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A “click” chemistry approach to phosphonated graft copolymers for potential fuel cell applications

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Over the past two decades, many efforts to synthesize new polymers for proton exchange membrane (PEM) fuel cells have been reported.¹ Among these polymer examples, the ion-containing block and graft copolymers are of particular interest, because they combine the features of controlled structure and ion conductivity.^{2,3} Phosphonated polymers have a potential as an alternative to the sulfonated analogs for PEM fuel cells due to their high thermal stability and lower methanol permeability.⁴

Herein, we present the synthesis of novel graft copolymers comprising a hydrophobic polysulfone (PSU) backbone and highly phosphonated poly(pentafluorostyrene) (PFS) side chains (Figure 1). The synthetic strategy involves the preparation of alkyne end-functionalized PFS *via* atom transfer radical polymerization (ATRP) and modification of PSU with azide side groups. In the second step the PFS chains were grafted to the PSU backbone through the highly efficient and selective copper-catalyzed azide-alkyne 1,3-cycloaddition (CuCAAC). Finally, the phosphonic acid moieties were introduced into the PFS grafts⁵ through a post-functionalization. The controlled polymerization process and the high efficiency of the modification reactions facilitate precise tuning of the copolymers' hydrophilic-hydrophobic balance. Thus, it is possible to achieve maximum content of ionic groups in the graft copolymers while maintaining their water insolubility and film-forming properties. The copolymers were characterized by size-exclusion chromatography, FTIR and ¹H NMR spectroscopy. Their thermal properties were investigated by differential scanning calorimetry and thermal gravimetric analyses. Initial measurements on solvent-cast polymer membranes showed promising results for conductivities at elevated temperatures.

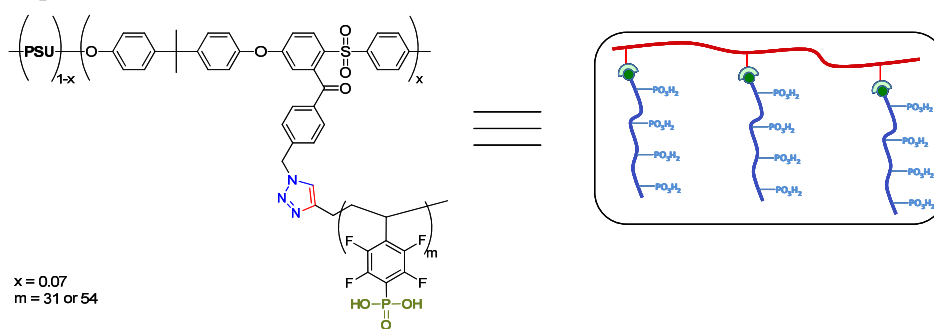


Figure 1. Structure of the phosphonated graft copolymers.

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⁴ Lafitte, B.; Jannasch, P. *Adv. Fuel Cells* **2007**, 1, 119-185.

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