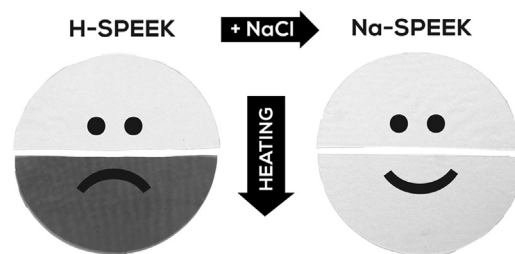


# Thermal Stability of Sulfonated Poly(Ether Ether Ketone) Films: on the Role of Protodesulfonation<sup>a</sup>

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Thin film and bulk, sulfonated poly(ether ether ketone) (SPEEK) have been subjected to a thermal treatment at 160–250 °C for up to 15 h. Exposing the films to 160 °C already causes partial desulfonation, and heating to temperatures exceeding 200 °C results in increased conjugation in the material, most likely via a slight cross-linking by H-substitution. It is well-known that the sulfonate proton plays a major role in the desulfonation reactions, and exchanging the protons with other cations can inhibit both protodesulfonation as well as electrophilic cross-linking reactions of the sulfonate group with other chains. Yet, the implications of such ion-exchange for the thermal processing of sulfonated polymer films has not been recognized. Our study demonstrates that the ion exchange stabilizes thin films and bulk SPEEK up to temperatures exceeding 200 °C, opening up ways for the thermal processing of SPEEK in the temperature range of 160–220 °C without adverse effects.



## 1. Introduction

Sulfonated poly(ether ether ketone) (SPEEK, Figure 1) is an anionic polymer that finds wide use as high-performance

membrane polymer that can be applied in water purification,<sup>[1–3]</sup> in proton exchange membrane (PEM) fuel cells,<sup>[4–6]</sup> and in dehydration of industrial gases.<sup>[7–9]</sup> For multiple reasons, SPEEK membranes are exposed to higher temperatures. PEM fuel cells have operating advantages at higher temperatures.<sup>[10,11]</sup> Additionally, during membrane preparation high temperature treatments are suggested to remove residual high boiling point solvents after membrane formation,<sup>[12]</sup> bring the material above its glass transition temperature to remove its thermal history,<sup>[4]</sup> or to perform temperature-promoted cross-linking.<sup>[13,14]</sup> Whereas, temperatures up to 200 °C are not uncommon in these procedures,<sup>[15]</sup> they can have detrimental effects on the integrity of SPEEK.<sup>[16]</sup>

Generally, thermal changes to SPEEK are reported to occur via three separate processes:<sup>[17,18]</sup> the removal of absorbed water and solvent ( $T = 50\text{--}150\text{ °C}$ ); temperature-promoted cross-linking, annealing and/or removal of the sulfonic acid group ( $T = 150\text{--}400\text{ °C}$ ); and backbone decomposition ( $T > 400\text{ °C}$ ). Especially the second temperature range is of interest, as it is associated with both desired and

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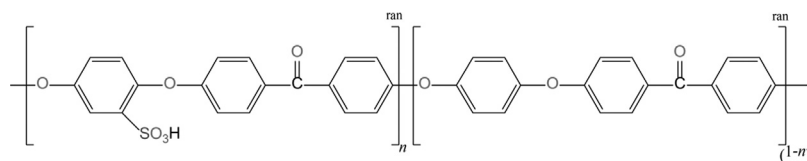
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<sup>a</sup>Supporting Information is available from the Wiley Online Library or from the author.



■ Figure 1. Structural formula of SPEEK with a degree of sulfonation  $n$ .

undesired reactions. Desulfonation is one of the major undesired reactions, because it affects the sulfonation degree and may enhance degradation reactions. Because the desulfonation reaction typically takes place through a protodesulfonation mechanism, the thermal stability of the sulfonate group is strongly dependent on the presence of a proton that takes the place of the sulfonate leaving group on the aromatic ring.<sup>[19]</sup> In the absence of a proton, desulfonation will not occur. Membrane performance studies and thermogravimetric analysis on bulk material, in which the sulfonate proton was exchanged by a sodium ion, showed indications of an enhanced thermal stability.<sup>[12,15,16,20]</sup> Nonetheless, the effect of exchanging the sulfonate proton for a different counter-ion on the thermal processing has hitherto not been fully appreciated and studied systematically for SPEEK films.

In this study, we have assessed the thermal stability of SPEEK thin films and bulk polymer in the temperature range of 160–250 °C over a time scale of 15 h, and have compared the stability of the proton-form H-SPEEK with that of the sodium-form Na-SPEEK. Thermogravimetric analysis (TGA) on the bulk polymer indicates an enhanced stability of the material in the sodium-form. By performing thermo-ellipsometric analysis (TEA), the stability of thin films has been studied in detail by tracking the thermally induced changes in the UV absorption spectrum of the material. These results indicate that already temperatures as low as 160 °C induce changes to H-SPEEK. Exchanging the proton by a sodium ion significantly enhances the thermal stability of the SPEEK films, allowing for thermal treatment at temperatures exceeding 200 °C without adverse effects.

## 2. Experimental Section

### 2.1. Materials

Poly(ether ether ketone) (PEEK) was purchased from Victrex. CaF<sub>2</sub> pellets were obtained from Crystran. NaCl (99.5% for analysis) was obtained from Acros Organics. Methanol (Emsure) and sulfuric acid 95–98% (EMPROVE) were purchased from Merck. DMSO-d<sub>6</sub> (99.5% atom D) for <sup>1</sup>H-NMR measurements was obtained from Sigma–Aldrich. Silicon wafers (100-oriented) were obtained from Okmetic. Water was deionized to 18.2 MΩ cm using a Milli-Q Advantage A10 system (Millipore). Nitrogen was dried with molecular sieve water absorbents, followed by removal of oxygen using an oxygen trap (outlet concentration <1 ppb O<sub>2</sub>).

### 2.2. PEEK Sulfonation

Sulfonated poly(ether ether) ketone was obtained by sulfonation of PEEK in sulphuric acid following the procedure described by Shibuya and Porter.<sup>[21]</sup> The obtained SPEEK was in the acidic form, where H<sup>+</sup> is the counter ion; from here on, it will be referred to as H-SPEEK. The degree of sulfonation was

determined by <sup>1</sup>H-NMR to be 84% following the procedure in literature<sup>[22]</sup> (see section <sup>1</sup>H-NMR for the details on the calculation).

