To a stirring solution of the appropriate benzyl alcohol (1.0 equiv) in DCM at RT, was added pyridiniumchlorochromate (PCC) (1.2 equiv). The mixture was exposed to air while stirring, and the progress of the reaction was monitored using TLC. The reaction is usually complete within 2–8 h depending on the scale of the reaction. After complete disappearance of the benzyl alcohol, the crude mixture was concentrated under

reduced pressure and purified by column chromatography (SiO $_2$ ).

# Procedure 7 for the Deprotection of MOM Group Using DOWEX Resin

The appropriate MOM-protected biaryl aldehyde (1.0 equiv) was dissolved in a mixture of (MeOH:  $H_2O$ : 1,4-dioxane) (1.0:0.5:0.1 v/v) at RT under argon. DOWEX resin (4.0 equiv with respect to each MOM group) was added and the solution was refluxed. The progress of the reaction was monitored for every 10 min using TLC. If the reaction is not complete within 30 min, then an additional amount of DOWEX resin (1.0 equiv) was added each time until the starting material disappeared completely. The mixture was filtered, and the resin was washed with MeOH. The filtrate was concentrated under reduced pressure, and the crude mixture was taken to the next step without further characterization.

### **Procedure 8 for Boc-Protection**

The appropriate biaryl hydroxy aldehyde (1.0 equiv) was dissolved in THF at RT under argon. The reaction mixture was cooled to 0 °C and DIPEA (1.5 equiv per hydroxyl group), (Boc)<sub>2</sub>O (1.5 equiv per hydroxyl group), and 4-Dimethylaminopyridine (0.05 equiv) were added. The reaction mixture was then warmed to RT and continued to stir at RT for overnight. THF was evaporated and the crude was taken up in ethyl acetate and washed twice with 1M NaOH and saturated NaCl solutions. The combined ethyl acetate layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the crude was purified by column chromatography (SiO<sub>2</sub>).

# **Procedure 9 for Wittig Reaction**

MePPh<sub>3</sub>Br (1.5 equiv) and KO<sup>t</sup>Bu (1.5 equiv) were taken in an oven-dried Schlenk flask at RT and dried under vacuum for 30 min. The flask was cooled to 0 °C using ice bath and anhydrous THF (50 mL) was added under argon. The solution immediately turned yellow, indicating the formation of ylide. The reaction mixture was allowed to stir at 0 °C for 30 min and was then warmed to RT. A solution of the appropriate Boc-protected biaryl aldehyde (1.0 equiv) in anhydrous THF was added using syringe and the reaction mixture was continued to stir at RT for 12 h. The reaction was quenched by the addition of water and extracted thrice with ethyl acetate. The combined ethyl acetate layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the crude was purified by column chromatography (SiO<sub>2</sub>).

# Synthesis of Biaryl (penta Boc) Monomer 9

Compounds  $1^{16}$  and  $2^{17}$  were synthesized following reported procedures (Scheme 1).

#### Synthesis of Compound 3

According to general procedure 1, 5-bromo-1,2,3-trimethoxybenzene (10.0 g, 40.5 mmol) was treated with boron tribromide (BBr<sub>3</sub>) (45.6 g, 182.1 mmol). The product was eluted with ethyl acetate/hexane (80:20 v/v) to afford 5-bromo-1,2,3-trimethoxybenzene (8.2 g, 100%) as yellow oil, which was carried to the next step without further characterization. According to general procedure 2, 5-bromo-1,2,3-trimethoxybenzene (8.2 g, 40.2 mmol) was treated with DIPEA (23.4 g,





SCHEME 1 Synthesis of Biaryl (penta Boc) monomer 9.

181.0 mmol) and MOMCl (14.6 g, 181.0 mmol). The product was eluted with ethyl acetate/hexane (25:75 v/v) to afford compound **3** (8.8 g, 65%) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.01 (s, 2H), 5.17 (s, 4H), 5.10 (s, 2H), 3.60 (s, 3H), 3.49 (s, 6H).<sup>13</sup>C NMR (100 MHz, CO(CD<sub>3</sub>)<sub>2</sub>)  $\delta$  152.81, 137.08, 116.23, 114.10, 98.95, 96.00, 57.13, 56.46. FAB/MS m/z 337.024 [M + H]<sup>+</sup> (expected m/z = 337.02).

