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ORIGINAL PAPER

Conductivity of highly sulfonated polyphenylene sulfide in the powder form as a function of temperature and humidity

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Abstract Block-copolymers with highly sulfonated ionomer blocks are considered as leading candidates for low-humidity high-temperature Polymer Electrolyte Fuel Cell membranes. We present a new approach that allows for faster measurement of conductivity of powdered ionomers in a wide range of temperature and humidity with a single 10–30 mg sample. Our method is exemplified by a case study of polyphenylenesufide with a degree of sulfonation 0.70. This material shows 0.12 S/cm conductivity at 127 °C and 50% relative humidity. At higher temperatures and lower humidities, this polymer undergoes irreversible cross-linking. Further routes to improving conductivity, chemical and mechanical properties of the polymer are discussed.

Keywords Polymer electrolyte · Protonic conductivity · Fuel cell · Polyphenylene sulfide

Introduction

The need for low-humidity high-temperature proton conducting membrane has been recognized by the Polymer Electrolyte Fuel Cell community in the last decade [1–7]. The US Department of Energy specified 0.1 S/cm conductivity at 120–150 °C at 25% relative humidity as the goal for 2010 [8]. Nafion and related polyperfluorooethersulfonic acids do not perform satisfactory under such conditions due to loss of liquid water, which is essential for proton transfer in their nanoporous structure, and because they undergo severe mechanical deformations in the temperature range of interest [9–13]. Inexpensive and thermostable phenylenic polymers are considered to be suitable alternatives to Nafion-like materials; however, the low-humidity

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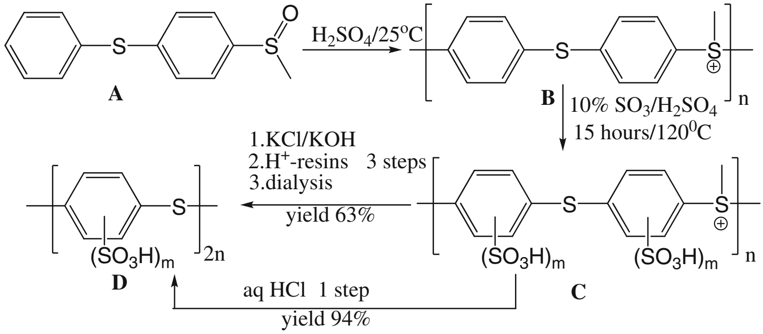
conductivity of such randomly sulfonated polymers is inferior to the conductivity of Nafion of similar equivalent weight [14–23]. Dramatic improvement of low-humidity conductivity of phenylenic polymers with the increase of their degree of sulfonation (i.e., lower equivalent weight) has been reported in numerous publications [13, 22, 24–29], and Schuster et al. suggested that “highly sulfonated systems with significantly smaller –SO_3H separations” should be considered in “the future research” [30]. Due to their water-solubility, swelling, and brittleness [13] highly sulfonated ionomers are expected to be used mostly as blocks in copolymers with non-ionic blocks [22, 23, 29, 31–33]. However, the intrinsic conductivity of such ionomers is of a great interest for membrane development. The brittleness of the highly sulfonated ionomers presents a challenge for membrane developers. For example, polyphenylenesulfones with degrees of sulfonation (DOS) of 0.5 and 0.85 can be studied as a film, whereas the same type of polymer with a DOS of 1 had to be characterized in the pellet form [13]. As we found with many other materials, pellets often disintegrate upon changes in humidity, thus making such measurements cumbersome and unreliable [34]. Our group reported recently an apparatus for measuring protonic conductivity of powders over a wide range of temperature and humidity with a single 10–30 mg sample [34]. This study presents data on the intrinsic conductivity and stability of highly sulfonated polyphenylenesulfide using the new apparatus.

Results and discussion

Polymer synthesis characterization

Poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hydrogen sulfate) (**B**) was prepared by polymerization of 4-(methylsulfinyl)diphenyl sulfide (**A**) in concentrated sulfuric acid [35], as shown in Scheme 1.

