Supporting Information for the article:

Thermal stability of sulfonated poly(ether ether ketone) films: on the role of protodesulfonation, *Macromolecular Materials and Engineering*, **301**(1), pp. 71-80. DOI: 10.1002/mame.201500075

^{1}H COSY NMR spectrum

Figure S1 shows the ^{1}H-COSY spectrum of fresh H-SPEEK for δ = 6.9 – 8.0. From the off-diagonal elements, the homonuclear correlation of protons can be determined. From the figure, the following peaks could be coupled:

- δ7.17 to δ7.82 (establishing that δ7.82 belongs to the H_A-proton);
- δ7.02 to δ7.76 (establishing that δ7.76 belongs to the $H_{A'}$-proton);
- δ7.22 to δ7.50 (confirming the coupling between $H_{C'}$ and $H_{E'}$);
- δ7.22 to δ7.11 (confirming the coupling between $H_{C'}$ and $H_{D'}$);

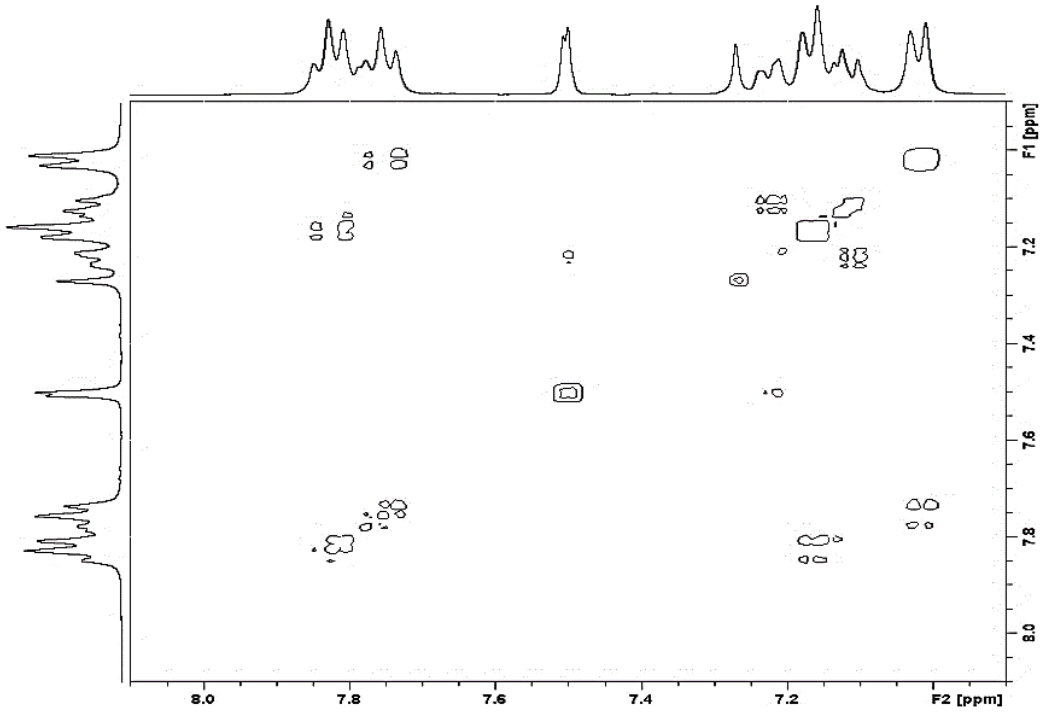

Figure S1: ^{1}H COSY spectrum in C_2D_6O at 400 MHz of fresh H-SPEEK.

Figure S2 shows the ^{1}H-COSY spectrum of H-SPEEK treated at 160 °C for 15 hours, for δ = 6.9 – 8.1. Again, the spectrum shows the correlation between the peaks as given above for the fresh SPEEK. However, in the spectrum, additional correlations can be found:

- δ6.85 to δ7.55
- δ7.0 to δ7.7 and to δ7.95
- δ7.15 to δ8.03

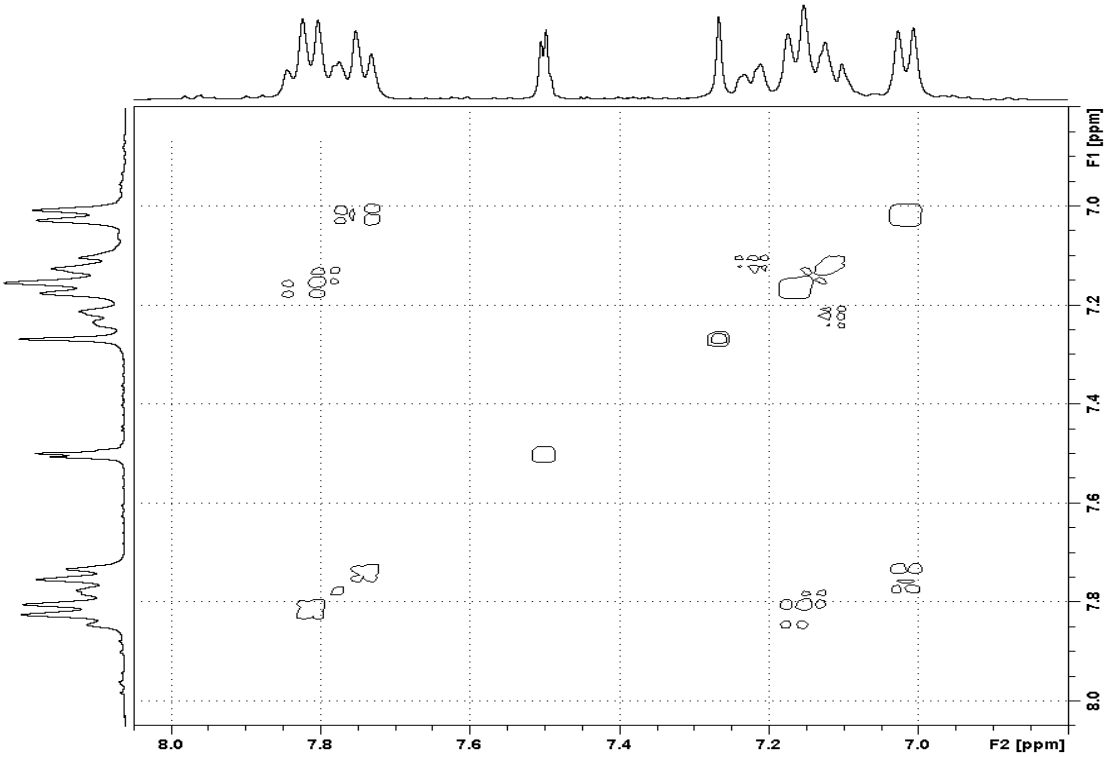

Figure S2: ^{1}H COSY spectrum in C_2D_6O at 400 MHz of H-SPEEK treated at 160 °C for 15 hours.

Figure S3 shows the ^{1}H-COSY spectrum of H-SPEEK treated at 190 °C for 15 hours, for δ = 6.9 – 8.5. Please note that the H-SPEEK was treated in a different batch as the H-SPEEK given in the article, and that as a result, the treatment temperature may be slightly different. Again, the spectrum shows the correlation between the peaks as given above for the fresh SPEEK. However, in the spectrum, additional correlations can be found:

- δ6.93 to δ7.6
- δ7.0 to δ7.7 and to δ7.95
- δ7.15 to δ8.03

Assigning these peaks to specific compounds is difficult, because of the numerous possible reactions that could occur in the material. The upfield shift of all these peaks is an indication of the increasing shielding of these protons. Furthermore, the correlation between the δ7.0, δ7.67 and δ7.95 indicates that these groups are part of the same structure.