#### Synthesis of Compound 4

According to general procedure 3, compound **3** (8.8 g 26.0 mmol) was treated with 1.6 M n-BuLi/hexane (32.5 mL, 52.0 mmol) and SnBu<sub>3</sub>Cl (12.7 g, 39.0 mmol) to afford compound **4** (10.0 g, 70%) as yellow oil. The product was eluted with ethyl acetate/hexane (3:97 v/v). The tributylstannane is not very stable and hence was used immediately in next steps. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.92 (s, 2H), 5.19 (s, 4H), 5.15 (s, 2H), 3.62 (s, 3H), 3.51 (s, 6H), 1.58–0.89 (m, 27H).

# Synthesis of Compound 5

According to general procedure 4, compound **2** (6.4 g, 18.3 mmol) were treated with compound **4** (8.36 g, 15.3 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.536 g, 0.8 mmol) to afford compound **5** (5.5 g, 55%) as white solid. The product was eluted with ethyl acetate/hexane (20:80 v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.52 (s, 2H), 6.89 (s, 2H), 5.20 (s, 2H), 5.19 (s, 4H), 5.12 (s, 4H), 4.40–4.37 (q, *J* = 7.10Hz, 2H), 3.66 (s, 3H), 3.48 (s, 6H), 3.37 (s, 6H), 1.40–1.38 (t, *J* = 7.10Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.16, 155.09, 150.54, 135.88, 131.09, 129.39, 126.20, 113.24, 110.07, 98.68, 95.64, 94.83, 61.35, 57.22, 56.34, 56.26, 14.51. FAB/MS *m/z* 527.206 [M + H] (expected *m/z* =527.20).

#### Synthesis of Compound 6

According to general procedure 5, compound 5 (5.4 g, 10.3 mmol) was treated with  $LiAlH_4$  (0.78 g, 20.6 mmol) to afford



compound **6** (4.8 g, 96%) as white solid. The product was eluted with ethyl acetate/hexane (25:75 v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.88 (s, 4H), 5.19 (s, 2H), 5.18(s, 4H), 5.08 (s, 4H), 4.69–4.67 (d, *J* = 6.10 Hz, 2H), 3.66 (s, 3H), 3.48 (s, 6H), 3.38 (s, 6H), 1.77 (t, *J* = 6.10 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.43, 150.45, 142.23, 135.56, 130.03, 120.85, 113.57, 107.47, 98.69, 95.65, 94.81, 65.45, 57.21, 56.24. FAB/MS *m/z* 485.192 [M + H]<sup>+</sup> (expected *m/z* = 485.19).

#### Synthesis of Compound 7

According to general procedure 6, compound **6** (4.3 g, 9.0 mmol) were treated with PCC (2.3 g, 10.7 mmol) to afford compound 7 (4.2 g, 98%) as light yellow solid. The product was eluted with ethyl acetate/hexane (25:75 v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.94 (s, 1H) 7.38 (s, 2H), 6.89 (s, 2H), 5.21 (s, 2H), 5.19 (s, 4H), 5.14 (s, 4H), 3.67 (s, 3H), 3.49 (s, 6H), 3.40 (s, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 191.59, 155.83, 150.62, 136.93, 136.00, 129.06, 127.60, 113.08, 109.86, 98.66, 95.63, 94.78, 57.23, 56.36, 56.26. FAB/MS *m*/*z* 483.178 [M + H]<sup>+</sup> (expected *m*/*z* = 483.17).