In order to determine the molecular weight of the resulting polymer, **B** was converted into polyphenylene sulfide (PPS) via refluxing in pyridine. Differential scanning calorimetry (DSC) yielded the melting temperature of PPS as 251 °C. This



Scheme 1 Synthesis of sulfonated polyphenylene sulfide **D**

finding along with polymerization time (40 h) allows us to estimate roughly the M_W of **B** as 20–25 kDa (see Fig. 3 in Ref. [24]).

Sulfonation of **B** in 10% oleum at 120 °C for 15 h afforded **C** with the number of sulfonic acid groups per phenyl ring (degree of sulfonation, DOS) equal to 0.70 (determined via the sulfur-to-carbon ratio in elemental analysis of **D**). However, multiple attempts to prepare a **C** with DOS = 2 as was claimed in Ref. [35] were unsuccessful in agreement with Ref. [36].

Polymer **D** was prepared by two separate procedures. The first route shown in Scheme 1 (demethylation–protonation–dialysis) produced **D** in three steps with a 63% overall yield. The reduced yield can be attributed to the loss during the dialysis step. On the other hand, the second route (demethylation by aqueous HCl) afforded **D** in 94% yield in one step.

The structures of polymers **B**, **C**, and **D** were evaluated by ^{1}H NMR (Fig. 1). The spectrum of **B** expectedly exhibited three signals which can be assign to three chemically distinguishable protons [24]: $\delta(H_a) = 3.81$, $\delta(H_b) = 7.65$, and $\delta(H_c) = 8.08$ ppm in the expected intensity ratio of 3:4:4 as reported earlier [37]. In the case of **C**, three additional signals appeared downfield: $\delta(H_{d'}) = 8.11$, $\delta(H_{e'}) = 8.3$, and $\delta(H_{f'}) = 8.9$ ppm. They can be attributed to three chemically nonequivalent protons of mono-sulfonated aromatic ring (Fig. 1). The area ratio of peak a′ area to the sum of

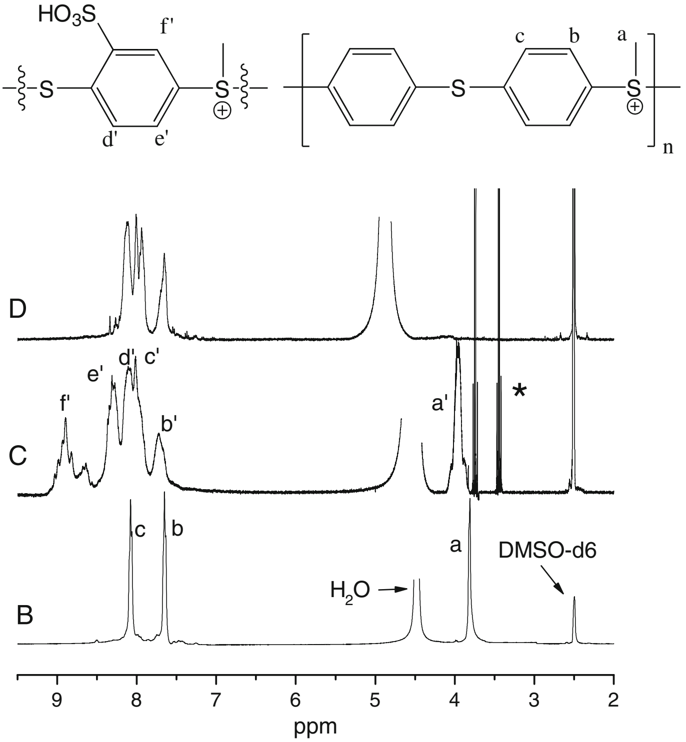


Fig. 1 ^{1}H NMR spectra (in DMSO-d_6) of **B**, **C**, and **D**. (*quartet from –CH_2– of EtOH which was used to precipitate **C**)

