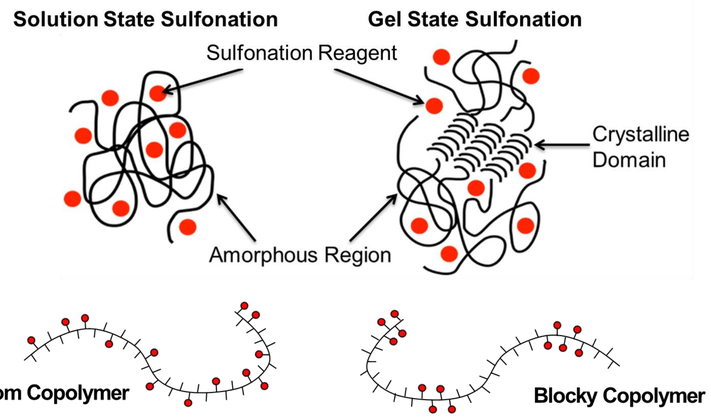
Generation and 2D NMR Analysis of Blocky Sulfonated PEEK With Multiple Sulfonations Per Sulfonated Monomer

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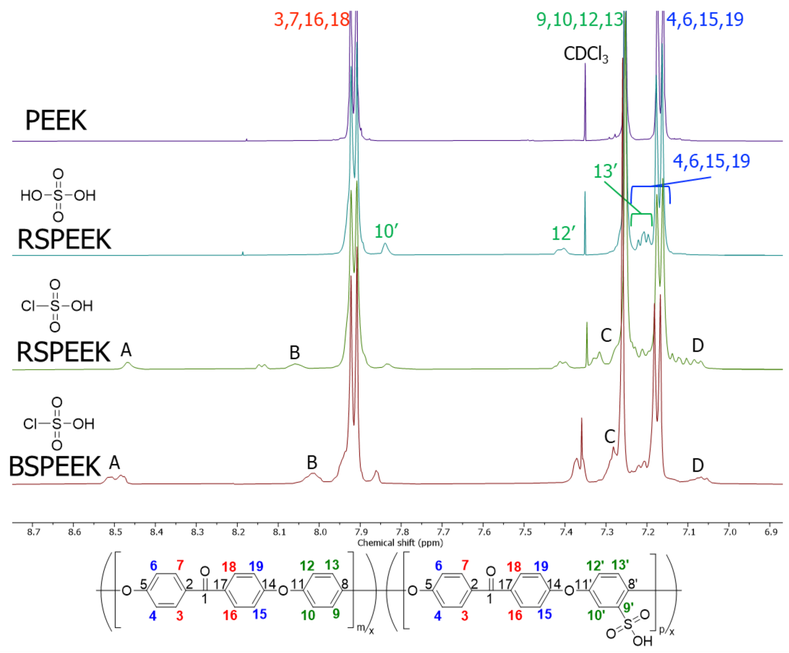
Blocky Sulfonated PEEK was Generated By Sulfonating in the Heterogeneous Gel State



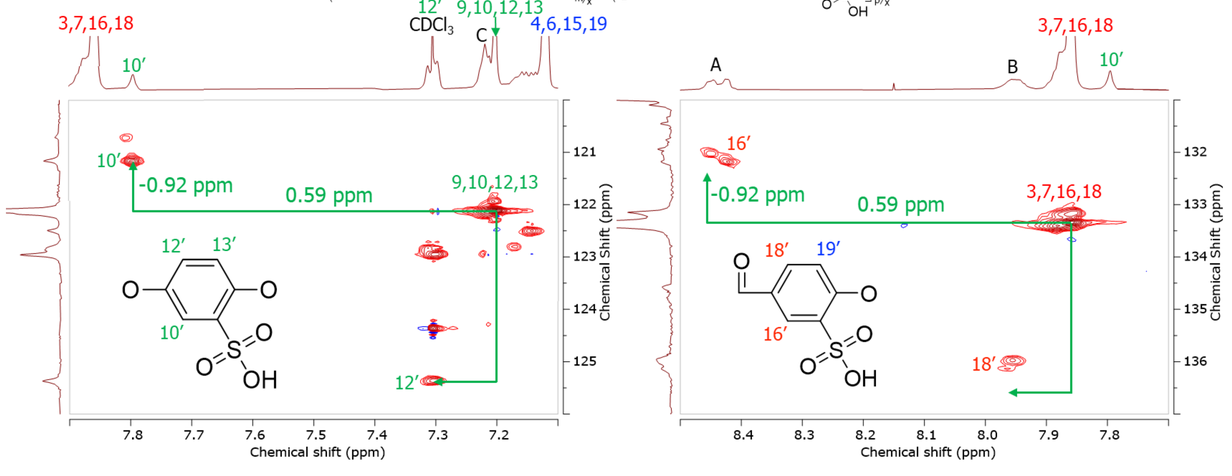
- Solution state sulfonation results in a random microstructure
- Sulfonation in the heterogeneous gel-state is restricted to the amorphous region
  - Forms non-random, blocky microstructure