#### Synthesis of Compound 8

According to general procedure 7, compound 7 (4.2 g, 8.7 mmol) was treated with DOWEX resin to afford 0.9 g (40%) of the crude penta hydroxy biaryl aldehyde. The hydroxyl groups were further protected with Boc according to general procedure 8 to obtain compound **8** (2.5 g, 95%) as white solid. The product was eluted with ethyl acetate/hexane (10:90 v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.98 (s, 1H), 7.65 (s, 2H), 7.18 (s, 2H), 1.54–1.53 (m, 27H), 1.35 (s, 18H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 189.79, 150.79, 149.98, 149.93, 149.03, 143.76, 137.20, 135.53, 133.65, 128.35, 122.09, 121.38, 84.81, 84.03, 83.95, 27.72, 27.37.

# Synthesis of Biaryl (penta Boc) Monomer 9

According to general procedure 9, compound **8** (2.5 g, 3.3 mmol) was reacted with MePPh<sub>3</sub>Br (1.8 g, 5.0 mmol) and K0<sup>t</sup>Bu (0.6 g, 5.0 mmol) to afford compound **9** (1.7 g, 68%) as white solid. The product was eluted with ethyl acetate/ hexane (8:92 v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.17 (s, 2H), 7.15 (s, 2H), 6.70–6.62 (dd, 17.56, 10.92 Hz, 1H), 5.80–5.75 (d, 17.56 Hz, 1H), 5.36–5.33 (d, 10.92 Hz, 1H), 1.54–1.52 (m, 27H), 1.35–1.33 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 151.14, 150.03, 149.27, 149.11, 143.57, 139.45, 135.09, 135.00, 129.40, 126.73, 122.33, 118.13, 116.36, 84.18, 83.84, 83.75, 27.74, 27.41.

# Synthesis of Biaryl Polymers General Procedures for Polymer Syntheses

All the Boc-protected biaryl monomers were polymerized via free radical polymerization with AIBN as the initiator. The Boc groups were then deprotected using trifluoroacetic acid (TFA) to obtain the corresponding biaryl phenolic polymers. The synthetic scheme for the synthesis of polybiaryl (penta OH) is shown in Scheme 2.

### Procedure 10 for Polymerization

A solution of the appropriate Boc-protected biaryl monomer in anhydrous THF was taken in a 10-mL oven-dried Schlenk flask under argon at RT. AIBN was added and the Schlenk flask was sealed and subjected to three freeze-pump-thaw cycles. The reaction mixture was stirred at RT for 5 min and the Schlenk flask was then transferred to an oil bath preheated to 70 °C. After the polymerization was complete, the polymer was diluted with THF and precipitated twice into large excess of hexane. The white precipitate was filtered, and was washed with either isopropanol or methanol to get rid of the residual monomer. The white powder obtained was dried under vacuum at 40 °C for 24 h to obtain the final polymers as white solids.

### Procedure 11 for the Deprotection of Boc Groups Using TFA

The Boc protecting groups were deprotected following a reported procedure.<sup>13</sup> The appropriate Boc-protected biaryl polymer was taken in 5 mL DCM at RT under argon and 5 mL TFA was added to it. The clear solution obtained was stirred at RT for 30 min, during which the solution initially turned turbid and finally a precipitate was obtained. An additional 10-mL DCM was added, and the solution was centrifuged. The precipitate obtained was washed thrice with excess DCM and was dried under vacuum at 40 °C for 24 h to obtain the corresponding biaryl phenolic polymer.

#### Polybiaryl (penta Boc)

According to general procedure 10, monomer **9** (1.35 g, 1.778 mmol) was reacted with AIBN (2.93 mg, 0.018 mmol) in THF (4.0 mL) for 7 h. The white precipitate was washed with excess isopropanol to obtain the polymer (0.85 g, 63%) as a white solid. Gel permeation chromatography (GPC) (THF) \*\*\* $M_n$ : 37,000 g/mol; PDI: 1.56. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.06 (s, 2H, ArH), 6.62 (br, 2H, ArH), 2.34 (br, 1H, --CH of polymer backbone), 1.44–1.23 (m, 47H, O--C(CH<sub>3</sub>)<sub>3</sub>, and --CH<sub>2</sub> of polymer backbone).





FIGURE 2 GPC (THF) chromatograms of Boc protected polymers.



FIGURE 3 FTIR spectra of biaryl polymers.

