

## Highly sulfonated poly(phenylene sulfones): optimization of the polymerization conditions

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**Abstract** The preparation of highly sulfonated poly(phenylene sulfone) (ion exchange capacity =  $4.45 \text{ meq g}^{-1}$ ) by polycondensation of sulfonated difluorodiphenyl sulfone with metal sulfide and subsequent oxidation with hydrogen peroxide is optimized. The monomer/metal sulfide ratio, polymerization time and temperature, and type of metal sulfide have been varied. For the best conditions high molecular weights of up to  $300 \text{ kg mol}^{-1}$  are obtained reproducibly. This high molecular weight polyelectrolyte is meant to be used as main constituent of heterogeneous membrane structures such as interpenetrating networks, polymer blends, or simple physical mixtures with other polymers, e.g., for application in PEM fuel cells.

**Keywords** Sulfonated poly(phenylene sulfone) · Sulfonated poly(phenylene sulfide sulfone) · Fuel cell · Proton conducting polyelectrolyte · Hydrocarbon membrane · Lithium sulfide

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## Introduction

There are a few properties of sulfonated poly(phenylene)s such as poly(*p*-phenylene ether ketone)s which makes them distinct from perfluorosulfonic acid (PFSA) ionomers such as Nafion. While their relatively low cost, high thermal stability and ion exchange capacity (IEC) have been driving their use in traditional applications such as electro dialysis, desalination, and water purification systems [1], their microstructural features are anticipated to be advantageous for the water management of PEM fuel cells if sulfonated poly(phenylene)s were used as a membrane material [2]. But, because of their low proton conductivity at low degrees of hydration they are just considered to be a low cost alternative to the commonly used PFSA membranes [3]. The recent development of sulfonated poly(phenylene sulfone)s with high stability, superior proton conductivity at high temperature [4] and low humidification and methanol rejection properties [5], however, may make them the material of choice for PEM fuel cell applications in the future provided they were available as membranes with acceptable mechanical properties under wet and dry conditions. Especially highly sulfonated poly(phenylene sulfone) (sPSO<sub>2</sub>-220) [6] with an IEC of 4.45 meq/g (compared to 0.9 meq/g for Nafion 1100) shows an unique combination of microstructural and transport properties [7]. It shows a proton conductivity even exceeding the one of Nafion by a factor of 5–7 in the temperature range 110–160 °C. Unfortunately, its pronounced ionic (salt-like) character makes this polyelectrolyte brittle in the dry state, very soft at medium relative humidity as a result of its tremendous water uptake and soluble in water at very high water activities.

Pure sPSO<sub>2</sub>-220 is therefore not suitable as a separator material for PEM fuel cells, but it may be used as main constituent of heterogeneous membrane structures such as interpenetrating networks, polymer blends, or simple physical mixtures with other polymers. In either case, a high molecular weight of sPSO<sub>2</sub>-220 is of great advantage, because this in itself is already expected to reduce the solubility and swelling and improve the film forming properties.

So far, only low molecular weights of up to 60 kg mol<sup>-1</sup> with a poor reproducibility have been obtained by non-optimized polycondensation procedures [6]. This article therefore presents a systematic optimization of the reaction conditions, and a set of parameters is given which allows for the reproducible formation of high molecular weight sPSO<sub>2</sub>-220.

A high molecular weight has a positive effect on the film forming properties, not only for the pure polyelectrolyte (which is water soluble) but also as a constituent of blends. For the latter, not only the viscoelastic properties are anticipated to benefit from a high molecular weight, but also a more efficient retention of the polyelectrolyte in blends is expected.

## Experimental

### Materials

Disodium 4,4'-difluorodiphenyl sulfone-3,3'-disulfonate (sDFDPhS) [8, 9] was dried at  $T = 120$  °C at  $p = 20$  Mbar before use.

