Structurally-Defined, Sulfo-Phenylated, Oligophenylenes and Polyphenylenes

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S *Supporting Information*

ABSTRACT: We report the synthesis and molecular characterization of structurally defined, sulfo-phenylated, oligo- and polyphenylenes that incorporate a novel tetra-sulfonic acid bistetracyclone monomer. The utility of this monomer in the [4 + 2] Diels—Alder cycloaddition to produce well-defined, sulfonated oligophenylenes and pre-functionalized polyphenylene homopolymers is demonstrated. Characterization of the oligophenylenes indicates formation of the meta—meta and para—para adducts in a ∼ 1:1 ratio. These functionalized monomers and their subsequent coupling provide a route to prepare novel, sterically encumbered, sulfonated polyphenylenes possessing unprecedented structural control.

In the past, methods to synthesize polyphenylenes,[1] such as those reported by Stille[1f,k—m] and Müllen,[1e,i,j] have drawn attention due to the polymer's inherent chemical stability and mechanical strength. Of more recent interest are routes to branched polyphenylenes bearing ionic functionality. Sulfonated versions of branched polyphenylenes are currently prepared by post-sulfonation of polyphenylenes, for the purpose of preparing polymers for electrochemical membranes.[2] Such membranes are reported to be mechanically robust and to possess high ionic (protonic) conductivity. Recently, they have been examined for use in proton exchange membrane fuel cells (PEMFCs), and post-quaternized ammonium derivatives have been examined in anionic exchange membrane fuel cells (AEMFCs).[2c,3]

Nonetheless, reports of sulfonated polyphenylenes are comparatively sparse because of the difficulty of forming rigid, sterically encumbered, aryl—aryl linkages and the need to manipulate near-intractable polymers in polar media for the purpose of later introducing ionic functionality. Moreover, current examples of sulfonated polyphenylenes are structurally ill-defined and relatively disorganized due to the uncertainty of meta- vs para-coupling of the phenyl linkages as well as the multitude of positions available, on multiple phenyl rings, for post-sulfonation.[2b] As consistently demonstrated for acid-bearing polymers, precise control of the polymer structure and accurate placement of ionic functionality along the polymer backbone enhances short and long-range order of ionic channels and thus ionic conductivity.[1c,4] Ding et al. demonstrated this with block and graft copolymers of sulfonated polystyrene.[5] Numerous examples have since been reported for many, primarily aromatic-based classes of ion-containing polymers.[1c,4b,d,6] A high degree of molecular control

is primarily achieved by spatially controlling the placement of sulfonic acid groups on the polymer, but such control is difficult, if not impossible, to achieve by post-sulfonation of polyphenylenes. To this end, we have explored strategies (Scheme 1) leading to the controlled synthesis of novel

Scheme 1. Synthesis of Sulfo-Phenylated Dienes and Polyphenylene Homopolymer[a]
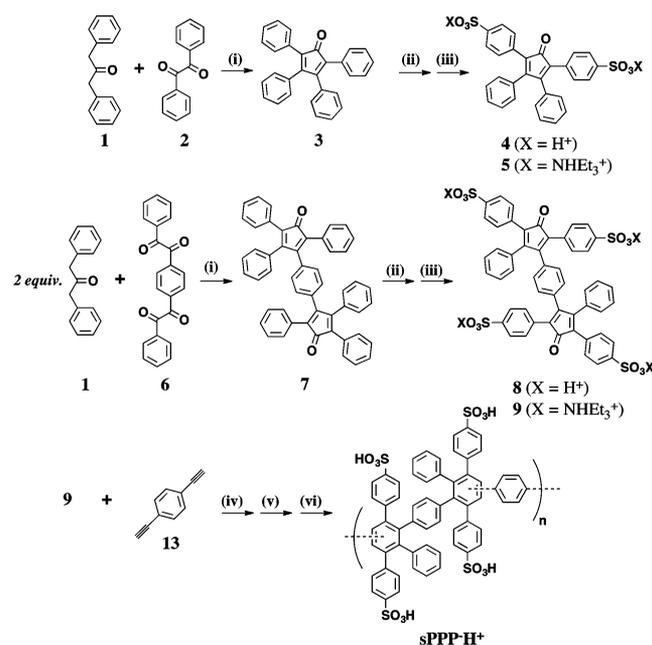
[a](i) KOH/EtOH, reflux; (ii) Me₃SiOSO₂Cl, 1,2-C₂H₄Cl₂; (iii) NEt₃, n-BuOH; (iv) PhNO₂: sand bath (180 °C, 12 h) or microwave reactor (195 °C, 2 h) (v) 2 M KOH; (vi) 0.5 M H₂SO₄.