#### Polybiaryl (penta OH)

According to general procedure 11, polybiaryl (penta Boc) (0.77 g, 1.013 mmol) was reacted with TFA/DCM (1:1 v/v) to obtain the polybiaryl (penta OH) (0.25 g, 95%) as a dark brown solid. <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$ : 8.53–7.93 (bd, 5H, —OH), 6.25–5.95 (bd, 4H, ArH), 2.2–0.8 (bs, 3H, —CH and —CH<sub>2</sub> of polymer backbone).

# **Characterization**

Molecular weights and the molecular weight distributions of the Boc protected biaryl polymers were determined by GPC using THF as eluent and toluene as internal reference. The molecular weights of biaryl hydroxy polymers (after Boc deprotection) were estimated based on the complete deprotection of Boc groups, which was confirmed by both <sup>1</sup>H NMR and FT-IR. Thermal properties of the biaryl hydroxy polymers were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Glass transition temperature ( $T_g$ ) of the polymers were obtained by DSC using TA instruments Dupont DSC 2910. The proton conductivity of biaryl hydroxy polymers was measured using electrochemical impedance spectroscopy under anhydrous conditions (see supporting information for details).

#### **RESULTS AND DISCUSSION**

#### Synthesis and Characterization

Boc protected biaryl monomers were obtained by coupling the appropriately functionalized top and bottom phenyl rings via Stille coupling reaction, followed by subsequent reduction, oxidation, deprotection, and protection steps. The synthetic scheme for the biaryl (penta Boc) monomer **9** is shown in Scheme 1. The synthetic schemes for the other monomers are shown in ESI. The monomers were polymerized via free radical polymerization with AIBN as the initiator (Scheme 2 and ESI). Monomer:AIBN ratio and the solvent were optimized to obtain control over the polymerization reaction. The synthesis and characterization of polystyrene (tri OH) are described in our previous report.<sup>13</sup>

GPC chromatograms of the Boc-protected biaryl and styrene polymers are shown in Figure 2. All polymers exhibit unimodal distribution. The Boc groups were further deprotected using TFA/DCM to obtain the corresponding biaryl hydroxy polymers. The polymers were obtained in good yield and the complete deprotection of Boc groups was confirmed by <sup>1</sup>H NMR based on the disappearance of the signal corresponding to the tert-butyl unit. The polymers were also characterized by FTIR spectroscopy (Fig. 3). Polybiaryl (penta Boc) and polybiaryl (tri Boc) polymers exhibit a peak at  $\sim 1750~{
m cm}^{-1}$ , characteristic of the C=O stretch of Boc protecting groups. The peak at 1750 cm<sup>-1</sup> hascompletely disappeared in polybiaryl (penta OH) and polybiaryl (tri OH) polymers, confirming the complete deprotection of Boc protecting groups. These polymers also exhibit a broad band at around 3000-3600 cm<sup>-1</sup>, with a maximum at  $\sim$  3400 cm<sup>-1</sup>, characteristic of hydrogen bonded O-H stretch. The molecular weight details of the polymers are summarized in Table 1.

**TABLE 1** Polymer Details, Thermal Stability ( $T_{d,5\%}$ , Under Nitrogen), Thermo-Oxidative Stability ( $T_{d,5\%}$ , Under Air), and Glass Transition Temperature ( $T_g$ ) of Biaryl Polymers

Polymer	<i>M</i> <sub>n</sub> <sup>a</sup> (g/mol)	PDI	Polymer	M <sub>n</sub> <sup>b</sup> (g/mol)	<i>T</i> <sub>d,5%</sub> <sup>c</sup> (°C)	<i>T</i> <sub>d,5%</sub> <sup>d</sup> (°C)	<i>T</i> <sub>g</sub> <sup>e</sup> (°C)
Polybiaryl (penta Boc)	37,000	1.56	Polybiaryl (penta OH)	12,500	347	223	309
Polybiaryl (tri Boc)	11,600	1.71	Polybiaryl (tri OH)	5,000	318	248	217
Polystyrene (tri Boc)	60,000	1.5	Polystyrene (tri OH)	20,000	265	267	233

<sup>a</sup> Estimated by GPC (THF) using PS standards.