### 2.3. SPEEK Conversion to Sodium Form

SPEEK with sodium as the counter ion, referred to as Na-SPEEK, was made by immersing H-SPEEK in a 2 M NaCl solution, ensuring a Na<sup>+</sup> excess of >500×. Each hour, the NaCl solution was substituted by a fresh solution to ensure complete conversion of the proton to the sodium form. After 3 h, the Na-SPEEK was rinsed with deionized water and dried for 48 h at 30 °C under vacuum. Part of the Na-SPEEK was converted back to the proton form. This back-converted SPEEK will be referred to as H<sup>+</sup>-SPEEK to distinguish it from H-SPEEK. H<sup>+</sup>-SPEEK was made by immersing Na-SPEEK in a stirred 1 M HCl solution for 17 h, ensuring a proton excess of >200×. Afterward, H<sup>+</sup>-SPEEK was rinsed with deionized water multiple times and dried for 48 h at 30 °C under vacuum.

### 2.4. Preparation of Freestanding H-SPEEK and Na-SPEEK Films

A 10 wt% solution of H-SPEEK in methanol was cast onto a glass plate. After methanol evaporation under atmospheric conditions for 24 h, the membranes were detached from the glass plate by immersion into deionized water. Subsequently, the membranes were dried for 48 h at 30 °C under vacuum. Na-SPEEK membranes were obtained by immersing H-SPEEK membranes in a 2 M NaCl solution accordingly, following the same procedure as described above for the SPEEK powder.

### 2.5. Preparation of H-SPEEK and Na-SPEEK Thin Films on Silicon Substrates

A 5 wt% solution of H-SPEEK or Na-SPEEK in methanol was spin-coated onto 2 × 2 cm<sup>2</sup> silicon wafers at 2000 rpm for 50 s. The spin-coated thin films were dried for 48 h at 30 °C under vacuum.

### 2.6. Characterization

#### 2.6.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a STA 449 F3 Jupiter (Netzch) fitted with a TG-only sample holder. Measurements were performed under 70 mL min<sup>-1</sup> nitrogen at a heating rate of 20 °C min<sup>-1</sup> from room temperature to 1200 °C. A temperature correction by melting standards and a blank correction with

an empty cup were carried out prior to the measurements. A sample mass of  $\approx 50$  mg was used, the exact mass being determined accurately by an external balance.

Gases evolving during the thermogravimetric analysis were transferred to a mass spectrometer (MS, QMS 403 D Aeolos, Netzsch). TGA and MS start times were synchronised, but no correction was applied for the time offset caused by the transfer line time (estimated  $< 30$  s, systematic offset). First, a bar graph scan for mass-to-charge ratio ( $m/z$ ) 1–100 amu was performed to determine the evolving  $m/z$ -numbers. The detected  $m/z$ -numbers were selected and recorded more accurately in multiple-ion-detection mode, with a dwell time of 0.5 sec per  $m/z$ -value and a resolution of 50.

### 2.6.2. Photographs of Heated SPEEK

Photographs of SPEEK were taken of fresh, freestanding films of H-SPEEK and Na-SPEEK, and of freestanding films of H-SPEEK and Na-SPEEK that were heated for 15 h at  $190 \pm 10$  °C in a furnace under ultrapure nitrogen.

### 2.6.3. ATR-FTIR

Fourier Transform Infrared Spectroscopy (FTIR) in Attenuated Total Reflection (ATR) mode was performed on freestanding films using a Tensor 27 Spectrometer equipped with a diamond crystal (Bruker Optics Inc., Germany), prior to and after a thermal treatment of the films under ultrapure nitrogen. The spectra were run against an empty background, baseline corrected using a rubberband baseline correction with a single iteration, and normalized before plotting.

### 2.6.4. $^1\text{H-NMR}$

The  $^1\text{H-NMR}$  spectra were recorded on an Ascend 400 (Bruker) at a resonance frequency of 400 MHz. For each analysis, 5 mg of polymer was dissolved in 1 ml of  $\text{DMSO-d}_6$ . NMR data were acquired for 16 scans. From the  $^1\text{H-NMR}$  spectra, the degree of sulfonation was calculated following the procedure outlined in literature.<sup>[22]</sup> In this method, the degree of sulfonation is calculated from the ratio of the surface areas of the peaks stemming from the proton neighbouring the sulfonic acid to that of the other protons.

### 2.6.5. UV–VIS Absorption Spectroscopy

UV–VIS spectra were recorded on a Cary 300 Spectrophotometer (Varian) with a spectral range of 200–800 nm, a resolution of 1 nm and a scan rate of  $600 \text{ nm min}^{-1}$ , on a solution of SPEEK in ethanol in a quartz cuvette.

### 2.6.6. Ellipsometry

Spectroscopic ellipsometry measurements were conducted on a M2000X ellipsometer (J.A. Woollam Co.) in the full wavelength range of 210–1000 nm. For measurements using the  $\text{CaF}_2$ -substrate, the ellipsometer was used in transmission mode, and the background was taken in air. For room temperature measurements using silicon wafers as substrate, measurements were performed at  $70^\circ$  angle of incidence. Temperature-controlled

experiments were performed on layers on silicon wafers. For these measurements, the M2000X was equipped with a HTC200 HeatCell accessory. Temperature calibration was performed using melting point standards.<sup>[23]</sup> Measurements were performed at a  $70^\circ$  angle of incidence. During experiments, the hot stage was continuously purged with nitrogen. The thermal treatment program consisted of a 2-h dwell at room temperature, followed by heating the material to the desired temperature with a heating rate of  $2.5 \text{ }^\circ\text{C min}^{-1}$ . The dwell time was 15 h, and after the dwell the sample was cooled to room temperature at  $2.5 \text{ }^\circ\text{C min}^{-1}$ .

### 2.6.7. Analysis of Ellipsometry Data

Analysis of the obtained optical spectra was performed using CompleteEase (version 4.86, J.A. Woollam Co.). The used optical constants for silicon were taken from the built-in library, and the thickness of the native oxide was fixed at 2 nm.

Parameterization of the optical dispersion of SPEEK was performed using Kramers–Kronig consistent B-Splines.<sup>[24]</sup> In order to obtain the optical dispersion reproducibly, the following steps were taken. First, the layer thickness was determined by fitting a Cauchy optical dispersion in the transparent range ( $\lambda = 500$ – $1000$  nm). Taking into account optical anisotropy in the layers<sup>[25]</sup> was not required to accurately model the absorption spectra. With fixed thickness, the layer was parameterized by B-Splines, with the node resolution set to 0.15 eV, the B-Splines forced to be Kramers–Kronig consistent, and  $\epsilon_2$  forced to be a positive number. Subsequently, the wavelength range of the B-Spline was expanded with increments of 0.15 eV, until it spanned the full wavelength range of the measurement. The node tie-offs at 0.640 and 0.840 eV were then forced to zero. This last step was performed to be able to output the nodes of the B-Spline in such a way that the optical dispersions could be reconstructed from the output data, using Matlab software and the approach outlined by Johs and Hale.<sup>[24]</sup> Finally, all parameters, i.e., thickness and optical dispersion, were fit using the B-Spline function.