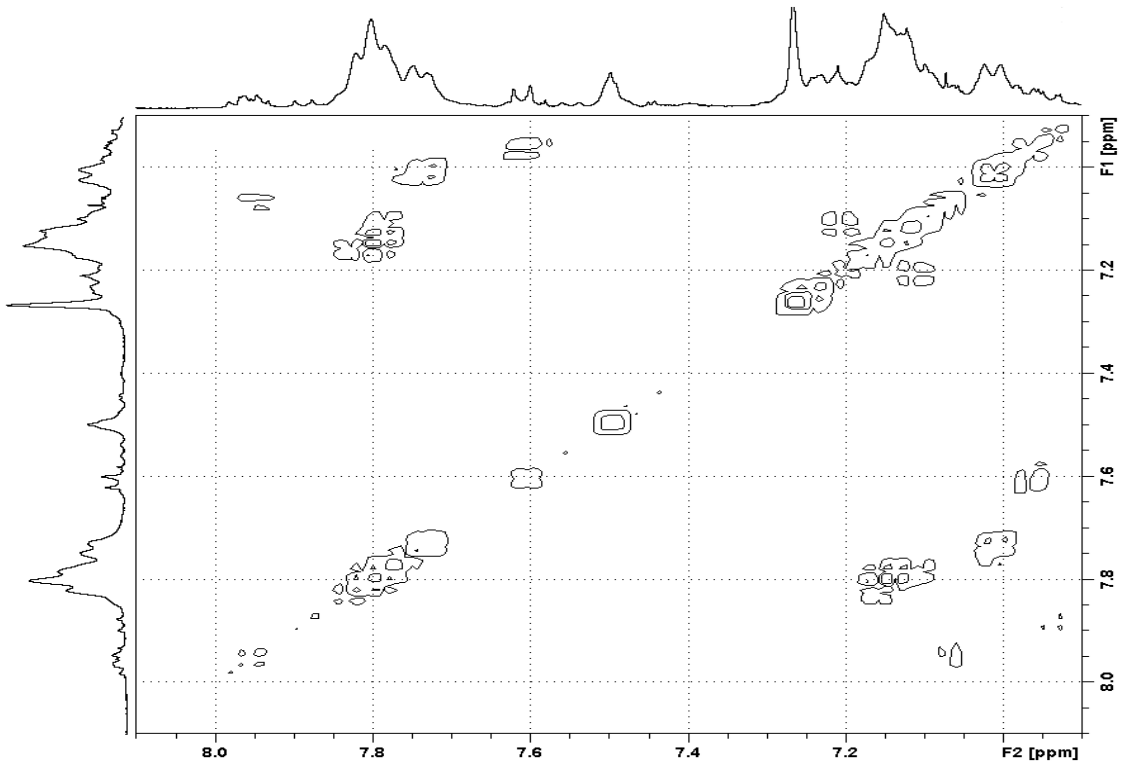

Figure S3: ^{1}H COSY spectrum in C_2D_6O at 400 MHz of H-SPEEK treated at 190 °C for 15 hours. The chemical shift is not locked to the solvent peak.

Absorption spectra H-SPEEK and Na-SPEEK

In addition to the spectra already given in the manuscript, the spectra in the Figures Figure S4-Figure S6 show the changes in the absorption of H-SPEEK and Na-SPEEK upon prolonged exposure to different temperatures between 180 and 250 °C.

Figure S4 shows that the changes in H-SPEEK follow the same trend for treatment at 163.8 and 183.3 °C. For the 183.3 °C treatment, the changes in the absorption peaks at ~250 nm is stronger, and a significant absorption peak develops over the course of a 15 hour treatment. For Na-SPEEK treated at the same temperatures, only minor changes are recorded.

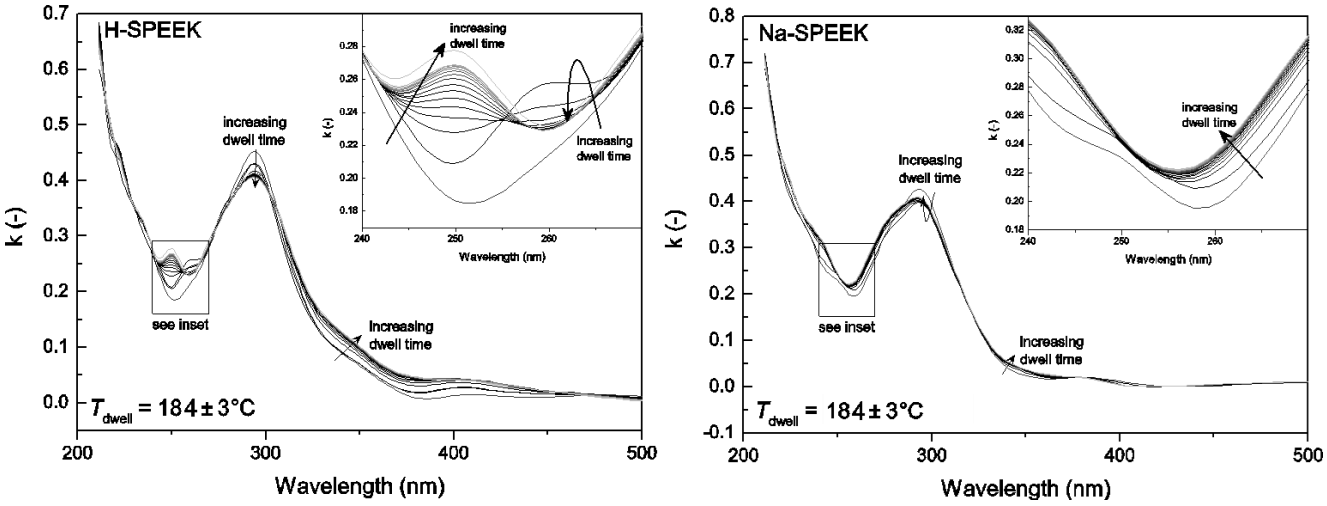

Figure S4: The absorption spectrum of H-SPEEK (left) and Na-SPEEK (right) under nitrogen before thermal treatment (red) and after 0 (black) to 15 hours (light grey) of dwell at 183.3 ± 2.8 °C. The change between the untreated and the 0 hour dwell samples is induced by the heating ramp.

Figure S5 shows that the changes in H-SPEEK at 193 °C are in line with those obtained at 183.3 °C. No significant differences are seen between the spectra.