 $^{\rm b}$  Estimated based on the complete deprotection of Boc groups, which was confirmed by both  $^1{\rm HNMR}$  and FT-IR (Fig. 3).

 $^{\rm c}$  Temperature at 5% weight loss when heated under nitrogen at 10  $^{\circ}\text{C}/$  min.



FIGURE 4 (a) Proton conductivity and (b) normalized proton conductivity of biaryl and styrenic polymers under anhydrous conditions.

#### **Thermal Analyses**

Since proton conductivity measurements were carried out under variable temperature conditions, and the conductivity could be affected by the glass transition temperature ( $T_{\rm g}$ ) of the polymers, it is necessary that we investigate the thermal properties of these polymers. The thermal stability of polymers was determined by TGA under nitrogen atmosphere. Since phenol based polymers are susceptible to oxidation, the polymers were also analyzed for thermo-oxidative stability, that is, the thermal stability of polymers was examined under air atmosphere. The thermal and thermo-oxidative stabilities of polymers are shown in Table 1 and Supporting Information Figure S4. The decomposition temperatures are reported at 5% weight loss. All polymers were found to be stable up to atleast 220 °C both under nitrogen and air atmosphere.

The glass transition temperature  $(T_g)$  of polymers was determined by DSC and is shown in Table 1 and Supporting Information Figure S5. The glass transition temperature steadily increases with increasing number of —OH groups. This is expected because the hydrogen bonding interactions among hydroxyl groups along the polymer chains would increase with increasing number of —OH groups, leading to increased polymer chain interactions and hence the  $T_g$ . Polybiaryl (penta OH) with maximum number of —OH moieties exhibits the highest  $T_g$  of 309 °C. Although polybiaryl (tri OH) and Polystyrene (tri OH) have same number of —OH groups, the former exhibits slightly lower  $T_g$  compared with the later one. This might be due to the lower molecular weight of polybiaryl (tri OH) since  $T_g$  is known to be dependent on the molecular weight of polymers.<sup>18</sup> Also, since the polymers are not crosslinked, the thin films of all these polymers are in general brittle. The thin films of polybiaryl (penta OH) and polybiaryl (tri OH) are comparatively more brittle than those of polystyrene (tri OH). This could be, in part, due to the low molecular weight of biaryl polymers.

# **Proton Conductivity**

The proton conductivity of biaryl hydroxy polymers is shown in Figure 4(a). In general, bulk proton conductivity is known to be influenced by several factors, especially the nature of the PT moiety (for e.g., imidazole, triazole, phenol etc.), variations in the polymer architecture,  $T_g$  of polymers, and charge carrier density (density of proton transporting moieties).<sup>4,5,9,19,20</sup> Since —OH is the proton-transporting moiety in all the polymers, the effect of the nature of PT moiety can be neglected. The weight fraction of —OH groups contained in each polymer was calculated by dividing the product of the equivalent weight of —OH unit (17 g/mol) and the

**TABLE 2** Charge Carrier Density, Apparent Activation Energy ( $E_a$ ), and Glass Transition Temperature ( $T_g$ ) of Phenolic Polymers

Polymer	Weight Fraction of –OH Units	Log [σ (Scm <sup>-1</sup> )] at 140 °C	E <sub>a</sub> ∕kJ mol <sup>−1</sup>	<i>T</i> g (°C)
Polybiaryl (penta OH)	32	-6.4	77	309
Polybiaryl (tri OH)	22	-7.6	74	217
Polystyrene (tri OH)	33	-4.5	94	233





Polybiaryl (tetra OH)

Polybiaryl (di OH)

Polystyrene (di OH)

CHART 2 Structures of biaryl and styrenic hydroxy polymers.

number of —OH units per polymer repeat unit by the equivalent weight of the polymer repeat unit. The charge carrier density for each polymer is shown in Table 2.