For the temperature-controlled measurements, exactly the same approach was followed, with the exception that the temperature-dependent optical model for silicon was selected.

### 2.6.8. Conversion of Extinction Coefficient to Absorption Coefficient

In order to be able to directly compare the results of spectroscopic ellipsometry, transmission intensity of spectroscopic ellipsometry, and UV–VIS analysis, the extinction coefficient  $k$  (–) was converted to the absorption coefficient  $\alpha$  ( $\text{nm}^{-1}$ ) by  $\alpha = 4\pi k \lambda^{-1}$ , with  $\lambda$  (nm) being the wavelength of the light. The transmission intensity  $I$  (–) was converted to the absorbance by  $A$  (–) by  $A = -\ln(I/I_0)$ , with  $I_0$  (–) the intensity of the incident beam before transmission.

## 3. Results and Discussion

### 3.1. Influence of the Counter-Ion on the Thermal Stability of SPEEK

Figure 2 shows the mass loss and evolved gases that are detected upon heating of H-SPEEK, Na-SPEEK, H<sup>+</sup>-SPEEK, and

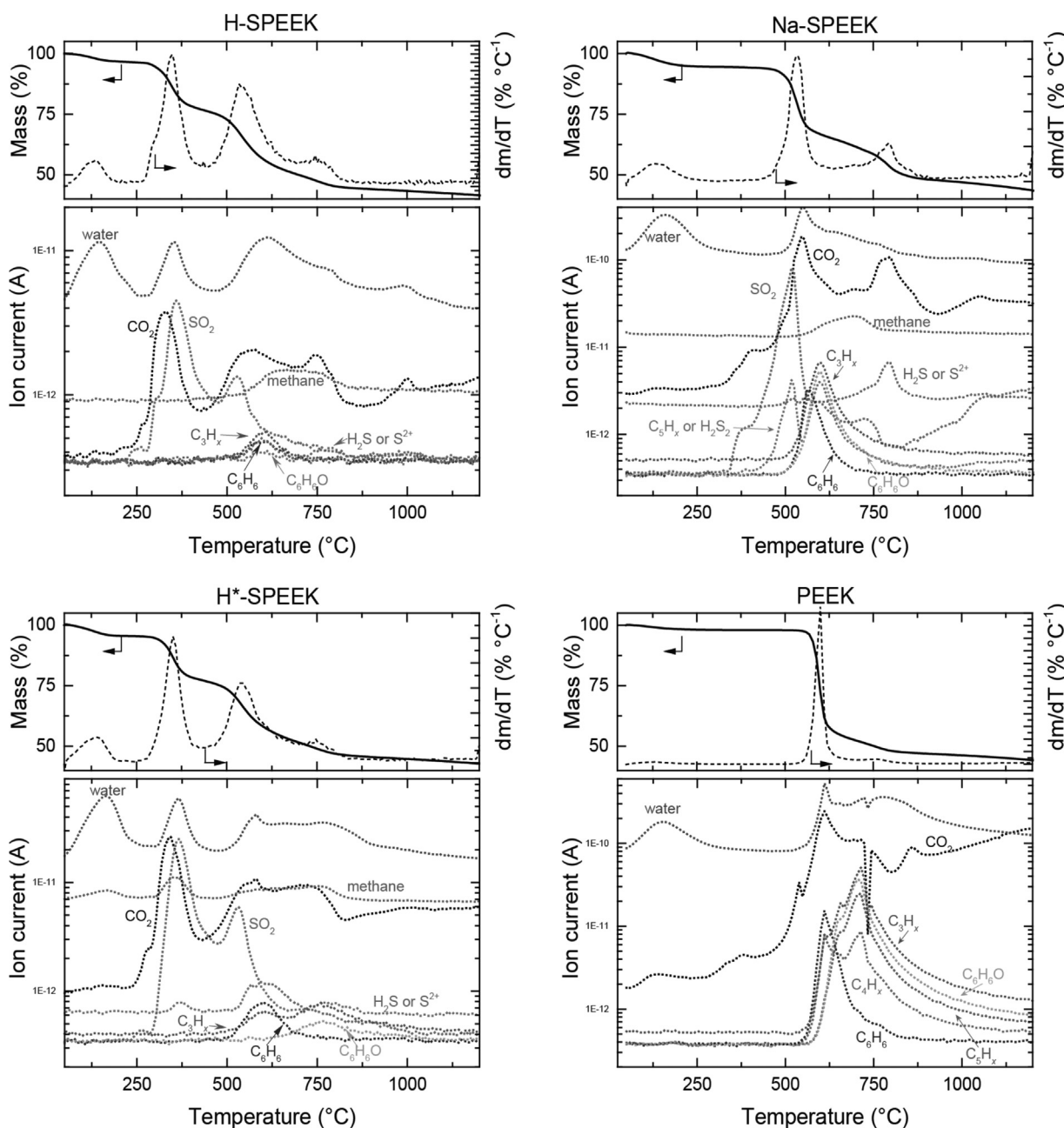


Figure 2. TGA-MS spectra of H-SPEEK (top left), Na-SPEEK (top right), H\*-SPEEK (bottom left) and PEEK (bottom right), all recorded with a heating rate of  $20\text{ }^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere. The raw  $m/z$ -data is available in the Supporting Information, Figure S9–S12.

PEEK. In these spectra, the identical low mass loss below  $200\text{ }^{\circ}\text{C}$  is accompanied by the release of water and can be attributed to removal of absorbed water from the material. For H-SPEEK, mass loss associated with removal of water,  $\text{CO}_2$  and  $\text{SO}_2$  sets on at  $250\text{ }^{\circ}\text{C}$  and reaches a peak at  $350\text{ }^{\circ}\text{C}$ . There are two possible sulfur sources for the evolution of  $\text{SO}_2$ : the sulfonate group or residual sulfuric acid. The presence of the latter has been proposed for SPEEK with high degrees of sulfonation.<sup>[6]</sup> Indeed, the release of  $\text{SO}_2$  takes place close to the boiling point of  $\text{H}_2\text{SO}_4$ .<sup>[26]</sup> To verify this

hypothesis, Na-SPEEK, for which the  $\text{SO}_2$  release at  $250\text{ }^{\circ}\text{C}$  was absent, was converted back to H\*-SPEEK, using hydrogen chloride to avoid the sulfuric counter ion. The mass loss spectrum obtained for the H\*-form is strikingly similar to that of the original H-form, thus rejecting the hypothesis that residual  $\text{H}_2\text{SO}_4$  is the source of  $\text{SO}_2$  formation. Hence, it can be concluded that the sulfonate group is the origin of the  $\text{SO}_2$ , and that exchange of the proton by sodium prevents the reaction that produces  $\text{SO}_2$ . The absence of this  $\text{SO}_2$ -loss in the sodium-exchanged