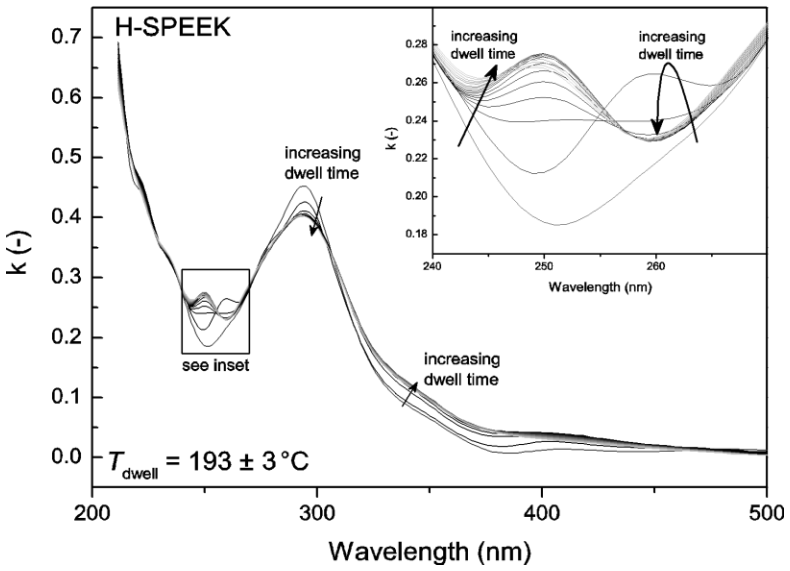

Figure S5: The absorption spectrum of H-SPEEK under nitrogen before thermal treatment (red) and after 0 (black) to 15 hours (light grey) of dwell at 193 ± 2.8 °C. The change between the untreated and the 0 hour dwell samples is induced by the heating ramp.

In addition to the figures in the manuscript, Figure S6 substantiates the pronounced differences in the absorption spectra of H-SPEEK when heating to temperatures higher than 210 °C.

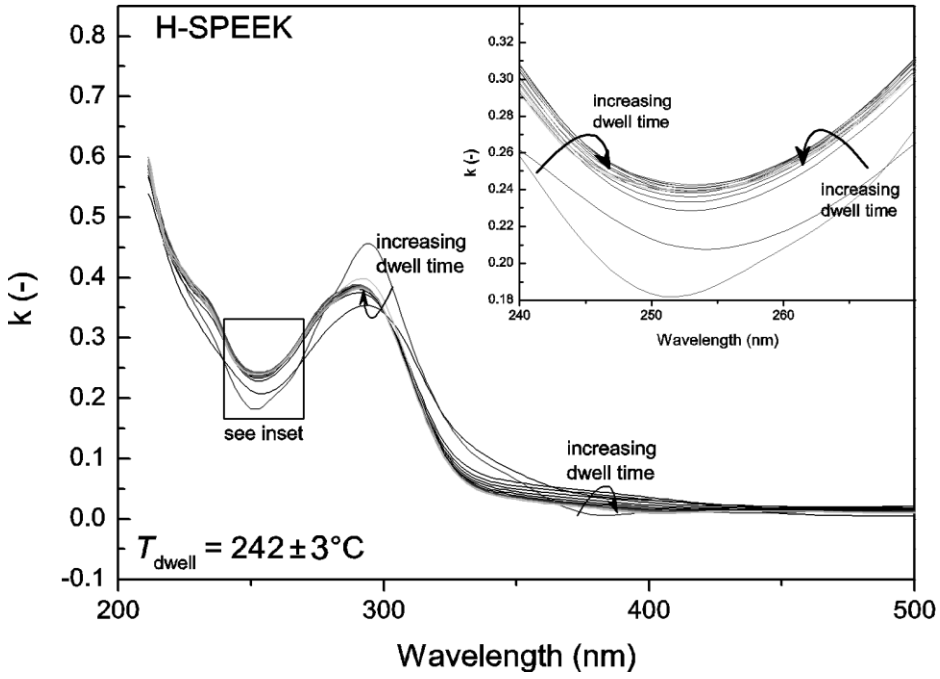

Figure S6: The absorption spectrum of H-SPEEK under nitrogen before thermal treatment (red) and after 0 (black) to 15 hours (light grey) of dwell at 241.8 ± 2.8 °C. The change between the untreated and the 0 hour dwell samples is induced by the heating ramp.

Infrared band assignment

Table S1 gives the infrared band assignment, based on general infrared bands in Pretsch et al. [1], supplemented with characteristic peaks for SPEEK from Xing et al.[2] and Maranesi et al.[3]

Table S1: Infrared band assignment for fresh SPEEK

Wavenumber (intensity)	Group	Extra information
3600-3200 (s, broad)	-OH	Stretching of O-H in water and/or acid
3100-3020	=C-H	Stretching of aromatic hydrogens
1644 (m)	C=O	Symmetric tretching
1595 (s)	Phenyl	Skeletal in-plane [3]
1490 (s)	Phenyl	Skeletal in-plane [2,3]
1472 (s)	Phenyl	Skeletal in-plane [3]
1416-1400 (m)	Phenyl	Symmetric stretching aromatic C-C [3]
1308 (m)*		
1281 (w, shoulder)*		1,2,4-substituted phenyl [3]
1251 (s)*		SO_3H [2,3]
1220 (s)*		1,2,4-substituted [2,3]
1186 (s)*		
1158 (s)*		Assigned to Ph-SO_2-Ph in [3]
1078 (m)	O=S=O	In SO_3H, Stretching [2,3]
1020-1005 (m)	SO_3H	Bending [2,3]
955 (w)	All: Possibly ar C-H δ, C-O-C γ, S-O st	
928 (s)		Most likely C-H or C-O-C
863 (s)		Most likely C-H or C-O-C
839 (m)		Most likely S-O (affected by Na-exchange)
767 (m)		Most likely C-H or C-O-C
708 (w)		
682 (w)		Most likely S-O (affected by Na-exchange)

* Strong overlap between the peaks, possibly all present in PEEK,[2] and therefore most likely vibrations in the phenyl rings and ether group. Because changes in these peaks are difficult to follow because of the strong overlap, specific assignment is difficult and could be inaccurate. Therefore, these peaks have not been assigned. Previously made assignments are given in the last column.