peaks of aromatic protons (b′, c′, d′, e′, and f′; 3:10) for **D** is smaller than for **B** (3:8), perhaps suggesting partial demethylation during the sulfonation. Quartet at 3.7 ppm and triplet at 1.1 ppm (not shown) can be assign to protons of the ethyl group of sulfonic acid ester, formation of which under acidic conditions was observed by others [38, 39]. The peak at δ 3.96 ppm assigned to the protons of methyl sulfonium group, the peak at δ 8.89 ppm assigned to the aromatic proton between sulfonic acid group and methyl sulfonium group, and peak at δ 8.1 ppm assigned to aromatic protons ortho to methyl sulfonium group (unsulfonated phenyl rings) completely disappeared in the ^{1}H NMR spectra of **D**, while peak at δ 7.73 ppm clearly increased in intensity. These findings support the idea of quantitative demethylation of ionomer **C**. The intensities ratio of peak at 7.6 ppm to peaks 7.94 ppm, 8.01 ppm, and 8.12 ppm allow the determination of DOS of ionomer **D**. For this polymer, the intensities imply that the DOS is equal to 0.75 which is close to the DOS determined by elemental analysis (0.70).

Protonic conductivity

The ionomer **D** was water soluble and extremely brittle, which prevented its film casting. This brittleness was observed despite the fact that power X-ray diffraction showed that the polymer is amorphous in agreement with Ref. [24]. We believe that this brittleness a manifestation of a general feature of solid ionic compounds well-known in Materials Science [40].

In order to measure the conductivity of powder samples as a function of temperature and humidity, an apparatus developed earlier in our laboratory was implemented [34]. A typical impedance spectrum of **D** is shown in a Fig. 2. Purely resistive behavior was found in our experiments which employed a four-point electrical probe and frequencies below 10 kHz.

A comparison of the conductivity dependence of ionomer **D** on humidity with Nafion at various temperatures is shown in Fig. 3.

At room temperature and humidities below 45%, Nafion 1100 has a higher conductivity than polyphenylene sulfide with DOS = 0.70 (**D**). As temperature is raised and relative humidity kept constant, the conductivity of Nafion does not change significantly till ca. 140 °C for humidities below 85% (data not shown) [9, 10]. The conductivity of **D** increases faster with temperature (Arrhenius dependence of σ versus 1/T with the activation energy of 0.152 eV at 41% RH). In fact, the conductivity of **D** at 127 °C attains the value of 0.12 S/cm at 50% RH. Also shown in Fig. 3 are conductivity data from earlier articles on sulfonated PPS [24, 41]. The conductivity measured in our experiments is two orders of magnitude higher than the conductivity reported earlier for PPS with an allegedly higher DOS [24] or at a higher temperature [41]. Taken into account the high IEC of the ionomer studied in this study, our values seem more reasonable than the values reported in Ref. [24].

Remarkably, no hysteresis in the conductivity of **D** was found in 10–50% humidity cycles below 130 °C, signifying fast and reversible water sorption and structural changes (if any) in the polymer. A different behavior was found at 150 °C, i.e., the conductivity of **D** decreases at low humidity and it stays at lower values upon return to higher humidities (see Fig. 4a). In order to investigate the