Na-SPEEK is a direct evidence of the enhanced thermal stability of the Na-SPEEK compared to H-SPEEK, and matches previous experiments.<sup>[16,20]</sup>

Between 450 and 650 °C, all SPEEK-forms show a strong mass loss, associated with the evolution of CO<sub>2</sub> and SO<sub>2</sub>, followed by a release of aromatic compounds. The evolution of SO<sub>2</sub> indicates that sulfur-containing groups were still present at these temperatures in both materials. Around 750 °C, a final mass loss step takes place that is accompanied by the release of CO<sub>2</sub>. A similar step is observed in the case of PEEK. This implies that the CO<sub>2</sub> loss is due to degradation of the polymer backbone, and is independent on the sulfonation history of the polymer.

For H-SPEEK, the release of SO<sub>2</sub> (*m/z* = 64) in two distinct steps with onsets at ≈250 and ≈500 °C is an indication for the presence of sulfur in two different forms in the material. The majority of the SO<sub>2</sub>-release occurs in the first step (note that the log-scale over-emphasises gases present in smaller amounts). Previous studies on SPEEK decomposition only reported SO<sub>2</sub> release in a unimodal peak between 200 and 400 °C (a temperature shift of some tens of degrees could be the result of differences in heating rate), although not all studies include an evolved-gas analysis up to a temperature of 500 °C.<sup>[13,15,17,27]</sup>

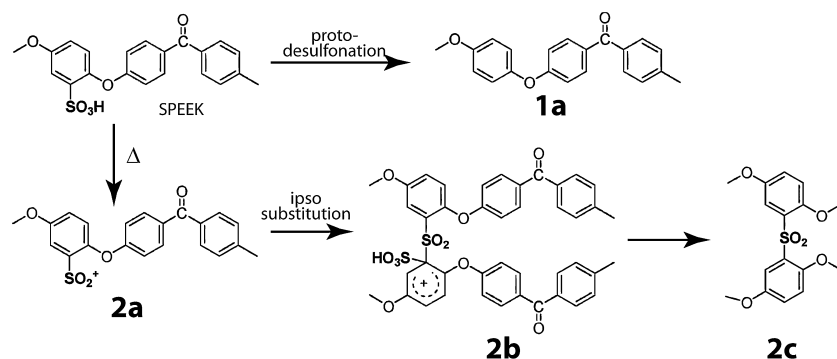
Scheme 1 summarizes the two possible routes for SO<sub>x</sub> loss from the material: protodesulfonation or ipso substitution. If a sulfone (R–SO<sub>2</sub>–R) bridge is formed by ipso substitution, this sulfone bridge can in turn decompose at higher temperatures, yielding the release of a second SO<sub>x</sub> species. Whether SO, SO<sub>2</sub>, or SO<sub>3</sub> is released from the material, depends on the reaction mechanism. Thermal protodesulfonation is typically said to yield an SO<sub>3</sub> group, although a two-stage process with cleavage of a SO<sub>2</sub> group has been registered in mass spectrometry.<sup>[28]</sup> Upon ipso substitution, SO<sub>2</sub> release would be expected. It has to be noted that the ipso substitution reaction was found to depend strongly on the presence of traces of solvent: it was found to occur in the presence of DMSO,<sup>[13,15]</sup> but not

with NMP, DMAc, or DMF.<sup>[29]</sup> A third possible reaction, H-substitution, results in cross-linking as well, but will not cause SO<sub>2</sub> release.<sup>[13]</sup> It will, however, result in the formation of cross-links inside the material under release of water, and can therefore be the origin for the different forms of sulfur in the material.

Discerning between the two possible mechanisms for the first SO<sub>2</sub> loss, which are given in Scheme 1, is not straightforward. Both routes are effectively blocked by the sodium exchange. In addition, differences between SO<sub>2</sub> and SO<sub>3</sub> are difficult to discern by MS, because SO<sub>3</sub> fragments upon electron impact to [SO]<sup>+</sup>, [SO<sub>2</sub>]<sup>+</sup>, and [SO<sub>3</sub>]<sup>+</sup> (in ≈2.1:1.2:1 ratio).<sup>[30]</sup> Mikhailenko et al. have suggested that the release of CO<sub>2</sub> prior to the SO<sub>2</sub> release could indicate the formation of an electrophile (RSO<sub>2</sub><sup>+</sup>) available for cross-linking via ipso or H-substitution, under the release of a hydroxyl radical that can directly react with the main chain.<sup>[27]</sup> However, as no further evidence for these degradation reactions is seen, and CO<sub>2</sub> that has been sorbed in the proton-rich watery environment present in the material cannot be excluded as alternative CO<sub>2</sub> sources, we consider this reaction unlikely in our system.

The combination of visual observation, NMR, and FTIR has been used to conclusively assert the thermally induced effects, and to better understand the differences between H-SPEEK and Na-SPEEK. Figure 3 visualizes the differences between the proton and sodium forms after thermal treatment of both films. Here, the films are shown before and after heating to 190 ± 10 °C for 15 h. Before thermal treatment, both films are transparent, and the H-SPEEK has a yellowish appearance. After heating the material, the strong color change into red in the H-SPEEK confirms the substantial chemical changes in the material. Although, at this temperature the TGA results do not reveal significant mass changes of the material, nor the release of gaseous degradation products, the long dwell time can significantly increase the progress of the reaction.<sup>[31]</sup> The red color of the treated H-SPEEK is a manifestation of the development of

chromophoric groups. If only desulfonation had taken place, the color could only shift to the brown-greyish color of PEEK, which would probably not be observed on such thin films. Because of the intense red color, the desulfonation reaction alone cannot be responsible for the color change. Most likely, a heating-induced cross-linking reaction through H-substitution increases the conjugation of the π-bonds, resulting in an increased light absorption. After the thermal treatment, H-SPEEK has lost its flexibility and has turned into a brittle material. The color change after the long-term treatment is irreversible. This is in contrast to the



**Scheme 1.** Two possible reactions involving loss of SO<sub>x</sub>: 1. Protodesulfonation, and 2. Formation of a SO<sub>2</sub><sup>+</sup> electrophile (2a) followed by cross-linking via ipso-substitution on the sulfonic acid moiety (2b and c), as suggested by Di Vona et al.<sup>[13]</sup>



