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Sulfonated hydrocarbon graft architectures for cation exchange membranes

Mads M. Nielsen, Katja Jankova, Søren Hvilsted *

Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, Building 227, DK-2800 Kgs. Lyngby, Denmark

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ABSTRACT

A synthetic strategy to hydrocarbon graft architectures prepared from a commercial polysulfone and aimed as ion exchange membrane material is proposed. Polystyrene is grafted from a polysulfone macroinitiator by atom transfer radical polymerization, and subsequently sulfonated with acetyl sulfate to various degrees. Series of grafting densities and graft lengths are prepared, and membranes are solvent cast from DMSO. The membrane properties in aqueous environments are evaluated from their water swelling behavior, and their thermal properties and stability are investigated by thermogravimetric analysis and differential scanning calorimetry.

1. Introduction

Cation exchange membranes have widespread uses, mainly within separation and power generation devices. More specifically, the amphiphilic polymers are applied for electrodialysis, desalination, water purification, sensors and fuel cells [1–4]. Depending on the application, hydrophobic polymers are functionalized with carboxylic acid, phosphonic acid or sulfonic acid [1,5]. Research drivers are ways either to improve the ion exchange properties or the lifetime of the membranes, or to come up with cheaper alternatives to the well established membranes such as DuPont's Nafion®.

Perfluorosulfonic acid membranes (PFSA) are vastly used as cation exchange membranes [2,6,7]. Currently, a trend is to investigate hydrocarbon-based cation exchange membranes as it can be argued that the advantages of such materials can make up for limitations like lower performance and shorter lifetime compared to PFSA's [2,8]. Advantages include lower price of raw materials, easier processing due to the eliminated fluorination step, and a reduced negative environmental impact [2]. For fuel cell applications, the membranes must be tailored to facilitate migration of protons from the anode to the cathode in the proton exchange membrane fuel cell (PEMFC) *via* percolated ionic channels [9–12]. The interplay between hydrophilic and hydrophobic domains is vital for the creation of a phase-separation that enables the passage between ionic sites [13–15]. Upon humidification the acidic groups dissociate, allowing for proton conduction [5]. Despite outstanding overall properties PFSAs suffer from limitations at elevated temperatures especially above 100 °C and at lower relative humidities [6,8,13]. Alternative systems are continuously being investigated, e.g., PFSA/inorganic composites [16], partially fluorinated ionomers [17], poly(arylene ethers) [4,18,19], polybenzimidazoles [20], polystyrene based copolymers [21,22] and blends [23–25]. When designing the proton exchange membrane (PEM) a compromise must be made when settling on an ion exchange capacity (IEC) as the presence of acidic groups is related to both proton conductivity and water

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* Corresponding author. Tel.: +45 4525 2965.
E-mail address: sh@kt.dtu.dk (S. Hvilsted).

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uptake. It is desirable that the membrane retains its dimensions and does not swell or even dissolve when it gets in contact with water. Block copolymers and graft copolymers are especially suited for this purpose due to the inherent phase-separation of incompatible components of which either a block or the grafts contain e.g., sulfonic acid groups [21,22]. Previous studies on block and graft structures have shown how grafts at low degree of grafting (DG) exhibit lower water uptakes without negatively affecting the conductivity [22,26].

Previous investigations of PEM systems based on the commercial polysulfone (PSU) Udel® as backbone have shown promising results, both with sulfonated aliphatic side chains [27] and phosphonated, partially fluorinated grafts [28]. Durability studies of an analogue, directly sulfonated PSU (with a biphenyl rather than bisphenol A segment) suggested that the stability was higher when sulfonated PSU copolymers had the acidic groups in the *ortho*-position to the SO_2 group [19]. In addressing the aim of a hydrocarbon structure with sulfonic acid sites, the polysulfone is modified to contain a chloromethyl group. In previous studies of partially fluorinated graft structures, the chlorine was substituted by an azide, thereby enabling the use of click chemistry [27–29]. However, styrene can be grafted directly from the macroinitiator by ATRP [30]. The polystyrene component is widely used in cation exchange membranes [1,2,21,31], and is established as sulfonated graft in various partially fluorinated PEM systems [24,25,32]. Handles in the partially sulfonated polysulfone-*g*-polystyrene (PSU-*g*-SPS) system are thus (i) DG, (ii) graft length, and (iii) degree of sulfonation (DS). Incomplete initiating efficiency (*f*) is a common issue when grafting from e.g., chlorotrifluoroethylene [26] that might be of little significance of model compounds, but more so in final applications. From a synthetic point of view it is therefore desirable to obtain complete *f* when developing a new macroinitiator. The aromatic spacer in the modified PSU is expected to reduce incomplete initiation caused by steric hindrance. The aim with the present study of the PSU-*g*-SPS system is to pursue a synthetic approach to cheaper cation exchange membrane materials, and – through tuning of the handles of the system and by performing preliminary studies of its water sorption and thermal properties – to evaluate its potential for this application.