^{1}H NMR Spectrum of BSPEEK Product Contained Unexpected Peaks

- For decades, the 10′ peak has been used to calculate degree of sulfonation (DS)[1]
- New peaks A, B, C, and D appeared when sulfonating using chlorosulfonic acid
  - Indicates additional sites could be sulfonated
- High field 1.2 GHz 2D NMR experiments were performed to find the source of these peaks



HSQC Spectrum of BSPEEK Reveals Source of Two Unknown Peaks: Benzophenone Sulfonation

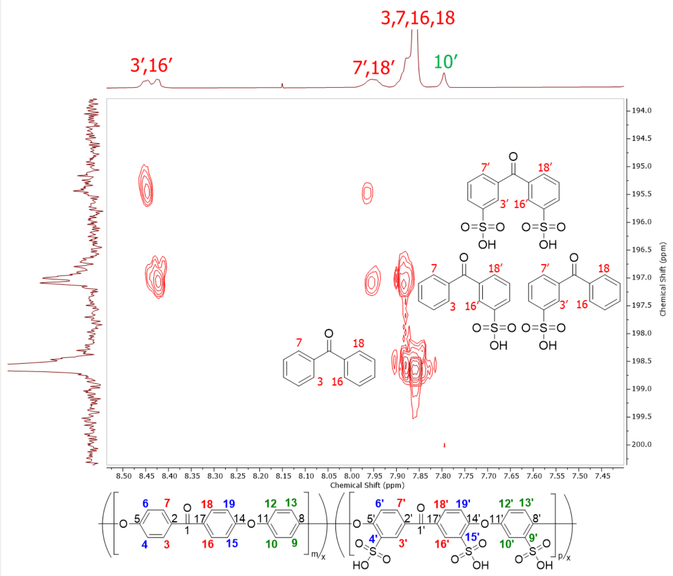


- **H**eteronuclear **S**ingle **Q**uantum **C**oherence (**HSQC**) reveals proton-carbon correlations
- Crosspeaks associated with A and B can only be explained by sulfonation of benzophenone

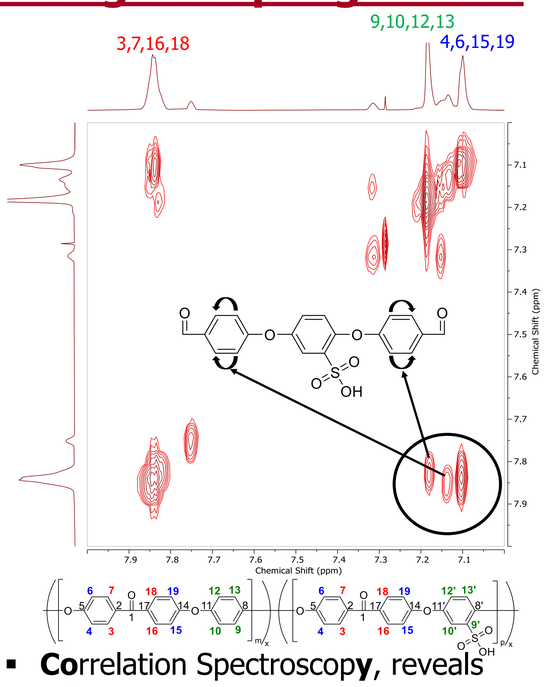
Citations

1. Anderson, L. J.; Yuan, X.; Fahs, G. B.; Moore, R. B.. Blocky Ionomers via Sulfonation of Poly(ether Ether Ketone) in the Semicrystalline Gel State. *Macromolecules* **2018**, *51* (16), 6226–6237. https://doi.org/10.1021/acs.macromol.8b01152.

