Commercial polyphenylsulfone was reacted with SiCl4 to afford a hybrid polymer and sulfonated to different degrees using sulphuric acid or ClSO3Si(CH3)3. Polymers having different degrees of sulfonation and different inorganic content were cross-linked via the formation of Si-O-Si bonds. The products were characterized by ATR/FTIR spectroscopy demonstrating the formation of covalent bonds between the organic and inorganic components and the absence of dispersed inorganic silicon. The physicochemical properties of the hybrids were suitable for the preparation of membranes which showed adequately high conductivity values to make them suitable candidates for application in PEMFCs.