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

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Polyether(ether ketone) (PEEK) is a high-performance thermoplastic that exhibits impressive mechanical robustness and chemical resistance. PEEK's repeat unit consists of two distinct units: the electronically activated hydroquinone and the deactivated benzophenone (Figure 1). Sulfonation of PEEK provides the polymer with proton-conduction properties, allowing the material to find an additional use as a robust proton exchange membrane in hydrogen fuel cells and water electrolyzers. Researchers most commonly synthesize sulfonated PEEK (SPEEK) through post-polymerization modification in concentrated sulfuric acid, where solid PEEK is added directly to the sulfuric acid and the polymer is sulfonated as it dissolves. In this method, only the activated hydroquinone unit is sulfonated. Recently, our group has developed two new methods for synthesizing SPEEK. In the first method, PEEK is dissolved in dichloroacetic acid, and a strong sulfonating agent like chlorosulfonic acid (CSA) is added to the solution, forming SPEEK with a random microstructure. In the second method, PEEK is sulfonated using CSA in the heterogeneous gel state, forming SPEEK with a statistically nonrandom, blocky microstructure. Unexpectadly, CSA sulfonated both the hydroquinone and benzophenone units. In this study, using 2D NMR, we developed a new protocol for using proton NMR to determine SPEEK's degree of sulfonation that considers these extra benzophenone sulfonations. Furthermore, we have shown that SPEEK's proton NMR spectrum exhibits long-range coupling effects, where a sulfonation on one aromatic ring affects the chemical shift of the protons on adjacent rings. This allows us to gain insight into the distribution and density of sulfonation sites across SPEEK's backbone. Interestingly, we found that when the chemistry is performed in the heterogeneous gel state, a higher ratio of benzophenone to hydroquinone sulfonations is observed than when the chemistry is performed in the solution state. We attribute this difference to the confinement effect, where the sulfonating agent is confined within the porous gel structure. This leads to a higher collision frequency within the gel than would occur in solution, allowing the less favorable benzophenone coupling to occur more frequently.

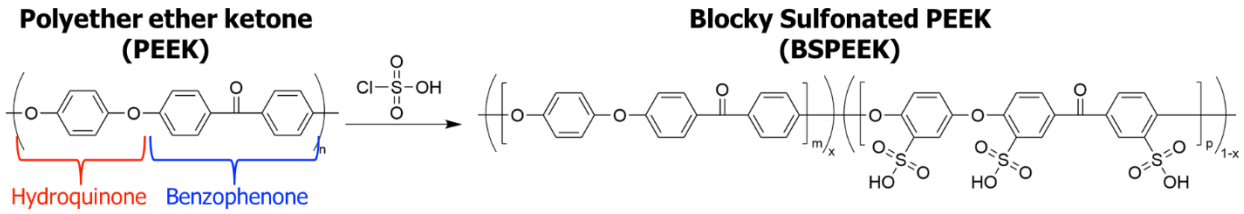


Figure 1. Using chlorosulfonic acid, PEEK can be sulfonated on both its hydroquinone and benzophenone units.