sulfonated monomers and demonstrated their utility in synthesizing sulfonated, branched oligophenylenes as well as the homopolymer (**sPPP-H⁺**), with precise control of the position and number of sulfonic acid groups.

Sulfonated dienes were prepared as shown in Scheme 1. The tetracyclone **3**[1g,7] was sulfonated using trimethylsilyl chlorosulfonate to produce the novel disulfonic acid tetracyclone **4**. The ¹H NMR spectrum of **4** (Figure S5) reveals a symmetrical structure, containing one doublet (integration 4 H) at 7.46 ppm. Using COSY (Figure S7), this doublet correlates with the

doublet at 7.11 ppm (4 H). These two doublets indicate disulfonation of **3** at the para position of the two phenylene rings juxtaposed to the ketone.[8] Sulfonation occurs at these positions due to delocalization of the electronic charge introduced by the ketone.[9] The remaining 10 protons are observed as doublets at 6.95 and 7.22−7.29 ppm for the unsulfonated phenylenes as well as the multiplet between 7.22 and 7.29 ppm and 6.95 ppm for the unsulfonated phenylene.[10] The acidic protons in **4** were exchanged for triethylammonium cations by treatment with triethylamine to produce **5**.

The symmetrical, tetrasulfonated monomer **8** was synthesized in a similar fashion to **4**. ^{1}H NMR analysis of **8** (Figure S15) reveals two doublets at low field (7.55 and 7.50 ppm). Using COSY (Figure S17), these protons correlate with doublets at 7.10 and 7.16 ppm, which is consistent with *p*-substitution of the phenyl ring adjacent to the ketone. The signal for the acidic proton appears at 7.57 ppm. ^{1}H NMR analysis indicates that **8** is symmetrical, with H_{core} represented by a singlet peak at 6.87 ppm. COSY and the 1D NOE analysis (Figure S19) were used to distinguish whether all four of the sulfonic acid groups are distant to one another ("**H**" conformation) or whether two are in close proximity ("**A**" conformation) (Figure S18). The $H\alpha_1$ and $H\beta_1$ protons (7.55 and 7.10 ppm, respectively) exhibit no through space correlation with protons (H_o, H_m, and H_p) on the unsulfonated phenyl rings, whereas $H\alpha_2$ and $H\beta_2$ (7.51 and 7.17 ppm respectively) do, indicating **8** exclusively adopts the "**A**" conformation in solution.

Compound **8** was converted to the ammonium derivative **9** for greater thermal stability, prior to Diels−Alder (D-A) coupling. ^{1}H NMR analysis of **9** revealed additional signals resulting from the Et_3NH^+:HN^+ (8.88 ppm); −CH_2− (two overlapping quadruplets at 3.09 and 3.10 ppm); and −CH_3 (1.16 ppm).

