Structurally-Defined, Sulfo-Phenylated, Oligophenylenes and Polyphenylenes

Thomas J. G. Skalski, Benjamin Britton, Timothy J. Peckham, and Steven Holdcroft*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

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, such as those reported by Stille and Müllen, 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. Sulfo-nated versions of branched polyphenylenes are currently prepared by post-sulfonation of polyphenylenes, for the purpose of preparing polymers for electrochemical membranes. 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).

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. Ding et al. demonstrated this with block and graft copolymers of sulfonated polystyrene. Numerous examples have since been reported for many, primarily aromatic-based classes of ion-containing polymers. 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 leading to the controlled synthesis of novel 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 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 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.

Scheme 1. Synthesis of Sulfo-Phenylated Dienes and Polyphenylene Homopolymer

![Scheme 1](image)

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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 phenylens 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. 13 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. 1H NMR analysis indicates that 8 is symmetrical, with Hcore 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 (“A” conformation) or whether two are in close proximity (“A” conformation) (Figure S18). The Hα1 and Hβ1 protons (7.55 and 7.10 ppm, respectively) exhibit no through space correlation with protons (Hα2, Hω2, and Hε2) on the unsulfonated phenyl rings, whereas Hε1 and Hβ2 (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. 13 H NMR analysis of 9 revealed additional signals resulting from the Et3NH+:HN+ (8.88 ppm); −CH2− (two overlapping quadruplets at 3.09 and 3.10 ppm); and −CH3 (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 diene 13 and 2 molar equiv of 5. As shown in Figure S30, the D-A proton (HDA) originates from the terminal alkyne of 13, Hα1 and Hβ1, are, respectively, protons ortho and meta to the sulfonic acid group of the phenyl ring adjacent to HDA while Hα2 and Hβ2 are the analogous protons located on the other sulfonated phenyl ring. The 1H NMR spectrum of 14 (Figure S28) reveals the presence of HDA at 7.38 ppm and Hcore 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 (Hα1) and 7.23 ppm (Hα2) correlated (Figure S30) with the peaks at 7.14 (Hβ1) and 6.77 (Hβ2) 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 HDA at 7.38 ppm reveals the proximity of Hcore at 6.88 ppm (single peak) as well as Hβ2 at 7.11 ppm. By irradiating Hβ1 at 7.11 ppm, the proximity of Hcore and HDA is also confirmed. Irradiation of Hβ1, however, does not indicate the relative proximity of HDA, but a correlation does exist with the unsulfonated phenylene (6.88 ppm, one peak) and Hcore (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,14 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 Hcore, 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 HDA 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 Hα1, 6.57 and 6.77 ppm due to Hβ1, 7.55 and 7.46 ppm due to Hα2, and 6.93 and 6.85 ppm due Hβ2. COSY was used to establish the pairing of Hα1 with Hβ1, as well as Hα2 with Hβ2, wherein the downfield shift of the Hα proton correlates with the upfield shift of the Hβ 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 Hcore 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-NHEt3+ (Scheme S12), was synthesized via the [4 + 2] D-A cycloaddition of comonomers 9 and 13. GPC analysis indicated a Mn of 186 000 Da and a polydispersity index of 1.44. 1H NMR analysis of sPPP-NHEt3+ (Figure S35) revealed methyl groups of NHEt3+ 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 NHEt3+ 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 Hcore 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 HDA protons, whereby they can be either para (HDA1) or meta (HDA2) to the central phenyl ring (i.e., Hcore), as shown in Figure S35 (between 7.60 and 7.45 ppm). However, the HDA 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 Hα1 situated at 7.43 ppm (assigned by COSY analysis and from 14 and 16). Model compound 16 shows a signal for Hα1 at 7.43 ppm, according to a COSY analysis (Figure S33), but according to a COSY analysis of sPPP-NHEt3+ (Figure S37), the peak at 7.22 ppm does not correlate with any of the other peaks, hence our assignment of this signal to HDA of the polymer. Protons on the sulfonated phenyl rings meta and para to the core phenyl ring appear at 7.43 (Hα2) and 7.18 (Hβ2) ppm which, by COSY analysis, are shown to correlate with 6.82 (Hβ2) and 6.64 (Hβ1) ppm, respectively. The protons on the unsulfonated, outer phenyl rings, namely...
H₂O, H₂SO₄, and H₂S have signals at 7.34, 6.53, and 7.02 ppm, respectively.

Following conversion of sPPP-NHEt₃⁺ 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, post sulfonated 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.²⁸ sPPP-H⁺ membranes dissolved when placed into Fenton’s reagent,¹¹ but a subsequent¹² 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, [−SO₃H⁻], 0.92 M for sPPP-H⁺ vs 1.55 M for NR211.⁶⁴,⁷¹

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 oligophenylene-nylenes 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)

## AUTHOR INFORMATION

### Corresponding Author

*holdcroft@sfu.ca

Notes

The authors declare no competing financial interest.

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## REFERENCES


(10) Additional evidence for $-\text{SO}_3\text{H}$ in 4 can be seen in Figure S8 with the presence of $-\text{OH}$, absent in 3 (Figure S4).

(11) Conditions of Fenton’s test: 3 ppm FeSO$_4$, 3 wt% H$_2$O$_2$, 80 °C, 1 h.


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