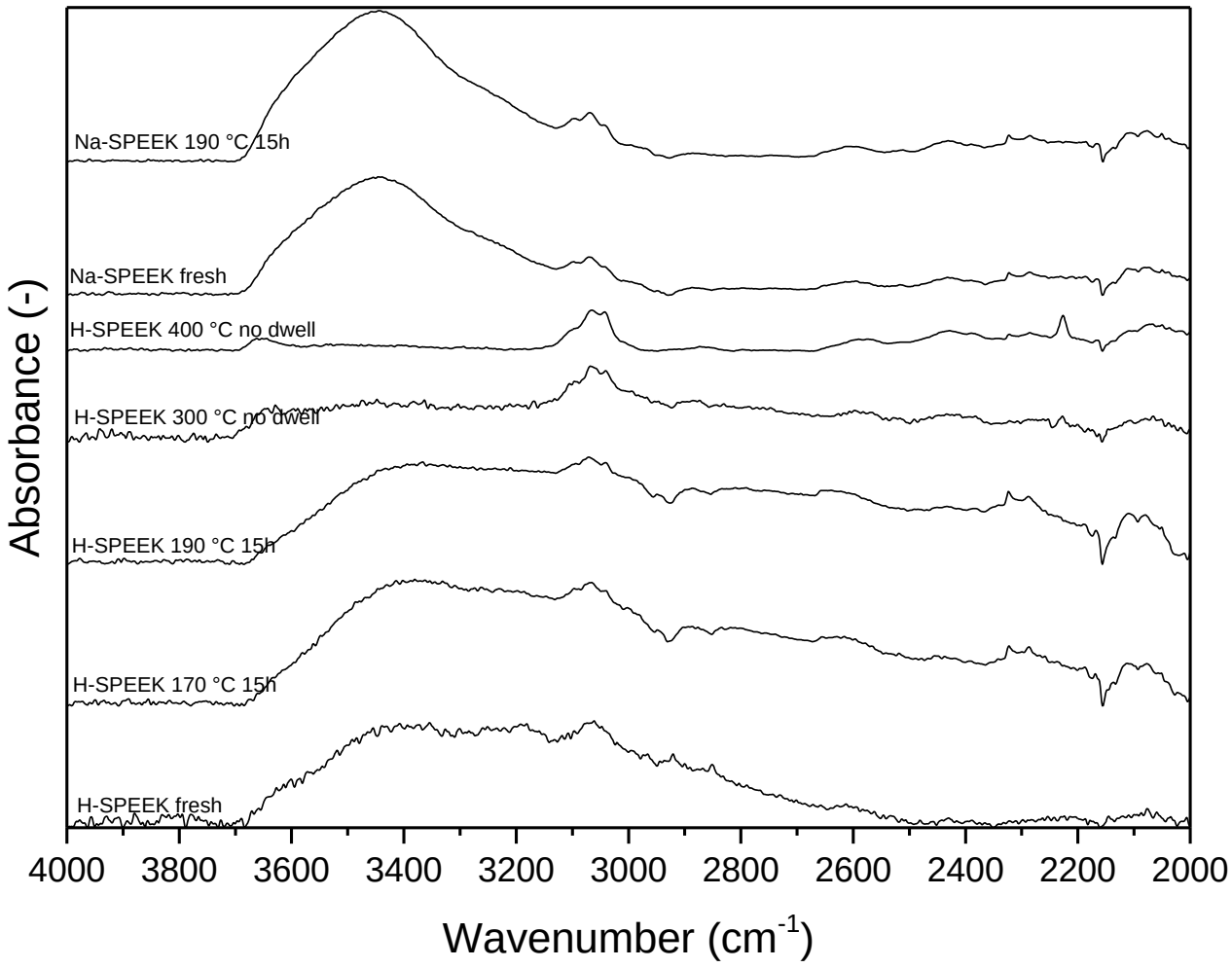

Figure S7: ATR-FTIR spectra of H-SPEEK and Na-SPEEK treated at different temperatures, in the wavenumber range of 4000-2000

Detection of evolved SO_2 by ICP-AES

To determine whether the detected chemical changes in the H-SPEEK structure are the result of a reaction by the sulfonic acid groups, the amount of SO_x in the gases that evolve during heating was measured. Gaseous products that were released during isothermal treatment of H-SPEEK at 183 °C were absorbed in water. ICP-AES was used to analyse the sulfur content in the water. Measurements were performed on a ICPE-9000 (Shimadzu). Samples were analyzed in triplicate and in axial direction.