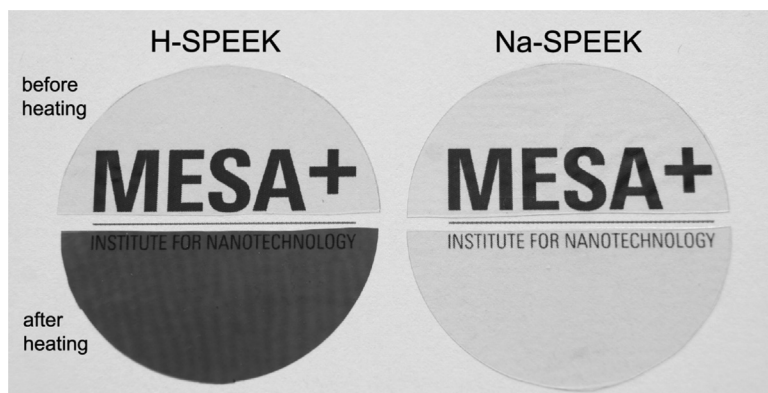


Figure 3. Photographs of H-SPEEK (left) and Na-SPEEK (right) before heating (top) and after heating (bottom) in nitrogen at 190 °C for 15 h.

reversible color changes that have been reported previously for short-term treatments<sup>[32]</sup> that are attributed to  $\pi$ - $\pi$  stacking induced by the removal of water at elevated temperatures.

Although, the effects of thermal treatment on the color of the H-SPEEK appear dramatic, the changes in the infrared spectrum upon this treatment are only limited. Figure 4 shows the infrared spectrum for both H-SPEEK and Na-SPEEK prior to and after thermal treatments. Again, strong changes are seen upon thermal treatment of H-SPEEK, whereas Na-SPEEK remains unchanged upon heating to 190 °C.

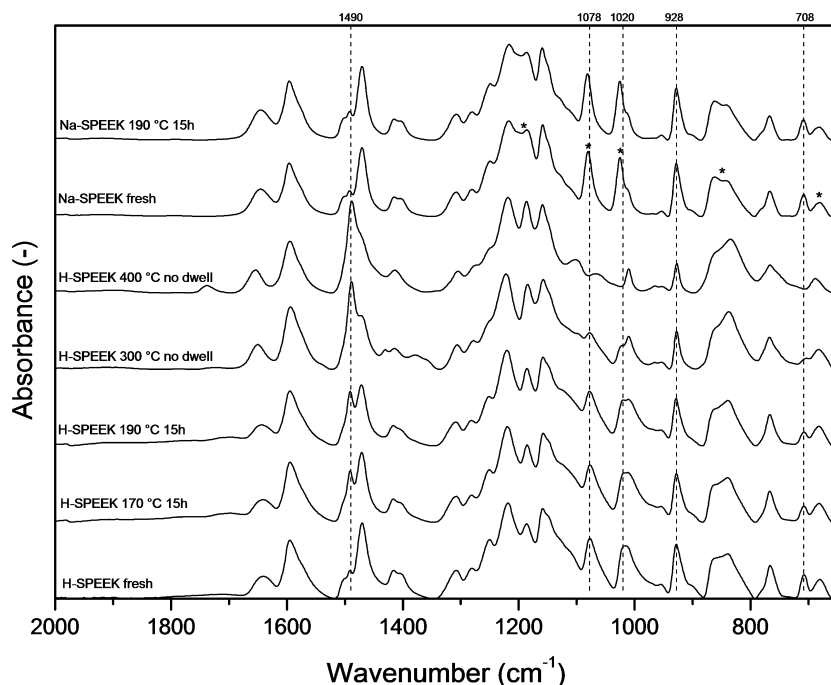


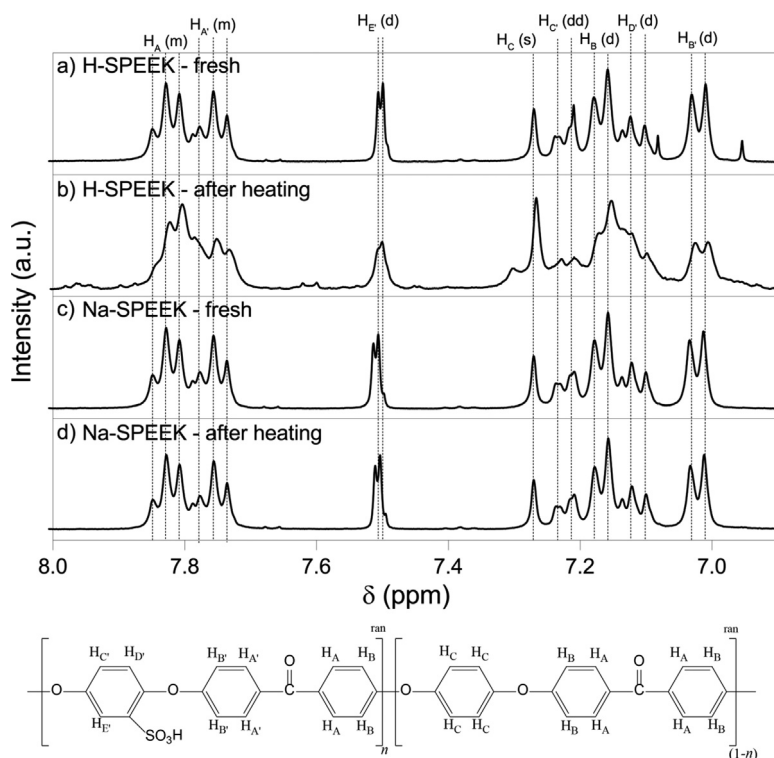
Figure 4. ATR-FTIR spectra of H-SPEEK and Na-SPEEK treated at different temperatures. The peaks marked by an asterisk (\*) in the spectrum of fresh Na-SPEEK show a difference from the fresh H-SPEEK spectrum, and therefore likely involve the sulfonate group. The band assignment is given in Table S1 and the spectra in the wavelength range 4000–2000  $\text{cm}^{-1}$  is given in Figure S7 in the Supporting Information.