Unlike *N*-heterocycle-based proton conducting polymers, the proton conductivity ( $\sigma$ ) in phenol-based polymers as a function of temperature follow an Arrhenius-type behavior over the entire temperature range investigated here. The proton conductivity can be described by equation  $\sigma = \sigma_0 \exp(-E_a/RT)$  (eq 1), where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the apparent activation energy, R is a universal gas constant, and T is the temperature in Kelvin. The conductivity plots were fitted by Arrhenius eq 1 and the activation energies ( $E_a$ ) were computed from the slope of the linear fit of log ( $\sigma$ ) versus 1/T and are shown in Table 2.

Polybiaryl (penta OH) and polybiaryl (tri OH) have similar polymer architecture. In addition, both polymers also present similar  $E_a$  values of 74–77 kJ/mol. Thus, the PT is equally feasible in both these polymers. Nonetheless, polybiaryl (tri OH) exhibits poor proton conducting ability, and its proton conductivity is lower by an order of magnitude compared with polybiaryl (penta OH). This might be due to the lack of —OH groups in one of the biaryl rings of polybiaryl (tri OH), resulting in lower weight fraction of the proton conducting —OH moieties. The reduced proton carrier density might impede —OH groups from forming continuous hydrogen bond pathway, thereby adversely affecting the overall PT.

Polybiaryl (penta OH) and polystyrene (tri OH) have similar —OH weight fractions. The  $E_a$  for proton transfer in polybiaryl (penta OH) is 17 kJ/mol lower than that in polystyrene (tri OH). Thus, the proton transfer in polybiaryl (penta OH) is more facilitated compared with polystyrene (tri OH). Although polybiaryl (penta OH) presents lower  $E_a$  for proton transfer, it is surprising that its net proton conductivity is almost two orders of magnitude lower than that of polystyrene (tri OH) over the entire temperature range. This might be, in part, due to the variations in polymer architecture and/or the differences in  $T_g$  values of polymers.

To eliminate the effect of  $T_{\rm g}$  on proton conductivity, log ( $\sigma$ ) is plotted against reduced temperature. Reduced temperature is defined as  $[(T-T_g)/T_g]$ , where all temperatures are considered in Kelvin, and the term is known to take into account the differences in  $T_{\rm g}$  values of polymers. The normalized conductivity versus reduced temperature plot is shown in Figure 4(b). Considering that polybiaryl (penta OH) and polystyrene (triOH) have similar proton carrier densities, the differences in their proton conductivities in log ( $\sigma$ ) versus reduced temperature plots can now be solely ascribed to the variations in biaryl versus styrenic polymer architectures. The normalized proton conductivities of polybiaryl (penta OH) and polystyrene (triOH) converge with each other with the difference being less than an order magnitude over the entire temperature range. Thus, the difference in conductivity can be attributed to the difference in the  $T_{\rm g}$  of the polymers, and the biaryl architecture does not seem to provide any inherent advantages for proton conductivity.

To further confirm this, we also synthesized another set of polymers shown in Chart 2 and investigated their thermal and proton conducting properties. polybiaryl (tetra OH) and

**TABLE 3** Polymer Details, Thermal Stability ( $T_{d,5\%}$ , Under Nitrogen), Thermo-Oxidative Stability ( $T_{d,5\%}$ , Under Air), and Glass Transition Temperature ( $T_g$ ) of Biaryl Polymers

Polymer	<i>M</i> <sub>n</sub> <sup>a</sup> (g/mol)	PDI	Polymer	M <sub>n</sub> <sup>b</sup> (g/mol)	<i>T</i> d,5% <sup>c</sup> (°C)	<i>T</i> <sub>d,5%</sub> <sup>d</sup> (°C)	<i>T</i> <sub>g</sub> <sup>e</sup> (°C)
Polybiaryl (tetra Boc)	37,000	1.6	Polybiaryl (tetra OH)	14,000	364	274	294
Polybiaryl (di Boc)	15,000	1.8	Polybiaryl (di OH)	7600	339	287	216
Polystyrene (di Boc)	64,000	1.4	Polystyrene (di OH)	25,000	258	239	227

<sup>a</sup> Estimated by GPC (THF) using PS standards.