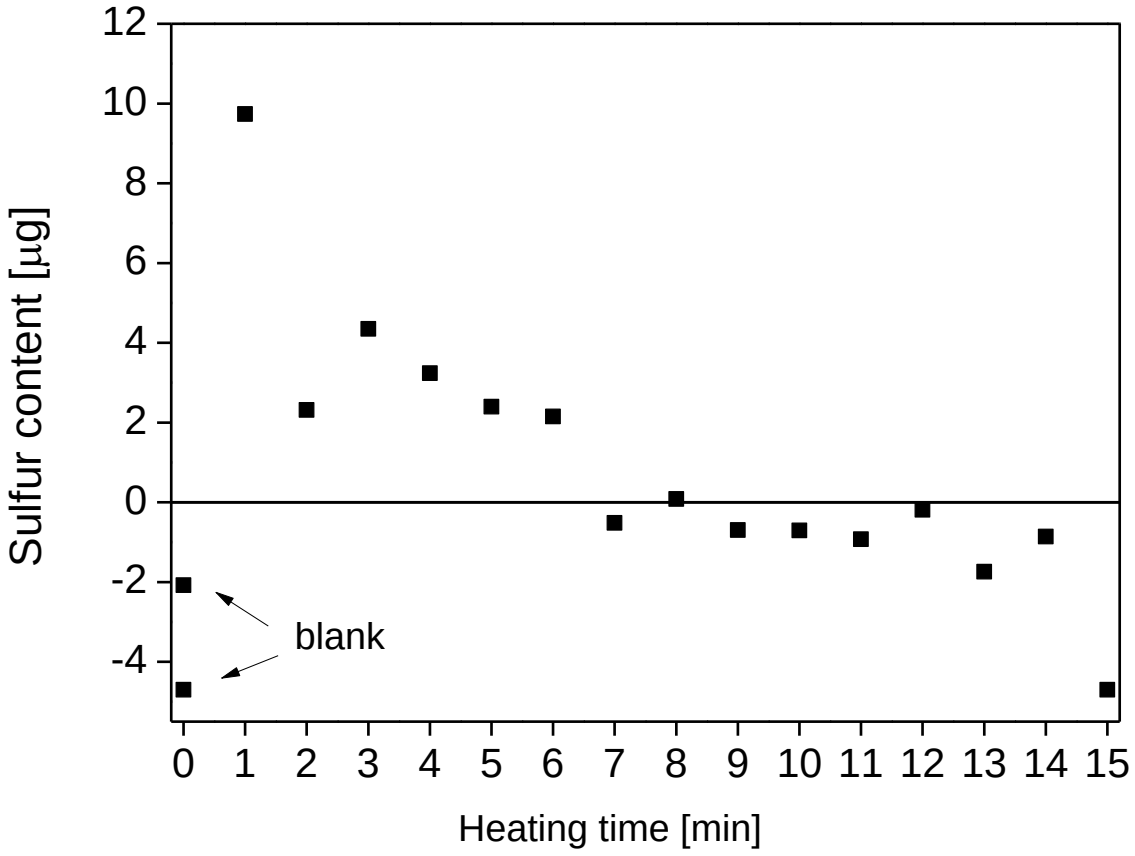

Figure S8: Overview of the evolved SO_2 per hour of the experiment as determined by ICP-AES at 183 °C

Full MS-data

Figures Figure S9-Figure **S12** display all individual *m*/*z*-values that were detected during TGA-MS measurements of H-SPEEK, Na-SPEEK, H*-SPEEK, and PEEK, respectively. The following compounds were represented by the following *m*/*z*-ratios in the manuscript: methane, 15; H_2O, 18; H_2S or S^{2+}, 34; C_3H_x, 39; CO_2, 44; SO_2, 64; C_6H_6, 78; C_6H_6O, 94; C_5H_x or H_2S_2, 66; C_4H_x, 51; C_5H_x, 65;