Alkaline or alkaline earth sulfides [ $\text{Li}_2\text{S}$  (Aldrich 98% metal basis),  $\text{Na}_2\text{S}$  (Aldrich 98% metal basis),  $\text{CaS}$  (Alfa 013121 99.9% metal basis), and  $\text{BaS}$  (Alfa 012848 99.7% metal basis)] were ground to a fine powder in a glove-box, *N*-methyl-2-pyrrolidone (NMP) ( $\geq 98\%$ , Fluka, water  $\leq 0.03\%$ ), *N*-ethyl-2-pyrrolidone (NEP) ( $\geq 98\%$ , Carl Roth, water  $\leq 0.5\%$ ), glacial acetic acid (Carl Roth), and  $\text{H}_2\text{O}_2$  (31% in water, BASF SE) were used as received. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

## Characterization

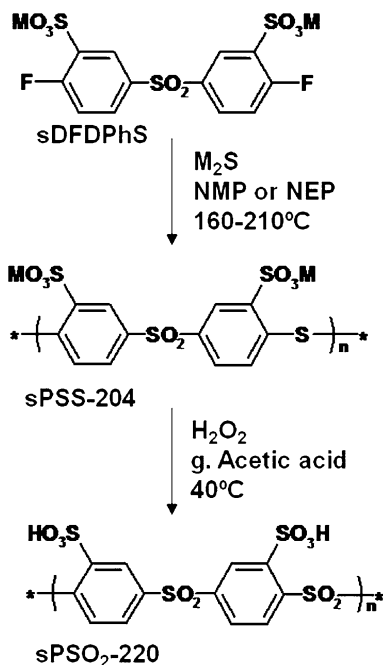
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature on a Bruker Advance spectrometer operating at a proton frequency of 300 MHz and a carbon frequency of 75.4 MHz. Deuterated dimethylsulfoxide ( $\text{DMSO}-d_6$ ) was used as solvent and its signals at 2.50 ppm ( $^1\text{H}$  NMR) and 39.52 ppm ( $^{13}\text{C}$  NMR) were used as references for the chemical shifts. For gel permeation chromatography (GPC) a Waters® pump model 590 was used with RI ERC-7512 detector and an UV–Vis light source Soma S-3702 (255 nm). The measurements were carried out at  $T = 60^\circ\text{C}$  with polystyrene (1 g/L) as a standard at a flow rate of 1.0 mL/min. “MZ-Gel” SDplus 500,  $10^4$ ,  $10^6$  Å of 10  $\mu\text{m}$  particle size were used as column fillings. IEC (meq  $\text{g}^{-1}$  dry polymer) of the synthesized polymers was analyzed by titration. The polymers were dissolved in water or 1 M NaCl solutions and then titrated with 0.1 N NaOH (Mettler Titrator DL21). Densities of the dry polymers (H-form) were determined by helium gas pycnometry using AccuPyc 1330 V2.01. IR spectra of the polymers (H-form) were recorded using a Bruker IFS 66 IR-spectrometer in the attenuated total reflectance (ATR) mode using a diamond tip. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 thermobalance with a heating rate of  $2^\circ\text{C min}^{-1}$  in a purge gas mixture of nitrogen and oxygen (80:20, 20 mL  $\text{min}^{-1}$ ). The outcoming gas stream containing the released products was continuously analyzed by a Balzer Prisma quadrupole spectrometer ( $m/z = 1\text{--}100$ ). UV and Fluorescent spectra were recorded using a Fluorolog (Horiba Jobin–Yvon) spectrofluorometer with fused-quartz cuvette of 1 cm optical path length. The concentration of the solutions ( $c = 10^{-4}$  g  $\text{L}^{-1}$ ) was chosen such that the absorbance was approximately 0.6 at a wave length of  $\lambda = 457$  nm.

## Synthesis of sPSO2-220

As shown in Scheme 1, the first reaction step is the formation of sulfonated poly(phenylene sulfide sulfone), in the following abbreviated sPSS-204.

