

## **Sulfonation Reaction Kinetics of Poly(ether ketone ketone) (PEKK) Using a Mixture of Concentrated and Fuming Sulfuric Acid**

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Sulfonated poly(ether ketone ketone) (SPEKK) ionomers were prepared by sulfonating PEKK with a mixture of concentrated and fuming sulfuric acid. Sulfonation occurs only on the phenyl rings attached to ether and ketone groups, resulting in a maximum sulfonation level of 4.33 mequiv/g. Three models for the reaction kinetics were investigated: (i) a second-order model and (ii) a pseudo-first-order model, each based on a single reaction step between active PEKK sites and  $\text{SO}_3$ , and (iii) a consecutive-reactions approach based on the notion that a previously reacted PEKK site deactivates remaining sites in the same repeat unit. Activation energies ranging from 71 to 76 kJ/mol were found for reaction temperatures from 16 to 74 °C. Although the sulfonation reaction could be predicted adequately up to a sulfonation level of 2.5 mequiv/g with all proposed models, the third model was needed to extend the simulation capability beyond this point. The validity of the consecutive-reactions model was confirmed by investigating the effect of the terephthaloyl-to-isophthaloyl ratio in PEKK and the effect of the initial  $\text{SO}_3$  concentration.