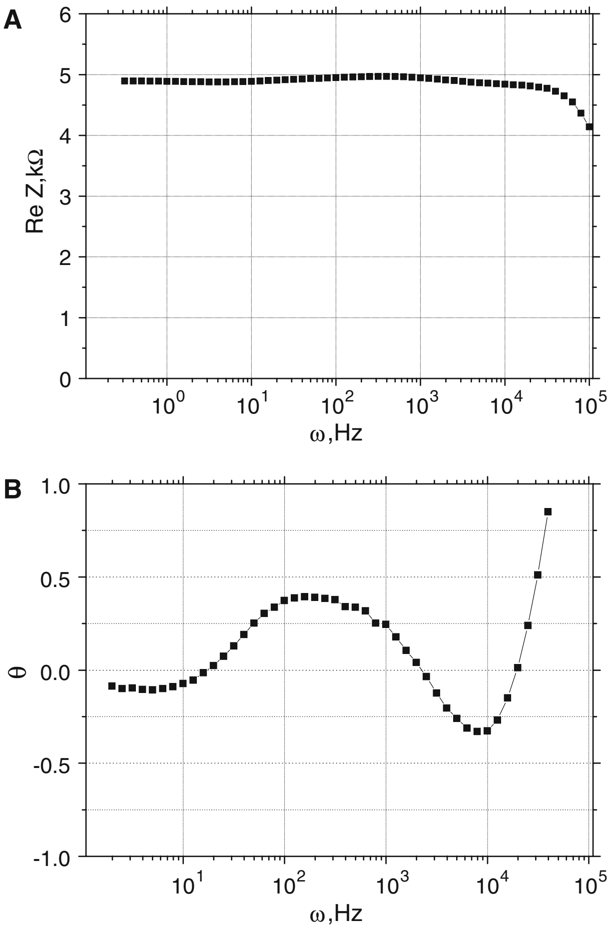


Fig. 2 Impedance spectra (in-phase component ReZ, and phase shift θ) of sulfonated polyphenylene sulfide with DOS = 0.70 (**D**) at 45.2% relative humidity and 23 °C. Inner probe distance is 5 mm. *Panel A*: reactance. *Panel B*: phase angle

origin of this effect, we looked at the time-dependence of the conductivity data at 150 °C. Figure 4b shows that upon stepping from mTorr vacuum to 28% humidity the conductivity reaches a plateau in about 2 h. In contrast, when the humidity was switched from 30 s exposure to vacuum to 11%, we found a ca. 1 h raise in the conductivity (due to hydration of the polymer) superimposed on an exponential decay which continued for over 24 h.

After completing the humidity cycle, the sample was taken out of the apparatus. The polymer did not dissolve in water or DMSO. The sulfate content in the sample did not change statistically compared to its content before the measurements (0.105 ± 0.005% w/w). The FTIR spectrum of the heated sample compared to the spectrum of the virgin sulfonated polyphenylene sulfide showed that an enlarged peak at 1,131 cm^{-1} assigned to the S=O symmetric stretching vibration of the

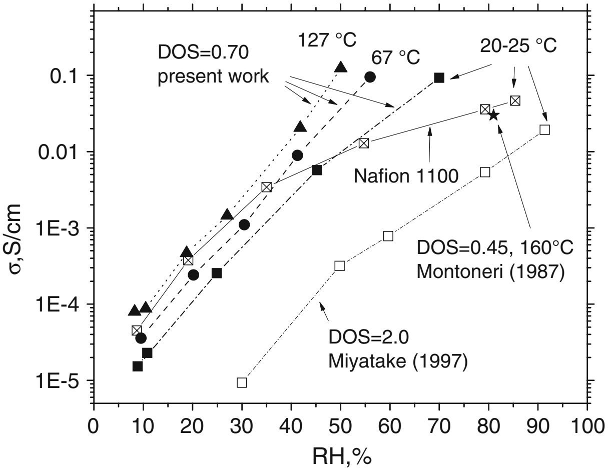


Fig. 3 Conductivity of sulfonated polyphenylene sulfide (*solid symbols*) with DOS = 0.70 (**D**), **D** with DOS = 2.0 (from Ref. [24]; *open symbols*), **D** with DOS = 0.45 (from Ref. [41]; *open symbols*), and Nafion 1100 film (*crossed symbols*) as a function of relative humidity (RH). Temperatures: 20 °C (*squares*), 67 °C (*circles*), 127 °C (*triangles*), and 160 °C (*star*)

sulfone group by earlier researchers [42]. This data indicates that most likely our material undergoes cross-linking at 150 °C. This could be the result of the attack of an electrophilic sulfonic group on an electron-rich thiophenyl ring with a resulting loss of acidic functionality.