For this all the glassware was dried at  $T \sim 400^\circ\text{C}$  and  $p = 10^{-3}$  Mbar before use. A flask equipped with mechanical stirrer was charged with sDFDPhS (10 g, 21.8 mmol), metal sulfide (1.023 g in the case of  $\text{Li}_2\text{S}$ , 21.8 mmol), and NMP or NEP (15 mL) in a glove-box. Then, the mixtures were heated to a constant temperature (depending on the batch in the range  $T = 160\text{--}215^\circ\text{C}$  measured in the oil bath) for times ranging from 2 to 24 h. The proceeding polycondensation reaction was clearly indicated by a severe increase of the viscosity. After cooling to  $T \sim 100^\circ\text{C}$ , water was added and the mixture was twice precipitated in

**Scheme 1** Formation of sPSO<sub>2</sub>-220 in a two step reaction (M = Na or Li)



isopropanol. The precipitate was separated and washed with isopropanol and then dialyzed for 3 days (Servapor cellulose 44144, MWCO 12,000–14,000, pore diameter 25 Å). Finally, water was evaporated and the product was dried at  $T = 110\text{ }^{\circ}\text{C}$  and  $p = 20\text{ Mbar}$ .

The final yield was 84% corresponding to 8.3 g of a pale-brownish polymer granulate which was sPSS-204 in the Na-form.

#### sPSS-204

Density:  $1.660\text{ g cm}^{-3}$  (H-form, dry). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 8.31$  (d, 2H, CH,  $J_{\text{HH}} = 1.7\text{ Hz}$ ), 7.79 (dd, 2H, CH,  $J_{\text{HH}} = 1.8, 8.0\text{ Hz}$ ), 7.28 (d, 2H, CH,  $J_{\text{HH}} = 8.2\text{ Hz}$ ). <sup>13</sup>C NMR (75.5 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 148.1$  (s), 141.4 (s), 138.1 (s), 134.2 (s), 128.0 (s), 126.2 (s). GPC (eluent DMF, standard PS):  $M_w$  330 kg mol<sup>-1</sup>, D 1.9. FT-IR (polymer powder, cm<sup>-1</sup>): 1638, 1572, 1550, 1446, 1378, 1378, 1319, 1236, 1200, 1166, 1146, 1115, 1087, 1059, 1016, 914, 829, 808, 731, 716, 692, 647, 617, 498.

The final product sPSO<sub>2</sub>-220 is obtained by oxidizing sPSS-204 in tenfold excess of hydrogen peroxide in glacial acetic acid as described before [6].

#### sPSO<sub>2</sub>-220

Density:  $1.763\text{ g cm}^{-3}$  (H-form, dry). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 8.47$  (m, 3H), 8.13 (s, 2H). <sup>13</sup>C-NMR (75.5 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 146.8$  (s), 143.1 (s), 142.7 (s), 131.7 (s), 128.4 (s), 128.3 (s). GPC (eluent DMF, standard PS):  $M_w$

150 kg mol<sup>-1</sup>, D 2.0. IEC exp.: 4.2–4.4 meq g<sup>-1</sup> (IEC calc.: 4.54 meq g<sup>-1</sup>) FT-IR (polymer powder, cm<sup>-1</sup>): 1710, 1594, 1560, 1457, 1375, 1336, 1248, 1168, 1151, 1115, 1088, 1051, 1011, 915, 831, 805, 721, 697, 647, 618, 599, 560, 457 (see supporting information). UV: absorbance  $\lambda_{\text{max}}$  457 nm; FS: excitation  $\lambda_{\text{max}}$  514 nm (see supporting information).

## Results and discussion

Since the molecular weight of the final product (sPSO<sub>2</sub>-220) is mainly controlled by the first reaction (polycondensation of sDFDPhS with metal sulfide) of the reaction sequence shown as Scheme 1, we have focused on finding the optimal molar ratio of the comonomers, polymerization temperature, and time. After this, the sulfur source (metal sulfide) was varied which turned out to have the most pronounced effect on the molecular weight obtained.