2. Experimental

2.1. Materials

The materials were purchased from Aldrich unless otherwise stated and used as received: copper(I)bromide (CuBr, 98%), *N*,*N*,*N′N″*,*N″*-pentamethyldiethylenetriamine (PMDETA, 99%), *n*-butyllithium (BuLi, in hexanes, 2.5 M, Acros), 3-(chloromethyl)benzoyl chloride (3-cmbc, Acros, 97%), acetic anhydride (AA, Bie & Berntsen A/S), sulfuric acid (H_2SO_4, 96%, chemically pure), methanol (MeOH, >99.9%), dichloroethane (DCE >99%, Bie & Berntsen A/S), propan-2-ol (IPA, Honeywell), dimethylsulfoxide (DMSO ⩾ 99%), chloroform-*d* ($CDCl_3$, 99.8%), dimethylsulfoxide-d_6 (DMSO, 99.9 atom% D). Styrene (St ⩾99%, ReagentPlus®, 4-tert-butylcatechol stabilized), was passed through a column of activated basic aluminum oxide (Al_2O_3, activated, basic, Brockmann I) and subsequently dried over calcium hydride (CaH_2, reagent grade, 90–95%) and distilled under reduced pressure. Tetrahydrofuran (THF, Fisher Scientific, 99.9%) was distilled and dried on 4 Å molecular sieves prior to use. PSU (Udel® P-3500 LCD MB8, $\overline{M}_n$ = 40 kDa, 195, Solvay Advanced Polymers) was dried in oven prior to use. Dialysis tubing of regenerated cellulose (cut off 12,000–14,000 Da, Membrane Filtration Products Inc.), and dialysis tubing benzoylated (cut off 1200 Da) were washed with DI water prior to use.

2.2. Polysulfone with pendant (chloromethyl)benzoyl groups (PSU-Cl)

PSU was functionalized according to a previously reported method [27,28]. In the typical reaction 7 g pre-dried PSU was dissolved in 350 mL dry THF and placed under argon in a glass reactor equipped with a magnetic stirring bar, a thermometer, a septum and a connection to a vacuum line. The mixture was cooled down to −65 °C on dry ice/IPA and degassed by first applying vacuum on the system, then putting it under a blanket of argon; This was repeated seven times. BuLi (20% excess of targeted degree of substitution) was added with a gas tight syringe to activate the *ortho* position to SO_2 of PSU [18,19,33,34]. After 1 h a 3-cmbc amount of 20% excess relative to BuLi was added with a gas tight syringe and the lithiated sites were quenched over 30 min. At RT the resulting **PSU-Cl** was precipitated in IPA, filtered, washed with water, filtered again and dried before stirring in MeOH, filtered once more and dried at 60 °C in vacuum oven overnight. **PSU-Cl** precursors bearing 3 and 18 chloromethyl groups per 100 repeat units were obtained, and they are referred to as **PSU-Cl-3** and **PSU-Cl-18**. ^1H NMR (300 MHz, $CDCl_3$, δ(ppm)): 8.05–6.80 (Ar *H*, *PSU* + substituted PSU), 4.66–4.56 (Ar—CH_2—Cl), 1.79–1.56 (C—$(CH_3)_2$). FTIR (cm^{-1}): 1683 (C=O), 1585 (Ar C=C), 1487 (CH_3), 1237 (C—O—C), 1169 and 1149 (O=S=O), 1105, 1081 and 1014 (Ar ring). Size exclusion chromatography (SEC) (DMF, Da) of **PSU-Cl-3** and **PSU-Cl-18**: $\overline{M}_p$ = 60,000 and 61,000, and polydispersity index ($PDI_{\mathbf{PSU\text{-}Cl}}$): 1.64 and 3.59 respectively.

2.3. Polysulfone grafted with polystyrene side chains (PSU-g-PS)

Graft copolymers were made according to Scheme 1. In the typical case, 100 mg **PSU-Cl** and 4 eq CuBr were mixed with 5000 eq St in a Schlenk tube and purged with nitrogen. The reaction mixture was degassed by employing three freeze–thaw cycles, then 4.1 eqs PMDETA were added and the mixture was degassed again before starting the bulk polymerization at 110 °C until the reaction mixture became too viscous to stir, after approximately 2 h. Chain propagation was followed by ^1H NMR and SEC (THF). See the Supporting information for more details. The reaction mixture was then dissolved in THF and precipitated from MeOH, washed with fresh MeOH twice