Our sodium exchange allows for direct identification of the peaks involving the sulfonate group, which are indicated by an asterisk in Figure 4. In combination with the peak changes upon sulfonation indicated in ref.<sup>[29]</sup> this allows for accurate identification of phenyl and sulfonate peaks. The full band assignment is given in Table S1 in the Supporting Information. Here, the most important peaks are found at 1490 and 1471  $\text{cm}^{-1}$ . The change in the ratio between these peaks upon heating shows the identical trend as for a chemically obtained lower degree of sulfonation of PEEK.<sup>[29]</sup> This conclusion is further supported by the

changes in the peaks at 1078, 1020, and 767  $\text{cm}^{-1}$ , which are all peaks associated with either sulfonic acid groups or the substitution of sulfonate groups on a phenyl ring. Heating does not introduce new peaks, except for the peaks at 1375  $\text{cm}^{-1}$  (w) after heating to 300 °C and at 1104 (w) and 1737  $\text{cm}^{-1}$  (w) after heating to 300 and 400 °C, respectively. All these peaks fall outside the typical range for sulfone cross-links ( $\text{R-SO}_2\text{-R}$ ) that is given as 1370–1290 and 1170–1110  $\text{cm}^{-1}$ , and which should be very strong.<sup>[33]</sup> Therefore, we conclude that, if any, the amount of sulfone cross-links formed in the H-SPEEK upon heating is too low to be obvious from the infrared analysis.

The thermally induced changes in the  $^1\text{H-NMR}$ -spectrum of SPEEK, shown in Figure 5, are another demonstration of the distinct characteristics of the proton and sodium form of SPEEK. The NMR spectrum for H-SPEEK agrees well with results previously reported in literature.<sup>[34]</sup> As can be seen from the spectrum, the exchange of the sulfonate proton by a sodium ion results in a slight deshielding of the  $\text{H}_{\text{E}}$ -proton, resulting in a small downfield shift. A similar effect is seen for the  $\text{H}_{\text{B}}$ -protons. The sodium exchange did not influence any of the other peaks. For the sodium form, the thermal treatment step induced no changes at all in the material's structure. For correctly discerning the  $\text{H}_{\text{A}}$  and  $\text{H}_{\text{A}}$ -protons, a 2D ( $^1\text{H COSY}$ ) spectrum was recorded (see Supporting Information, Figures S1 and S2).

For H-SPEEK, definite changes are introduced by the thermal treatment, resulting in strong changes in the chemical environment of the protons. Although most peaks still remain visible,



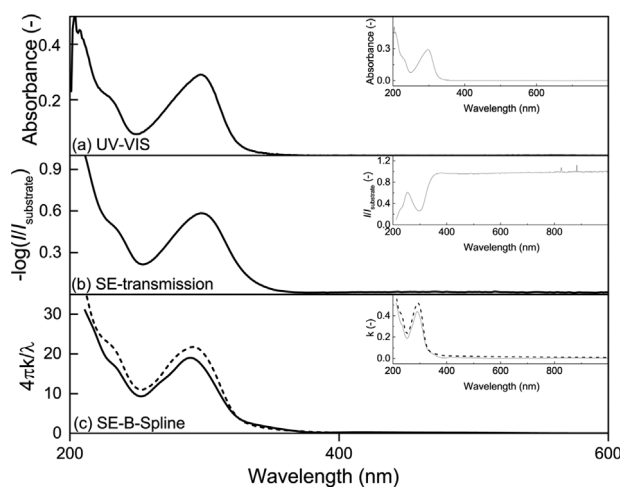
**Figure 5.** Absorption spectra of H-SPEEK (solid line) and PEEK (dashed line) determined by (a) UV–VIS on SPEEK dissolved in ethanol, (b) spectroscopic ellipsometry in transmission mode, and (c) spectroscopic ellipsometry B-spline modeling. All data were converted to a parameter that is linearly proportional to the absorbance. The inserts show the original data over the whole wavelength range.

From the NMR-spectrum of SPEEK, the degree of sulfonation can be determined.<sup>[22]</sup> For the untreated H-SPEEK and both untreated and treated Na-SPEEK, this calculation could be applied accurately. For all three SPEEK-types, the degree of sulfonation was determined to be unchanged at 84%, indicating no structural changes in these polymers. For the heat-treated H-SPEEK, the apparent degree of sulfonation was calculated to be 78% after heating at 160 °C for 15 h and 65% after heating at 190 °C for 15 h. Because some changes in the spectrum could not be assigned to specific groups, wrong groups can be included in the peak integration, and these values should be considered with caution. For the treatment at 183 °C at 15 h, the loss of sulfonate groups from the material is supported by the detected release of SO<sub>2</sub> (see Supporting Information, Figure S8).

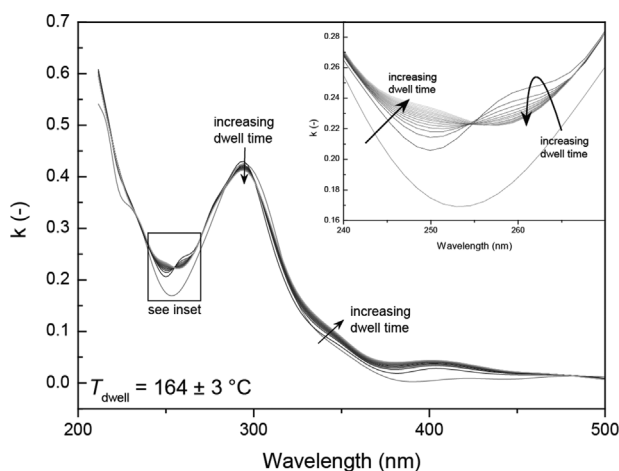
### 3.2. Long-Term Stability of Thin Films

Figure 6 shows the absorption spectra obtained by UV–VIS absorption spectroscopy, by transmission mode ellipsometry, and reflectance mode ellipsometry.

strong peak broadening has occurred. Peak broadening can be a result of reduced mobility of the studied molecules and can therefore be an indication of cross-linking reactions. Alternatively, it can be the result of a mixture of molecules for which the peaks overlap, for instance through cross-linking by H-substitution. As a single peak without overlap with other peaks, the H<sub>C</sub>-peak is an ideal peak to study the effects of the thermal treatment. Upon desulfonation, the removal of one sulfonate group results in the creation of four H<sub>C</sub>-protons at the expense of the H<sub>C'</sub>, H<sub>D'</sub>, and H<sub>E'</sub> peaks. In the case of a thermally induced ipso substitution reaction, the electron-withdrawing SO<sub>3</sub><sup>-</sup> group gets exchanged for an SO<sub>2</sub> group that is electron-withdrawing as well. Consequently, the changes in the <sup>1</sup>H-NMR spectra would be minor peak shifts. The significant increase in the H<sub>C</sub>-peak confirms the occurrence of desulfonation reactions. This conclusion is further supported by the decrease of the H<sub>A'</sub>, H<sub>B'</sub>, H<sub>D'</sub> and H<sub>E'</sub>-peaks, and in line with spectra of SPEEK at lower sulfonation degrees.<sup>[22]</sup> The 2D (<sup>1</sup>H COSY) spectra (see Supporting Information, Figure S2 and S3) confirms the presence of three new groups of coupled protons with apparent downfield shifts from the base material, indicating the occurrence of side reactions during the desulfonation.