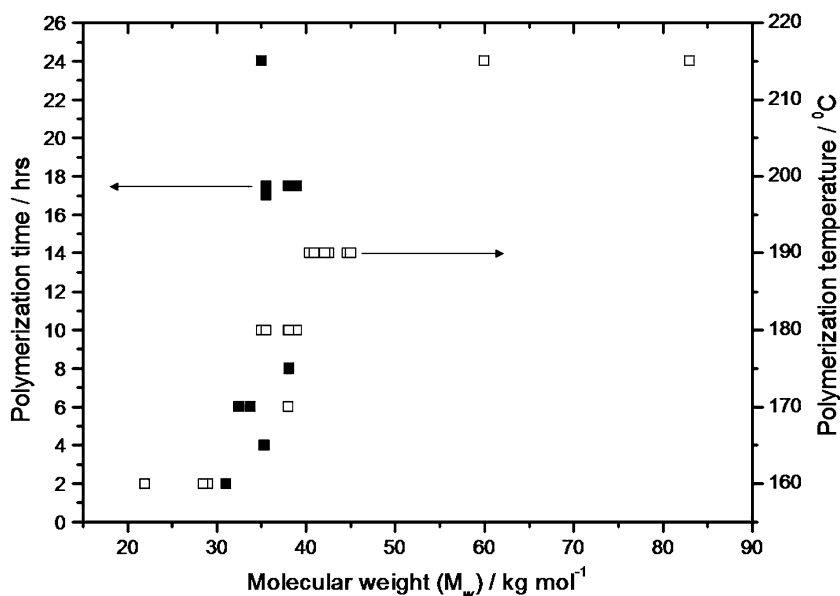
For the polymerization reaction only the two comonomers sDFDPhS and metal sulfide dissolved in NMP were used, in particular any additives such as acetates or hydroxides have been avoided, and oxygen was excluded since this is known to lead to unwanted side reactions [10, 11]. Because of the high hygroscopicity of NMP, sDFDPhS, and metal sulfides, traces of water may still be present. In fact, water is thought to react with metal sulfide and NMP to form H<sub>2</sub>S and 4-(*N*-methyl-amino)butanoate [10]. Therefore, the solution of metal sulfide in NMP has been preheated several times to partially eliminate water and H<sub>2</sub>S. The loss of sulfide (as H<sub>2</sub>S) has been compensated by adding an adequate amount of metal sulfide [12–16]. In order to avoid such complex procedures we kept the reaction conditions as dry as possible, and, for the initial batches, we varied the water content from 1 to 40% in a defined way. But this could not confirm any effect of the water content on the molecular weight of the final product (data are not shown).

The equivalent ratio of the comonomers (Na<sub>2</sub>S/sDFDPhS) was varied between 0.95 and 1.28, and the highest molecular weights  $M_w$  were obtained in the range 1.00–1.02 [taking into account purity of Na<sub>2</sub>S (98%)].

Reaction temperature and time was optimized for reactants concentrations of 0.6–0.7 g mL<sup>-1</sup>, which was found to be the highest concentration still allowing for effective stirring over the entire reaction period.

At a constant reaction temperature of  $T = 180$  °C, the molecular weight increases to  $M_w \sim 30$  kg mol<sup>-1</sup> within the first 2 h followed by a regime (2–18 h) of a modest increase of  $M_w$  to values around 40 kg mol<sup>-1</sup> (Fig. 1). For longer reaction times, the molecular weight tends to slightly decrease (e.g., to  $M_w \sim 35$  kg mol<sup>-1</sup> after 24 h).