The synthesis of bis-dienophile **13** is described in the Supporting Information. Oligomers **14** and **16** were synthesized (Scheme S1) to investigate the mode of D-A coupling of comonomers **9** and **13**. Compound **14** was obtained by D-A cycloaddition of dienophile **13** and 2 molar equiv of **5**. As shown in Figure S30, the D-A proton (H_{DA}) originates from the terminal alkyne of **13**, $H\alpha_1$ and $H\beta_1$ are, respectively, protons ortho and meta to the sulfonic acid group of the phenyl ring adjacent to H_{DA}, while $H\alpha_2$ and $H\beta_2$ are the analogous protons located on the other sulfonated phenyl ring. The ^{1}H NMR spectrum of **14** (Figure S28) reveals the presence of H_{DA} at 7.38 ppm and H_{core} of the central phenyl ring at 6.93 ppm. As for the peripheral phenyl rings, the protons on the sulfonated rings reflect the different chemical environments with signals at 7.36 ppm ($H\alpha_1$) and 7.23 ppm ($H\alpha_2$) correlated (Figure S30) with the peaks at 7.14 ($H\beta_1$) and 6.77 ($H\beta_2$) ppm, respectively. The signals corresponding to the unsulfonated phenyl rings are observed between 6.96 and 6.83 ppm. The possibility of conformational isomers was investigated using 1D NOE (Figure S31). Irradiation of H_{DA} at 7.38 ppm reveals the proximity of H_{core} at 6.88 ppm (single peak) as well as $H\beta_1$ at 7.11 ppm. By irradiating $H\beta_1$ at 7.11 ppm, the proximity of H_{core} and H_{DA} is also confirmed. Irradiation of $H\beta_1$, however, does not indicate the relative proximity of H_{DA}, but a correlation does exist with the unsulfonated phenylene (6.88 ppm, one peak) and H_{core} (two peaks). This suggests that compound **14** also adopts the "**A**" conformation in solution.

Compound **16** was synthesized by D-A cycloaddition of **9** with **15**. Protons in **16** originating from the phenyl ring of **15**

are observed at 7.00, 6.68, and 6.62 ppm (Figure S32). According to the literature,[1j,k,m] this reaction does not afford a pure isomer as both meta and para additions can occur as shown in Scheme S10. As a result, three regio-isomers for **16** are evidenced by three main NMR signals at 6.41, 6.31, and 6.14 ppm for H_{core}, which correspond to the para−para (p−p), meta−meta (m−m), and meta−para (m−p) isomers, respectively. Signals at 7.28 ppm are attributed to H_{DA} protons, according to the lack of correlation on the COSY with other protons of the molecule (Figure S33). The spectrum for compound **16** also shows signals at 7.23 and 7.11 ppm due to $H\alpha_1$, 6.57 and 6.77 ppm due to $H\beta_1$, 7.55 and 7.46 ppm due to $H\alpha_2$, and 6.93 and 6.85 ppm due $H\beta_2$. COSY was used to establish the pairing of $H\alpha_1$ with $H\beta_1$, as well as $H\alpha_2$ with $H\beta_2$, wherein the downfield shift of the $H\alpha$ proton correlates with the upfield shift of the $H\beta$ proton (e.g., the peaks at 7.23 and 6.57 correlate) with a similar situation for the downfield pairs (e.g., the peaks at 7.46 and 6.85 ppm correlate). We have interpreted this to mean that **16** consists of a mixture of "**H**" and "**A**" conformers, in contrast to the almost exclusive formation of the "**A**" conformer for **14**. For each conformer, a set of three regio-isomers can be formed, and thus, a total of six peaks, corresponding to the H_{core} protons of the three regio-isomers of each conformer, are observed between 6.00 and 6.50 ppm (Figure S32).