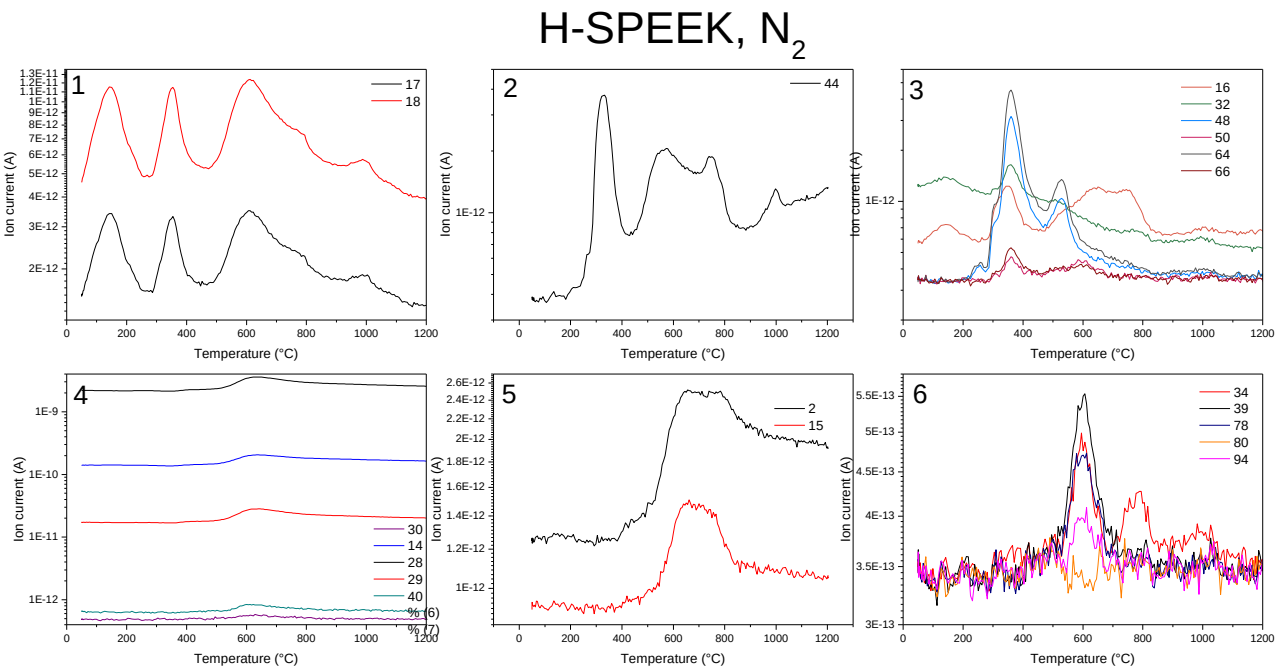

Figure S9: Overview of all the detected MS-signals during the TGA-MS measurement of H-SPEEK