The fast initial increase of the molecular weight is reflecting the high rate constants of both the fluorine substitution by metal sulfide resulting in a thiolate and the reaction of this aromatic thiolate with sDFDPhS until all sulfide dissolved in NMP is consumed [17]. After this period, more sulfides can only be produced by the slow dissolution of H<sub>2</sub>S (products of interaction between metal sulfide with NMP and water, see above), which is probably rate limiting for the overall polycondensation reaction. The reason for the degradation of the molecular weight at long times is not clear yet.



**Fig. 1** Polymerization time at a fixed temperature of  $T = 180\text{ }^{\circ}\text{C}$  (filled square) and temperature at a fixed reaction time of  $t = 18\text{ h}$  (open square) as a function of  $M_w$  of the obtained sPSS-204

For a fixed polymerization time ( $t = 18\text{ h}$ ), the molecular weight progressively increases with reaction temperature (Fig. 1), i.e., molecular weights of  $20\text{--}30\text{ kg mol}^{-1}$  are obtained at  $T = 160\text{ }^{\circ}\text{C}$ ,  $40\text{--}45\text{ kg mol}^{-1}$  at  $T = 180\text{ }^{\circ}\text{C}$ , and  $60\text{--}85\text{ kg mol}^{-1}$  at  $T = 215\text{ }^{\circ}\text{C}$  (autoclave).

Subsequently, we have varied the sulfide source, either by adding catalytic amounts of CsF or by substituting  $\text{Na}_2\text{S}$  by CaS or BaS. For the first, the idea was that  $\text{Cs}_2\text{S}$  formed through the reaction of CsF with  $\text{Na}_2\text{S}$  may more efficiently eliminate the fluoride group of sDFDPhS [18], for the latter the formation of poorly soluble fluorides ( $\text{CaF}_2$  or  $\text{BaF}_2$ ) was expected to drive the local reaction equilibrium toward the polycondensation product. In either case, no positive effect on the molecular weight of the product sPSS-204 was observed (see supporting information).

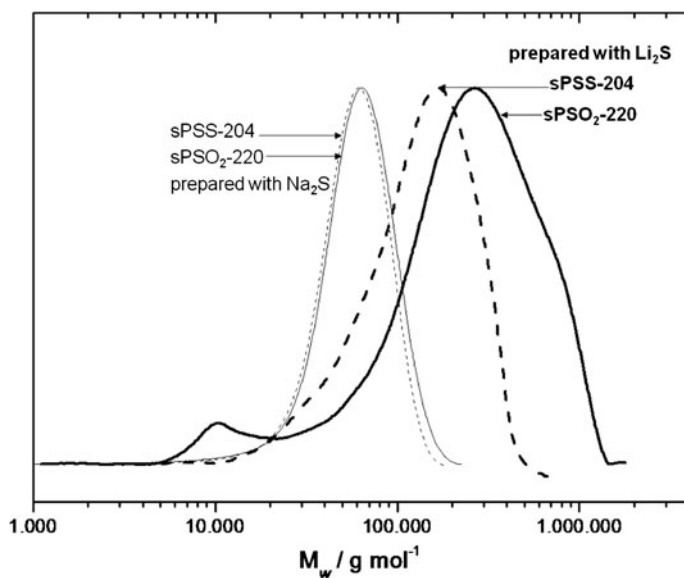
We have also tried  $\text{Li}_2\text{S}$  as a comonomer, and this led to an increase of the molecular weight of sPSS-204 by a factor of 2–5 (Table 1).

Instead of the expected increase of the molecular weight, oxidation of sPSS-204 (second step of reaction Scheme 1) leads to a slight decrease of the molecular weight and the polydispersity index (PDI) (see GPC profile in Fig. 2). While the latter is simply the consequence of the loss of low molecular weight fractions during the dialysis, the reason for the decrease of  $M_w$  remains unclear.