The protected sulfonated poly(phenylene), **sPPP-NHEt$_3^+$** (Scheme S12), was synthesized via the [4 + 2] D-A cycloaddition of comonomers **9** and **13**. GPC analysis indicated a M_n of 186 000 Da and a polydispersity index of 1.44. ^{1}H NMR analysis of **sPPP-NHEt$_3^+$** (Figure S35) revealed methyl groups of **NHEt$_3^+$** at 1.12 ppm (36 H), which were subsequently used as an internal reference for quantification of the remaining protons. The methylene protons (24 H) are represented as two overlapping quadruplets at 3.05 ppm, and the ammonium protons (4 H) are found at 8.92 ppm. Signals for the protons of the polymer backbone are observed in the region between 5.90 and 7.60 ppm. The integration ratio between the methyl from the NHEt$_3^+$ salt for one unit and the polymer backbone is observed to be 1:1, proving that the sulfonate group in the salt form remains intact during the D-A reaction. As with the model compounds, the polymer shows evidence for regio-isomers: signals for H_{core} are found for the m−m (6.32 ppm), p−p (6.17 ppm), and m−p (5.98 ppm) isomers. Integration of these peaks yields an isomeric composition of 42%, 40%, and 18%, respectively (Figure S36).

The effect of regio-isomerization is also observed for the H_{DA} protons, whereby they can be either para (H_{DA1}) or meta (H_{DA2}) to the central phenyl ring (i.e., H_{core}), as shown in Figure S35 (between 7.60 and 7.45 ppm). However, the H_{DA} protons are observed as a broad peak in the vicinity of 7.23 ppm due to their low intensity as well as being partially obscured by $H\alpha_1$ situated at 7.43 ppm (assigned by COSY analysis and from **14** and **16**). Model compound **16** shows a signal for $H\alpha_1$ at 7.43 ppm, according to a COSY analysis (Figure S33), but according to a COSY analysis of **sPPP-NHEt$_3^+$** (Figure S37), the peak at 7.22 ppm does not correlate with any of the other peaks, hence our assignment of this signal to H_{DA} of the polymer. Protons on the sulfonated phenyl rings meta and para to the core phenyl ring appear at 7.43 ($H\alpha_2$) and 7.18 ($H\alpha_1$) ppm which, by COSY analysis, are shown to correlate with 6.82 ($H\beta_2$) and 6.64 ($H\beta_1$) ppm, respectively. The protons on the unsulfonated, outer phenyl rings, namely

H_o, H_m, and H_p, have signals at 7.34, 6.53, and 7.02 ppm, respectively.

Following conversion of **sPPP-NHEt$_3$$^+$** to **sPPP-H$^+$**, films were cast from DMSO. The ion exchange capacity (IEC) was determined by acid−base titration to be 3.47 mequiv g^{-1}, close to the theoretical value of 3.70 mequiv g^{-1}. This is a very high IEC value for an aromatic polymer, and yet the polymer was found to be insoluble and free-standing in water at room temperature (Figure S41) (water content, 85 wt %). For comparison, a previously reported, postsulfonated polyphenylene, possessing an average of four sulfonic acid groups per repeat unit and an IEC of 2.2 mequiv g^{-1}, formed a hydrogel in water.[2b] **sPPP-H$^+$** membranes dissolved when placed into Fenton's reagent,[11] but a subsequent ^{1}H NMR analysis (Figure S42) revealed no changes in chemical structure, suggesting an extraordinarily high oxidative stability.

The proton conductivity of **sPPP-H$^+$** (Figure S43) was studied at 30 °C on water-saturated samples and partially hydrated (30−95% RH) membranes. As is commonly observed for aromatic membranes, proton conductivity increases as a function of RH from a low of 8.65 mS cm^{-1} at 40% RH to 106 mS cm^{-1} at 95% RH. In contrast to most aromatic membranes, however, **sPPP-H$^+$** exhibits conductivity competitive to NR211 at low RH. The conductivity of **sPPP-H$^+$** is reduced when water-saturated (77 vs 106 mS cm^{-1} at 95% RH), which reflects the high water uptake of **sPPP-H$^+$** in contact with liquid water and a reduction of the analytical acid concentration, $[-SO_3H]$, 0.92 M for **sPPP-H$^+$** vs 1.55 M for N211.[4c,12]