<sup>b</sup> Estimated based on the complete deprotection of Boc groups, which was confirmed by both <sup>1</sup>HNMR and FT-IR (Fig. S3).

 $^{\rm c}$  Temperature at 5% weight loss when heated under nitrogen at 10  $^{\circ}\text{C}/$  min.



FIGURE 5 (a) Proton conductivity and (b) normalized proton conductivity of biaryl and styrenic hydroxy polymers under anhydrous conditions.

polybiaryl (di OH) polymers were synthesized following similar synthetic protocols described for polybiaryl (penta OH) and polybiaryl (tri OH), respectively. The synthetic details are described in detail in ESI. The synthesis, thermal analysis, and proton conducting properties of polystyrene (di OH) are described in our previous report.<sup>13</sup> The polymer details and thermal properties are shown in Table 3 and Supporting Information Figures S2, S3, S4, and S5. All polymers are stable up to atleast 230 °C. Polybiaryl (tetra OH) with the maximum number of —OH moieties exhibits the highest  $T_{\rm g}$  of 294 °C.

The conductivity and normalized conductivity plots are shown in Figure 5(a,b), respectively. It can be seen from Figure 5(a) that the proton conductivity of polybiaryl (tetra OH) is slightly lower than that of polystyrene (di OH) in the higher temperature range and the difference is less than an order of magnitude over the entire temperature range. On the other hand, the normalized proton conductivity of polybiaryl (tetra OH) is about 1-2 orders of magnitude higher compared with polystyrene (di OH). Since polybiaryl (tetra OH) and polybiaryl (di OH) have similar charge carrier densities (27 and 25, respectively), the differences in their normalized proton conductivities can be ascribed to the variations in polymer architecture. Thus, given a constant charge carrier density and similar  $T_g$  values, the biaryl architecture might prove advantageous over the linear styrenic polymers, especially in the lower temperature range. Nevertheless, considering that the placement of hydroxyl groups in both rings of the biaryl hydroxy polymers is always accompanied by a corresponding increase in  $T_{g}$ , the advantage of the biaryl architecture, if any, on the net proton conductivity is not substantial. Thus, the orthogonal placement of proton transporting functional groups that could promote both intra and interchain hydrogen bonding seem to lower the activation energies, but is complicated by the fact that the glass transition temperature of the polymers significantly increases.

# CONCLUSIONS

A series of biaryl hydroxy polymers with varying number of hydroxyl groups have been successfully synthesized and characterized. The biaryl architecture is observed to enhance the thermal stability of phenol-based polymers. Incorporation of proton transporting -OH moieties on both phenyl rings of the biaryl scaffold increases the  $T_{g}$  of biaryl polymers. The proton conductivities of the biaryl and styrenic polymers are compared to elucidate the role of orthogonal disposition of PT -OH moieties in biaryl architecture on net PT. The orthogonal disposition of -OH moieties in biaryl polymers does provide low  $E_{\rm a}$  for PT compared with the linear styrenic hydroxy polymers. However, this did not afford a net increase in the proton conductivity, compared with the styrenic polymers over the temperature range investigated here. This is attributed to the observed increase in  $T_{g}$  since the normalized proton conductivities of polybiaryl (penta OH) and polybiaryl (tetra OH) are either comparable or slightly higher than that of the corresponding styrenic polymers. From a practical materials perspective, the proton conductivities of the phenol-based polymers are lower than Nafion.<sup>21</sup> However, phenols are indeed useful model systems for pKa-independent design strategies for PT polymers. We are encouraged by the fact that the functional group placement strategy does provide lower activation energy. The remaining challenge, though, is to design polymers where the glass transition temperature does not change when incorporating such functional group placements. Addressing this challenge should be the focus of further work in this area. The two-dimensional disposition of



PT functionalities could also be achieved by using block copolymers that provide hexagonal cylindrical selfassembled nanostructures with the PT moieties constituting the hexagonal cylinder. Moreover, block copolymers also provide an opportunity to fine tune the glass transition temperature by varying the nonconducting block without adversely affecting the PT characteristics.

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