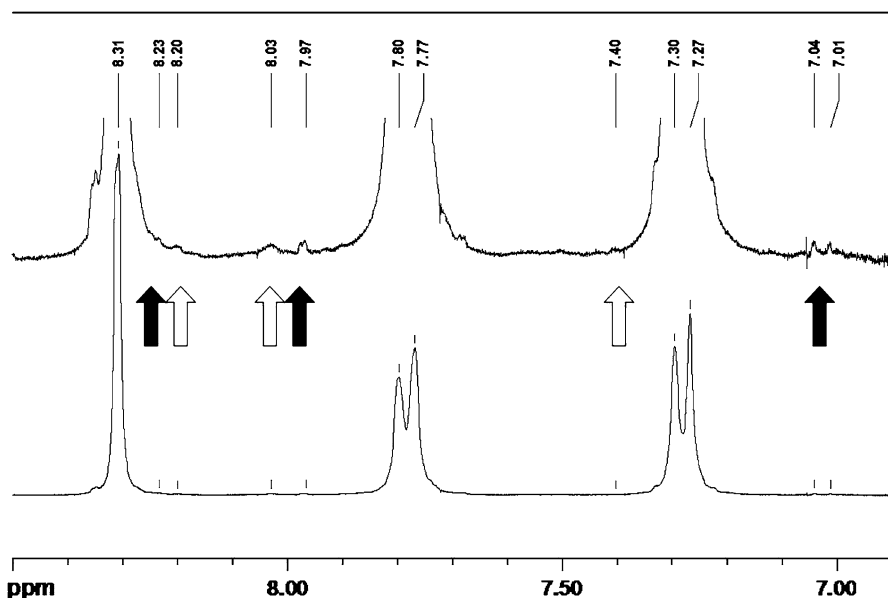
A first hint for a certain degree of branching is a shoulder at  $M_w \sim 10^6\text{ g mol}^{-1}$  in the GPC profile of sPSS-204 (see Fig. 2). This is actually supported by the corresponding  $^1\text{H}$  NMR spectra (Fig. 3) which shows, apart from the three main signal groups assigned to the three chemically distinguishable aromatic protons,

**Table 1** Molecular weights  $M_w$  and polydispersity index PDI of sPSS-204 and sPSO<sub>2</sub>-220 as obtained by the Li<sub>2</sub>S route

Temperature (°C)	Time (h)	Monomer/Li <sub>2</sub> S	$M_w$ (kg/mol)	PDI	$M_w^a$ (kg/mol)	PDI <sup>a</sup>
210	10	1.0011	150	2.3	130	1.6
210	10	1.0020	330	4	150	2.0
215	10	1.0030	170	3.4	130	1.6
215	10	1.0001	160	3.6	130	1.6
215	12	1.0000	120	2.2	95	1.7

<sup>a</sup> After oxidation (see second step in Scheme 1)**Fig. 2** GPC profiles of sPSS-204 prepared by using Na<sub>2</sub>S and Li<sub>2</sub>S. The profiles of the corresponding oxidized forms (sPSO<sub>2</sub>-220) are shown for comparison

some extra signals. Few of these signals can not be explained by end-functionalities (indicated with solid arrows on Fig. 3) and polymer weights calculated from the intensities of all extra signals (assuming linear chains) are lower than the values directly obtained by GPC (see above). This is further indication for polymer branching, and recent investigations on possible side reactions provided evidence for a reaction of the sulfonic group of the main polymer chain with fluoride functions of a monomer/oligomer under certain polymerization conditions [19]. Assuming that the unassigned <sup>1</sup>H-NMR signals originate from such branching points a density of such points between 0.6 and 0.8% (1 on every 120–170 sulfonic group) is calculated. In other words, sPSS-204 synthesized in the way described above is close to be linear but probably with some minor degree of branching with sulfonic groups being the branching points.