We undertook preliminary studies of **sPPP-H$^+$** incorporated into cathode catalyst layers (CCL) of PEMFCs. A reasonable performance for aromatic ionomer was found for the **sPPP-H$^+$**-based CCL (at 90% RH) compared to those in which Nafion D520 was used in the CCL (Figure S44) (in both cases, N211 was used as the membrane). However, when the cathode inlet was reduced to 0% RH, not only does the **sPPP-H$^+$**-based CCL perform better than at 90% RH, it also outperforms Nafion-based CCLs by a significant margin, e.g., a current density of 3000 mA cm^{-2} can be extracted for a **sPPP-H$^+$**-based CCL, whereas only 800 mA cm^{-2} can be achieved for Nafion-based CCLs. Calculation of in situ membrane conductivity (using eq S6 and the iR drop in the Ohmic region) (Figure S45) reveals that **sPPP-H$^+$** increases the in situ conductivity of the membrane by 4−6 times.

A preliminary FC analysis of **sPPP-H$^+$** as membrane and ionomer (Figure S46) indicates that **sPPP-H$^+$** gave a lower performance compared to N212, but this is due to its possessing a 3 times greater thickness, as an in situ membrane conductivity calculation (Figure S47) revealed that **sPPP-H$^+$** is 6 times higher than NR212 under the FC conditions operated. The results are unprecedented for an aromatic membrane, particularly for a fully aromatic-based MEA, in an operating fuel cell, and suggest that thinner **sPPP-H$^+$** membranes would provide competitive, if not greater, performance than Nafion.[13]

In summary, through the synthesis of a novel sulfonated diene, **9**, we have accessed well-defined, sulfonated oligophenylenes and a polyphenylene homopolymer. The stereochemistry of the phenyl−phenyl linkages formed was elucidated using model compounds to be a mixture of m−m, p−p, and m−p in a ratio of 42:40:18 for the homopolymer. **sPPP-H$^+$** was found to be relatively stable to Fenton's reagent. Membranes possessed a high IEC, yet remained water-insoluble, and exhibited high proton conductivity. Preliminary studies of fuel cells incorporating **sPPP-H$^+$** are highly encouraging. Investigation of copolymer derivatives, with a view to controlling polymer morphology, limiting water sorption, enhancing proton conductivity, and strengthening the mechanical properties of thin films, are warranted.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07865.

　　Experimental procedures and characterization details (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1928**, *460*, 98. (b) Durand, J. F.; Hsun, L. W. *Comptes Rendus* **1930**, *191*, 1460. (c) Harrison, W. L.; Hickner, M. A.; Kim, Y. S.; McGrath, J. E. *Fuel Cells* **2005**, *5*, 201. (d) Haussler, M.; Lam, J. W. Y.; Zheng, R. H.; Peng, H.; Luo, J. D.; Chen, J. W.; Law, C. C. W.; Tang, B. Z. *C. R. Chim.* **2003**, *6*, 833. (e) Morgenroth, F.; Müllen, K. *Tetrahedron* **1997**, *53*, 15349. (f) Mukamal, H.; Harris, F. W.; Stille, J. K. *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2721. (g) Ried, W.; Freitag, D. *Chem. Ber.* **1960**, *93*, 1769. (h) Ried, W.; Freitag, D. *Naturwissenschaften* **1966**, *53*, 306. (i) Rusanov, A.; Shifrina, Z. B.; Bulycheva, E. G.; Keshtov, M. L.; Averina, M. S.; Fogel, Y. I.; Muellen, K.; Harris, F. W. *Macromol. Symp.* **2003**, *199*, 97. (j) Shifrina, Z. B.; Averina, M. S.; Rusanov, A. L.; Wanger, M.; Müllen, K. *Macromolecules* **2000**, *33*, 3525. (k) Stille, J. K.; Noren, G. K. *Macromolecules* **1972**, *5*, 49. (l) Stille, J. K.; Rakutis, R. O.; Mukamal, H.; Harris, F. W. *Macromolecules* **1968**, *1*, 431. (m) Vankerck, Hf; Stille, J. K.; Gilliams, Y. K. *Macromolecules* **1972**, *5*, 541.