HMBC and COSY Reveal Long-Range Coupling Effects

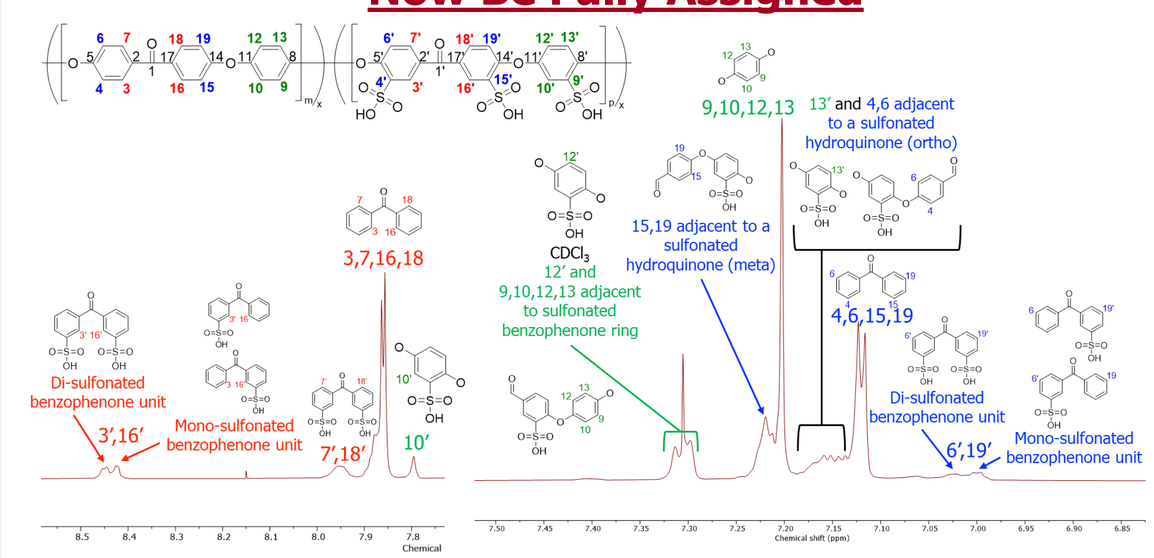


- **H**eteronuclear **M**ultiple **B**ond **C**orrelation, reveals long range (2-4 bond) proton-carbon correlations
- Non-, mono-, and di-sulfonated benzophenones can be differentiated in proton NMR



- **Co**rrelation Spectroscopy, reveals adjacent protons
- Protons on benzophenone rings ortho and meta to sulfonated hydroquinone rings have different chemical shifts

BSPEEK's Proton NMR Spectrum Can Now Be Fully Assigned



- Fully assigned SPEEK spectrum contains 45 unique proton signals
- New method for using proton NMR to determine % sulfonated was developed
- Previous method underreported %sulfonation by up to 50%

$Equation\ 1: \int 3',16' + 7',18' + 3,7,16,18 = 4$ $Equation\ 2: DS = 100\% * \int 3',16' + 10'$

Conclusions

Utilizing 2D NMR spectroscopic techniques, the proton NMR spectrum of our blocky sulfonated PEEK could be fully assigned. During this process, it was found that when sulfonating PEEK with chlorosulfonic acid, both the hydroquinone and benzophenone units are sulfonated. This observation runs contrary to what has been understood by the field for decades, where it was thought that only the hydroquinone unit of PEEK could be sulfonated. With a fully assigned proton NMR spectrum, we developed a new method for calculating SPEEK's degree of sulfonation that takes into account both the hydroquinone and benzophenone sulfonations. Using this new method, we found that our BSPEEK product was sulfonated to a degree of 75%, more than double what was found using the method traditionally used in the field.

Acknowledgements

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