**Fig. 3**  $^1\text{H}$  NMR of sPSS-204: signals of fluorine end-groups (empty arrows) and signals of sulfon-branching (solid arrows)

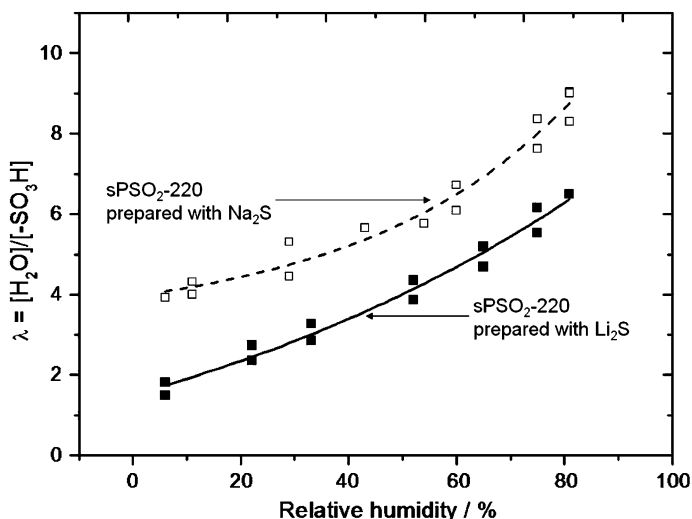
In order to examine the effects of the increased molecular weight on the properties of sPSO<sub>2</sub>-220, TGA, and water sorption experiments were performed on the sample with the highest molecular weight ( $M_w = 330$  kg/mol).

The TGA did not reveal any increase of stability against desulfonation and oxidation of sPSO<sub>2</sub>-220 which is not surprising considering the fact that even low molecular weight sPSO<sub>2</sub>-220 is known for its superior stability [6]. As observed for lower molecular weight samples, the combined TGA and mass spectrometry of the released products shows the onset of desulfonation only at  $T \sim 300$  °C before backbone degradation starts to occur around 350 °C. As reported and explained before, indications for the decomposition of the precursor sPSS-204 are already seen in the temperature range  $T = 230$ –250 °C. Properties as IEC, hydrolytic stability, and conductivity are similar to the material with lower molecular weight published earlier [6].

When it comes to the sorption of water, high molecular weight sPSO<sub>2</sub>-220 is still soluble in liquid water. But the residues obtained by evaporation of aqueous solutions are compact transparent membranes compared to powders obtained for low molecular weight materials. At low relative humidity (e.g., RH = 6%), high molecular weight sPSO<sub>2</sub>-220 takes up significantly less water ( $\lambda = 2$  for high molecular weight sPSO<sub>2</sub>-220 compared to  $\lambda = 4$  for low molecular weight sPSO<sub>2</sub>-220, see Fig. 4), and its characteristic microstructure is preserved up to higher temperatures and relative humidities (to be published).

In very dry states, there is no apparent change of the mechanical properties; even for very high molecular weights the high density of ionic groups makes sPSO<sub>2</sub>-220 very brittle.





**Fig. 4** Hydration number  $\lambda$  as function of relative humidity for sPSO<sub>2</sub>-220 with low (*dashed line*) and high molecular weight (*solid line*)

## Summary and outlook

The preparation of highly sulfonated poly(phenylene sulfone) (IEC = 4.45 meq g<sup>-1</sup>) by polycondensation of sulfonated difluorodiphenyl sulfone with metal sulfide and subsequent oxidation with hydrogen peroxide is optimized. The use of Li<sub>2</sub>S as a sulfide source, a high reaction temperature ( $T = 210$  °C), and a reaction time around 10 h are the clue to high molecular weight products (up to 300 kg/mol). The final yield is 84%.

The product is still water soluble and brittle in the dry state, but the water uptake at low relative humidity is significantly reduced compared to the water uptake of low molecular weight material. For combining the excellent stability and transport properties of sPSO<sub>2</sub>-220 with the mechanical properties required for PEM fuel cell applications, sPSO<sub>2</sub>-220 prepared in such a way is currently tested as main constituent of heterogeneous membrane structures such as interpenetrating networks, polymer blends, or simple physical mixtures with other polymers.

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