(2) (a) Cherry, B. R.; Fujimoto, C. H.; Cornelius, C. J.; Alam, T. M. *Macromolecules* **2005**, *38*, 1201. (b) Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* **2005**, *38*, 5010. (c) Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromolecules* **2009**, *42*, 8316.

(3) (a) Hibbs, M.; Cornelius, C. J.; Fujimoto, C. H. Poly(phenylene)-based anion exchange membrane. US7888397, February 15, 2011. (b) Hibbs, M. R. Functionalization of poly(phenylene) by the attachment of sidechains. US8809483, August 19, 2014. (c) Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *ECS Trans.* **2009**, *19*, 89.

(4) (a) Elabd, Y. A.; Hickner, M. A. *Macromolecules* **2011**, *44*, 1. (b) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29. (c) Kreuer, K. D.; Paddison, S. J.; Spohr, E.; Schuster, M. *Chem. Rev.* **2004**, *104*, 4637. (d) Peckham, T. J.; Holdcroft, S. *Adv. Mater.* **2010**, *22*, 4667.

(5) Ding, J. F.; Chuy, C.; Holdcroft, S. *Chem. Mater.* **2001**, *13*, 2231.

(6) (a) He, L. L.; Fujimoto, C. H.; Cornelius, C. J.; Perahia, D. *Macromolecules* **2009**, *42*, 7084. (b) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587. (c) Miyahara, T.; Hayano, T.; Matsuno, S.; Watanabe, M.; Miyatake, K. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2881. (d) Ng, F.; Bae, B.; Miyatake, K.; Watanabe, M. *Chem. Commun.* **2011**, *47*, 8895. (e) Stanis,

R. J.; Yaklin, M. A.; Cornelius, C. J.; Takatera, T.; Umemoto, A.; Ambrosini, A.; Fujimoto, C. H. *J. Power Sources* **2010**, *195*, 104. (f) Atanasov, V.; Burger, M.; Lyonnard, S.; Porcar, L.; Kerres, J. *Solid State Ionics* **2013**, *252*, 75. (g) Cui, W.; Kerres, J.; Eigenberger, G. *Sep. Purif. Technol.* **1998**, *14*, 145. (h) Kerres, J.; Ullrich, A.; Hein, M.; Gogel, V.; Friedrich, K. A.; Jorissen, L. *Fuel Cells* **2004**, *4*, 105. (i) Kerres, J. A. *J. Membr. Sci.* **2001**, *185*, 3. (j) Kerres, J. A. *Polym. Rev.* **2015**, *55*, 273.

(7) Ogliaruso, M. A.; Shadoff, L. A.; Becker, E. I. *J. Org. Chem.* **1963**, *28*, 2725.

(8) Coan, S. B.; Trucker, D. E.; Becker, E. I. *J. Am. Chem. Soc.* **1953**, *75*, 900.

(9) (a) Daoust, D.; Devaux, J.; Godard, P. *Polym. Int.* **2001**, *50*, 925. (b) Koleva, G.; Galabov, B.; Kong, J.; Schaefer, H. F.; Schleyer, P. V. *J. Am. Chem. Soc.* **2011**, *133*, 19094.

(10) Additional evidence for $-SO_3H$ in **4** can be seen in Figure S8 with the presence of $-OH$, absent in **3** (Figure S4)

(11) Conditions of Fenton's test: 3 ppm $FeSO_4$, 3 wt% H_2O_2, 80 °C, 1 h.

(12) Peckham, T. J.; Schmeisser, J.; Rodgers, M.; Holdcroft, S. *J. Mater. Chem.* **2007**, *17*, 3255.

(13) Research aimed at fabricating reproducibly thinner membranes and composite membranes is under way.