**Figure 6.** Absorption spectra of H-SPEEK (solid line) and PEEK (dashed line) determined by (a) UV–VIS on SPEEK dissolved in ethanol, (b) spectroscopic ellipsometry in transmission mode, and (c) spectroscopic ellipsometry B-spline modeling. All data were converted to a parameter that is linearly proportional to the absorbance. The inserts show the original data over the whole wavelength range.



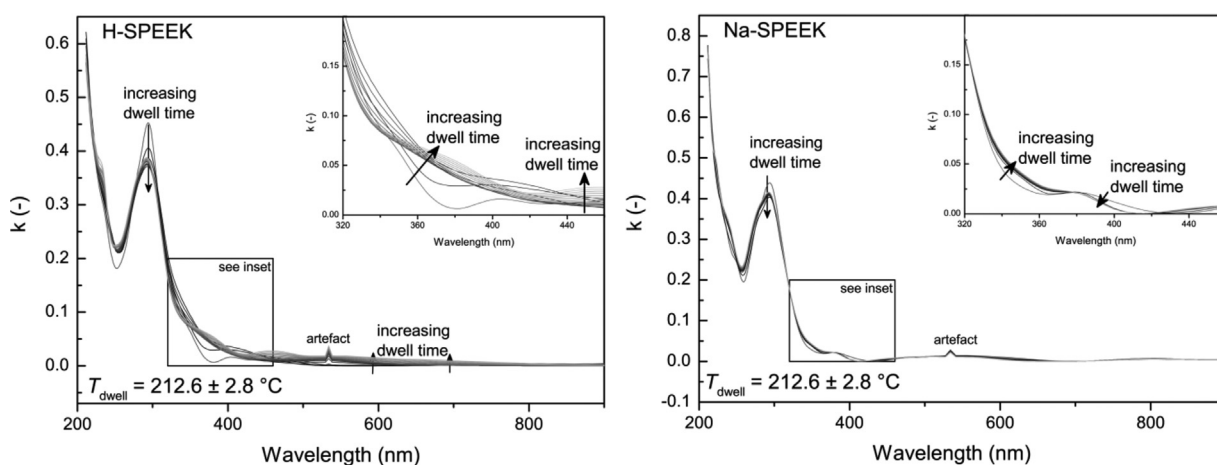
**Figure 7.** Absorption spectra of H-SPEEK under nitrogen before thermal treatment (red) and after 0 h (black) to 15 h (light grey) of dwell at  $164 \pm 3$  °C, obtained by in-situ ellipsometry. The change between the untreated and the 0 h dwell samples is induced by the heating ramp.

The close agreement between the spectra establishes ellipsometry as a suitable technique to study the changes in the thin supported films. This is in particular beneficial for polymers such as PEEK that have low solubility in common solvents, and are therefore difficult to study with, e.g., UV-VIS. The close resemblance between the PEEK and H-SPEEK ellipsometry spectra indicate that the sulfonation of the polymer does not induce large changes in its light absorption properties.

The changes in the absorption spectrum of H-SPEEK upon prolonged exposure to a temperature of 164 °C are given in Figure 7. The red line corresponds to untreated H-SPEEK and has the same shape as in Figure 6. The prolonged exposure to 164 °C for 15 h induced multiple changes in the

absorption spectrum. The increase in absorbance at wavelengths higher than 320 nm, and the slight decrease of the peak at  $\lambda = 300$  nm, are in line with earlier observations made by temperature-controlled UV-VIS.<sup>[32]</sup> Notable is the development of two peaks at 250 and 260 nm. The peak at 250 nm shows a progressive growth with increasing dwell times; the peak at 260 nm first appears but later disappears during the prolonged exposure to this temperature. The clear development of individual peaks corresponds to changes in the structure of SPEEK. Absorptions around 250 nm are generally associated with  $n-\pi^*$  transitions or with  $\pi-\pi^*$  transitions in conjugated systems.<sup>[33]</sup> It is therefore difficult to assign this peak specifically, as it can be due to non-bonding electrons of oxygen in either the sulfonate, the ether, or the carbonyl groups, or due to an increase in conjugation within the material because of thermal cross-linking. Given the results of the TGA-MS, FTIR, and NMR on the bulk SPEEK, a higher electron density in the aromatic rings resulting from protodesulfonation would be the most plausible explanation. Treatment of H-SPEEK at temperatures of 183 and 193 °C (see Supporting Information, Figure S4–S6) resulted in similar, but more pronounced, trends. For Na-SPEEK, treatment at 183 °C introduces only minor changes in the spectrum, indicating that the absence of the sulfonate proton prevents the thermal reactions from taking place (see Supporting Information, Figure S4).

At a treatment temperature of  $\approx 220$  °C (Figure 8) and higher (Supporting Information, Figures S4–S6), the differences between the proton and sodium form are even more pronounced. Here, the region of interest is the wavelength range of 300 nm upward, in which chromophoric behavior is typically limited to strongly conjugated structures.<sup>[33]</sup> For H-SPEEK, light absorption increases over nearly the full wavelength range, and strong changes take



**Figure 8.** The absorption spectrum of H-SPEEK (left) and Na-SPEEK (right) under nitrogen before thermal treatment (red) and after 0 h (black) to 15 h (light grey) of dwelling at  $213 \pm 3$  °C, obtained by in-situ ellipsometry. The change between the untreated and the 0 h dwell samples is induced by the heating ramp.



place around  $\lambda = 380$  nm. The increase in absorption is in line with the visual observations presented in Figure 3. For Na-SPEEK, the changes in the spectrum are limited to minor changes in the absorption in the 300–400 nm wavelength range.

#### 4. Conclusion

The thermal stability of SPEEK (H-SPEEK) and its sodium-exchanged form (Na-SPEEK) have been studied at temperatures of 160–250 °C, in shorter heating rate experiments and for longer experiments by dwelling for 15 hours. For H-SPEEK, desulfonation reactions are found to occur already at temperatures as low as 160 °C, followed by increased conjugation in the material, most likely via slight cross-linking on phenyl rings by H-substitution at temperatures exceeding 200 °C.

