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Publication date:
2011

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Citation (APA):
Nielsen, M. M., Dimitrov, I., Takamuku, S., Jannasch, P., Jankova Atanasova, K., & Hvilsted, S. (2011). *Sulfonic Acid Functionalized Polysulfone by "Click" Chemistry*. Abstract from Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Pacific Grove, CA, USA.

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Sulfonic Acid Functionalized Polysulfone by ‘click’ chemistry

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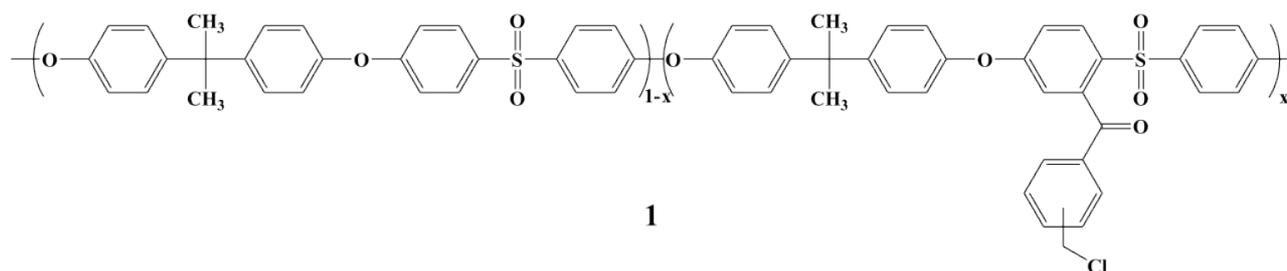
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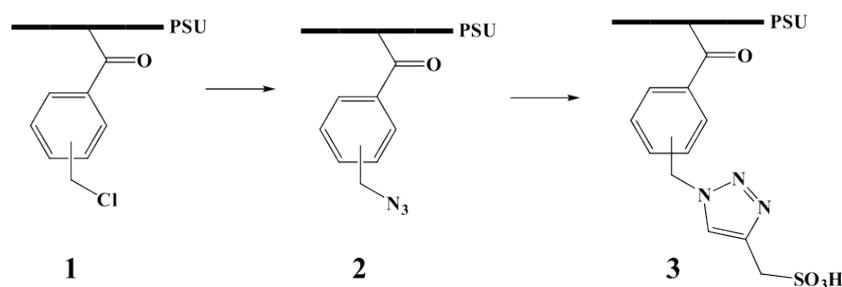
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The current benchmark material for membranes in proton exchange membrane (PEM) fuel cells, Nafion, is a perfluorinated polymer. Though it is still the best overall choice, perfluorinated PEM's in general suffer from drawbacks like inability to operate at elevated temperatures (>80 °C), loss of sulfonic acid moieties due to hydrolytic and thermal decomposition, relatively high oxygen and methanol permeability and high cost. Thus, a great incentive exists to prepare novel membrane materials with high ionic conductivity, good durability, electrically insulating, gas impermeable, ionic conductivity in absence of water, both high and low temperature performance, mechanical strength, and low cost. Previous research has taught us that material solubility and film forming capabilities are very important properties¹. Therefore among other approaches we are exploiting the potential in modifying the excellent film forming polysulfones (PSUs). Besides having been investigated in various multiblock systems^{2,3} and in blends⁴ modified PSUs have already shown promising results, both as tethered with benzimidazole⁵, phosphonated⁶ or sulfonated⁷⁻¹⁰, the latter being of interest in the work presented here.

‘Click’ chemistry performed directly from the PSU backbone is an alternative to the insertion of proton conducting moieties by e.g. lithiation¹¹. In the current study an alkyne-azide ‘click’ reaction is performed from a spacer, (chloromethyl)benzoyl, which is introduced onto a commercially available PSU at different degrees of substitution (**1**).



The chloromethyl substituted PSU (**1**) is readily turned into an azidomethyl PSU (**2**), which is used for clicking a sulfonic acid containing alkyne (e.g. propargyl sulfonate) onto the backbone, resulting in a sulfonic acid containing PSU (**3**):



The complete conversion of the ‘click’ reaction (as proofed by ^1H NMR) makes the ion exchange capacity (IEC) value dependent on the degree of conversion in the step where the spacer is introduced and the use of spacer and sulfonated alkyne. The idea in introducing a spacer is to obtain a better separation of the hydrophobic and hydrophilic domains; however it also decreases the IEC.

The trend is evident, and the high conversion of the ‘click’ reaction is a useful tool in obtaining a controlled dispersion of the sulfonic acid moieties. The highest obtained degree of substitution in the structure shown above is $x=0.61$, meaning that the resulting sulfonated product has a theoretical IEC value of 1.08. Even though this value is rather low, there are other ways to increase the sulfonic acid content, so this contribution should be seen as a proof of concept reaction of ‘clicking’ a sulfonic acid moiety onto a PSU backbone via a spacer.

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