Thermal degradation of **D** was studied by Thermal gravimetric analysis (TGA) in dry nitrogen. The result is shown in Fig. 5. Below 250 °C, the sample loses ca. 7% of its weight. Interestingly, a small weight loss between 140 and 240 °C has been reported earlier in similar, relatively electron-rich sulfonated polyphenylene sulfide systems [36, 41, 42]. The data shown in this study suggest that this is due to cross-linking at high temperatures and low humidities which is accompanied by a loss of water. The further weight loss between 250 and 375 °C is attributed to the loss of SO_3. The third step, between 380 and 475 °C, is most likely due to the polymer backbone degradation.

Conclusions

Using a new apparatus, we measured the protonic conductivity of a powdered ionomer in a wide range of temperature and humidity. We found that sulfonated polyphenylene sulfide with 0.70 sulfonic group per aromatic ring is chemically stable up to 130 °C. This polymer shows an impressive protonic conductivity of 0.12 S/cm at 50% and 127 °C. Further increase in low-humidity conductivity can be expected at higher degrees of sulfonation. The stability toward cross-linking can be improved by converting the sulfide links into sulfoxide [28] and the mechanical properties can be improved using a block-copolymer. All three approaches are under way in our laboratory.

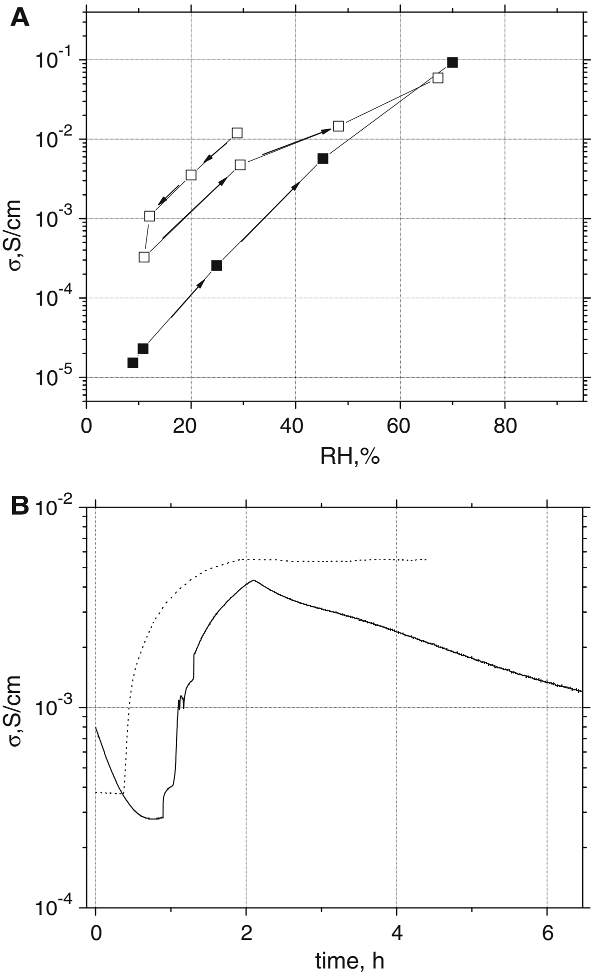


Fig. 4 **a** Conductivity of sulfonated polyphenylene sulfide with DOS = 0.70 (**D**) as a function of relative humidity (RH) at 20 °C (*solid square*) and 150 °C (*open square*). **b** Conductivity of sulfonated polyphenylene sulfide with DOS = 0.70 (**D**) at 150 °C as a function of time (RH) and at relative humidities 28% (upward scan in **a**; *dotted line*) and 11% (downward scan in **a**; *solid line*)

Experimental section

A, **B**, PPS, and **C** were prepared according to previous articles [24, 35].