The thermal stability of SPEEK is found to be strongly enhanced upon ion exchange of the sulfonate proton with a sodium ion. For the bulk polymer, this exchange shifts the onset of the first SO<sub>2</sub> removal to higher temperatures by 100 °C. This shift is attributed to the inhibition of the protodesulfonation reaction. Experiments in which the Na-SPEEK is converted back to the proton form eliminate residual sulfuric acid as a possible cause for sulfur release at 250–350 °C.<sup>[6]</sup> The absence of sulfonated solvents in our synthesis, and the fact that H<sub>2</sub>SO<sub>4</sub> could be excluded as a sulfur source, is a strong indication for the involvement of the sulfonate groups for both mass losses. For H-SPEEK, TGA-MS, FTIR, and <sup>1</sup>H-NMR are separately not conclusive whether the SO<sub>2</sub> loss from the material is due to protodesulfonation or cross-linking through sulfone bridges via ipso substitution. However, the fact that all three techniques individually show evidence for desulfonation and only limited evidence for the formation of sulfone bridging groups at temperatures exceeding 160 °C, suggest that the SO<sub>2</sub> loss is mainly due to the protodesulfonation mechanism. Although this would indicate a possibility of using a specifically designed thermal treatment program to obtain SPEEK with a targeted degree of desulfonation, the fact that not all sulfur can be removed from the material before main-chain degradation occurs, indicates that some sulfur moieties remain stable inside the material. As a result, full desulfonation of a SPEEK thin film into a PEEK thin film appears to be impossible.

#### 5. Abbreviations

PEEK	polyether ether ketone
SPEEK	sulfonated PEEK
H-SPEEK	proton form of SPEEK
Na-SPEEK	sodium form of SPEEK

H\*-SPEEK proton form of SPEEK obtained after back-exchange of Na-SPEEK with H<sup>+</sup>

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- [1] T. He, M. Frank, M. H. V. Mulder, M. Wessling, *J. Membr. Sci.* **2008**, *307*, 62.
- [2] C. Ba, J. Economy, *J. Membr. Sci.* **2010**, *362*, 192.
- [3] W. R. Bowen, T. A. Doneva, H. Yin, *J. Membr. Sci.* **2002**, *206*, 417.
- [4] A. Carbone, R. Pedicini, G. Portale, A. Longo, L. D'Ilario, E. Passalacqua, *J. Power Sources* **2006**, *163*, 18.
- [5] L. Jörisen, V. Gogel, J. Kerres, J. Garche, *J. Power Sources* **2002**, *105*, 267.
- [6] S. Kaliaguine, S. Mikhaïlenko, K. Wang, P. Xing, G. Robertson, M. Guiver, *Catal. Today* **2003**, *82*, 213.
- [7] M. L. F. Giuseppin, P. J. Smits, G. W. Hofland, Subcritical gas assisted drying of biopolymer material. US2012/0316331 A1, **2012**.
- [8] L. Jia, X. Xu, H. Zhang, J. Xu, *J. Appl. Polym. Sci.* **1996**, *60*, 1231.
- [9] H. Sijbesma, K. Nymeijer, R. van Marwijk, R. Heijboer, J. Potreck, M. Wessling, *J. Membr. Sci.* **2008**, *313*, 263.
- [10] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D. P. Wilkinson, Z.-S. Liu, S. Holdcroft, *J. Power Sources* **2006**, *160*, 872.
- [11] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, *J. Membr. Sci.* **2001**, *185*, 73.
- [12] A. L. Khan, X. Li, I. F. J. Vankelecom, *J. Membr. Sci.* **2011**, *372*, 87.
- [13] M. L. Di Vona, E. Sgreccia, S. Licocchia, G. Alberti, L. Tortet, P. Knauth, *J. Phys. Chem. B* **2009**, *113*, 7505.
- [14] S. D. Mikhaïlenko, K. Wang, S. Kaliaguine, P. Xing, G. P. Robertson, M. D. Guiver, *J. Membr. Sci.* **2004**, *233*, 93.
- [15] B. Maranesi, H. Hou, R. Polini, E. Sgreccia, G. Alberti, R. Narducci, P. Knauth, M. L. Di Vona, *Fuel Cells* **2013**, *13*, 107.
- [16] X. Jin, M. T. Bishop, T. S. Ellis, F. E. Karasz, *Br. Polym. J.* **1985**, *17*, 4.
- [17] P. Knauth, H. Hou, E. Bloch, E. Sgreccia, M. L. Di Vona, *J. Anal. Appl. Pyrolysis* **2011**, *92*, 361.
- [18] H. Hou, M. L. Di Vona, P. Knauth, *J. Membr. Sci.* **2012**, *423–424*, 113.
- [19] A. C. M. Wanders, H. Cerfontain, *Recl. des Trav. chimiques des Pays-Bas* **1967**, *86*, 1199.
- [20] C. Bailly, D. Williams, F. Karasz, W. MacKnight, *Polymer (Guildf)* **1987**, *28*, 1009.

- [21] N. Shibuya, R. S. Porter, *Macromolecules* **1992**, *25*, 6495.
- [22] S. M. Zaidi, S. Mikhailenko, G. Robertson, M. Guiver, S. Kaliaguine, *J. Membr. Sci.* **2000**, *173*, 17.
- [23] E. J. Kappert, M. J. T. Raaijmakers, W. Ogieglo, A. Nijmeijer, C. Huiskes, N. E. Benes, *Thermochim. Acta* **2015**, *601*, 29.
- [24] B. Johs, J. S. Hale, *Phys. Status Solidi* **2008**, *205*, 715.
- [25] B. T. Koziara, K. Nijmeijer, N. E. Benes, *J. Mater. Sci.* **2015**, *50*, 3031.
- [26] In *CRC Handbook of Chemistry and Physics*, D. R. Lide, Ed., Taylor and Francis, Boca Raton, FL **2007**.
- [27] S. D. Mikhailenko, G. P. Robertson, M. D. Guiver, S. Kaliaguine, *J. Membr. Sci.* **2006**, *285*, 306.
- [28] S. Fornarini, In *The Chemistry of Sulphonic Acids, Esters and their Derivatives*, S. Patai, Z. Rappoport, Eds., J. Wiley & Sons, New York **1991**, p. 73.
- [29] P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, S. Kaliaguine, *J. Membr. Sci.* **2004**, *229*, 95.
- [30] J. P. Briggs, R. R. Hudgins, P. L. Silveston, *Int. J. Mass Spectrom. Ion Phys.* **1976**, *20*, 1.
- [31] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, *Thermochim. Acta* **2011**, *520*, 1.
- [32] C. Jarumaneeroj, K. Tashiro, S. Chirachanchai, *Macromol. Rapid Commun.* **2014**, *35*, 1397.
- [33] E. Pretsch, P. Bühlmann, M. Badertscher, *Structure Determination of Organic Compounds. Tables of Spectral Data.*; 4th, revis., Springer: Heidelberg, **2009**.
- [34] G. P. Robertson, S. D. Mikhailenko, K. Wang, P. Xing, M. D. Guiver, S. Kaliaguine, *J. Membr. Sci.* **2003**, *219*, 113.