Preparation of poly(thio-1,4-phenylenesulfonic acid) (**D**)

First route

This procedure was reported earlier [19]. It includes demethylation of **C** in KOH + KCl solution, exchange of K^+ for H^+ using ion exchange resin (Amberlite

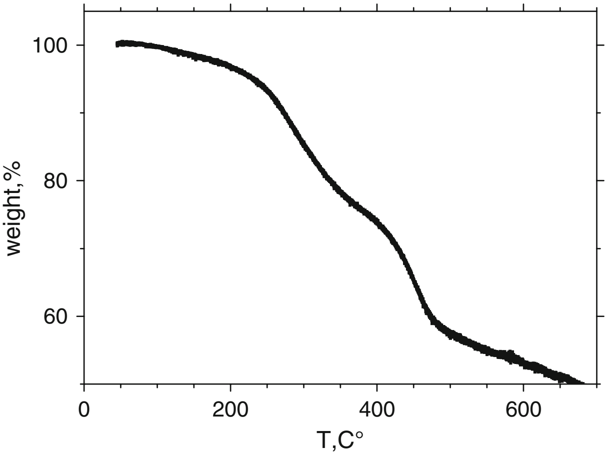


Fig. 5 TGA of **D** in nitrogen atmosphere; heating rate 1 K/min

IR-120H), and dialysis with (SnakeSkin Pleated Dialysis Tubing 3,500 MWCO, 22 mm × 35 feet in diameter (34 mm dry flat width) 3.7 ml/cm) membrane over 1 week.

Second route

One gram of **C** was stirred overnight in 50 mL of 12.1 M HCl at room temperature. The solution was evaporated and the residue was washed with THF.

Nafion treatment

A film of Nafion N105 (nominal thickness 127 μm, equivalent weight 950 g/mol H^+ form, Ion Power Inc.) was boiled in 3% H_2O_2 for 4 h, in deionized water (18.2 MΩ cm conductivity) for 2 h, in 1.0 M $HClO_4$ for 2 h, and then again in deionized water thrice for 2 h.

Conductivity measurements

The conductivity of Nafion film was measured using a four-electrode conductivity clamp BekkTech BT-110. The conductivity of ionomer **D** was measured with custom-made powder cell, details of which are given in our previous report [34]. Both the powder cell and the film clamp were placed into a 1 L custom-made high-pressure environmental chamber capable of 20 atm operating pressure. The chamber temperature was maintained using a temperature controller (Omega CN 8200) connected to a thermistor positioned inside the chamber and to an electrical heating tape (Barnstead International #BIH101-060) wrapped around the chamber. At temperatures below 80 °C, the relative humidity in the chamber was controlled using saturated salts solutions [41, 42] placed in a glass beaker on the bottom of the chamber. At higher temperatures, a bubbler humidifier (Fideris, model FCTS HB, custom-made for 20 atm operation) connected to the chamber with a tube heated to 200 °C was used. The humidity was established by evacuating the preheated chamber to 1 kPa and then, within less than 1 min, opening a ball valve connecting the chamber to the humidifier preset at the desired dew point. The humidity was measured using a sensor (Vaisala HMT338), and it was stable within 0.2%.

Other measurements

^{1}H NMR spectroscopy was performed on a Bruker Avance 400 MHz spectrometer. DSC measurements were performed using a TA Instruments Differential Scanning Calorimeter 2920 at heating and cooling rates of 5 °C/min. FTIR spectra were obtained using a Bruker Tensor 27 spectrometer with a ZnSe ATR probe. TGA was performed with a TGA 2950 thermogravimetric analyzer. Elemental analysis was performed using a Leco CHNS-932 instrument. Sulfate content was determined in aqueous solutions or extracts using a DX-100 Ion Chromatograph. Powder X-ray diffraction data were acquired overnight with a Siemens D5000 instrument. Samples for XRD were mixed with vacuum grease and placed on an amorphous glass plate.

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