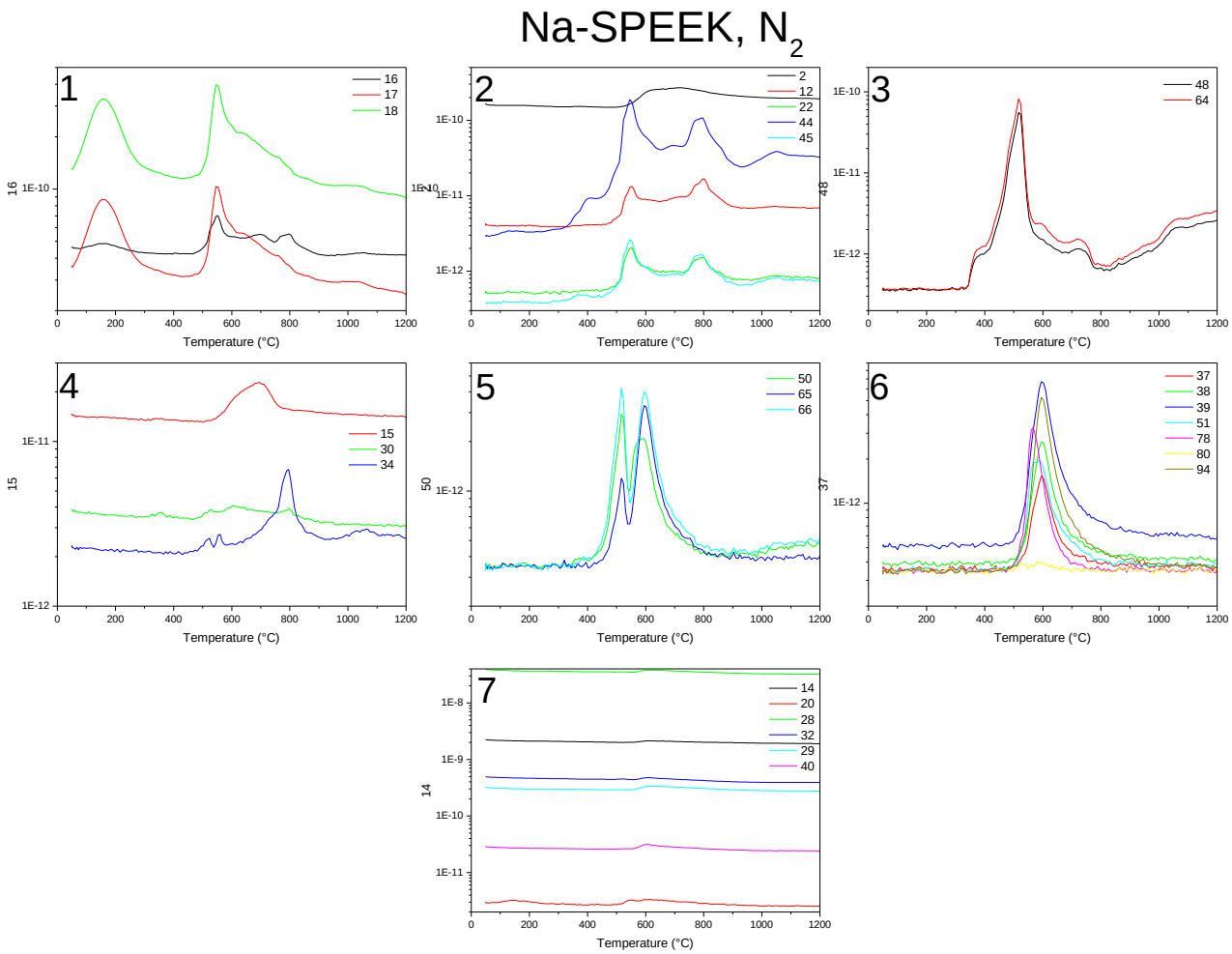

Figure S10: Overview of all the detected MS-signals during the TGA-MS measurement of Na-SPEEK

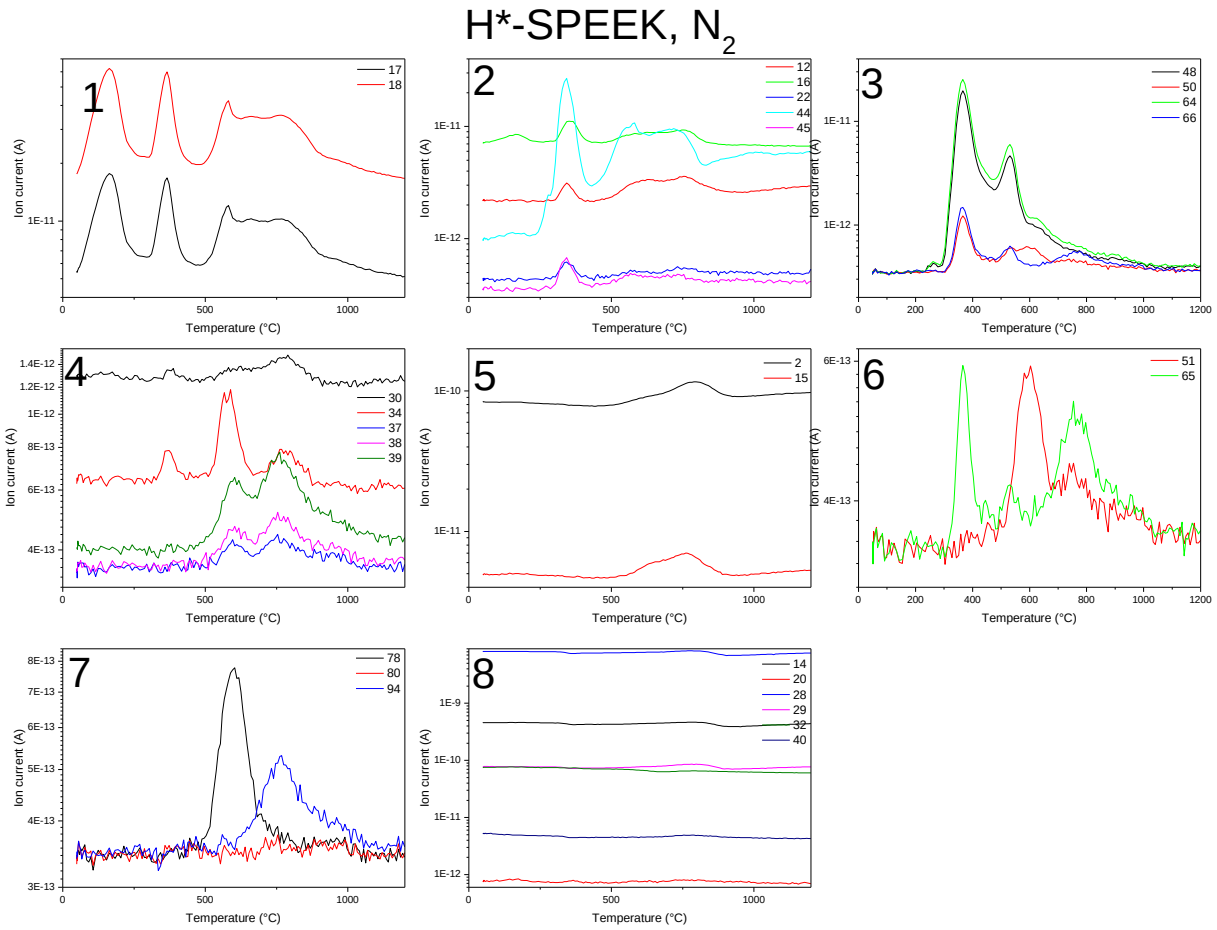

Figure S11: Overview of all the detected MS-signals during the TGA-MS measurement of H*-SPEEK

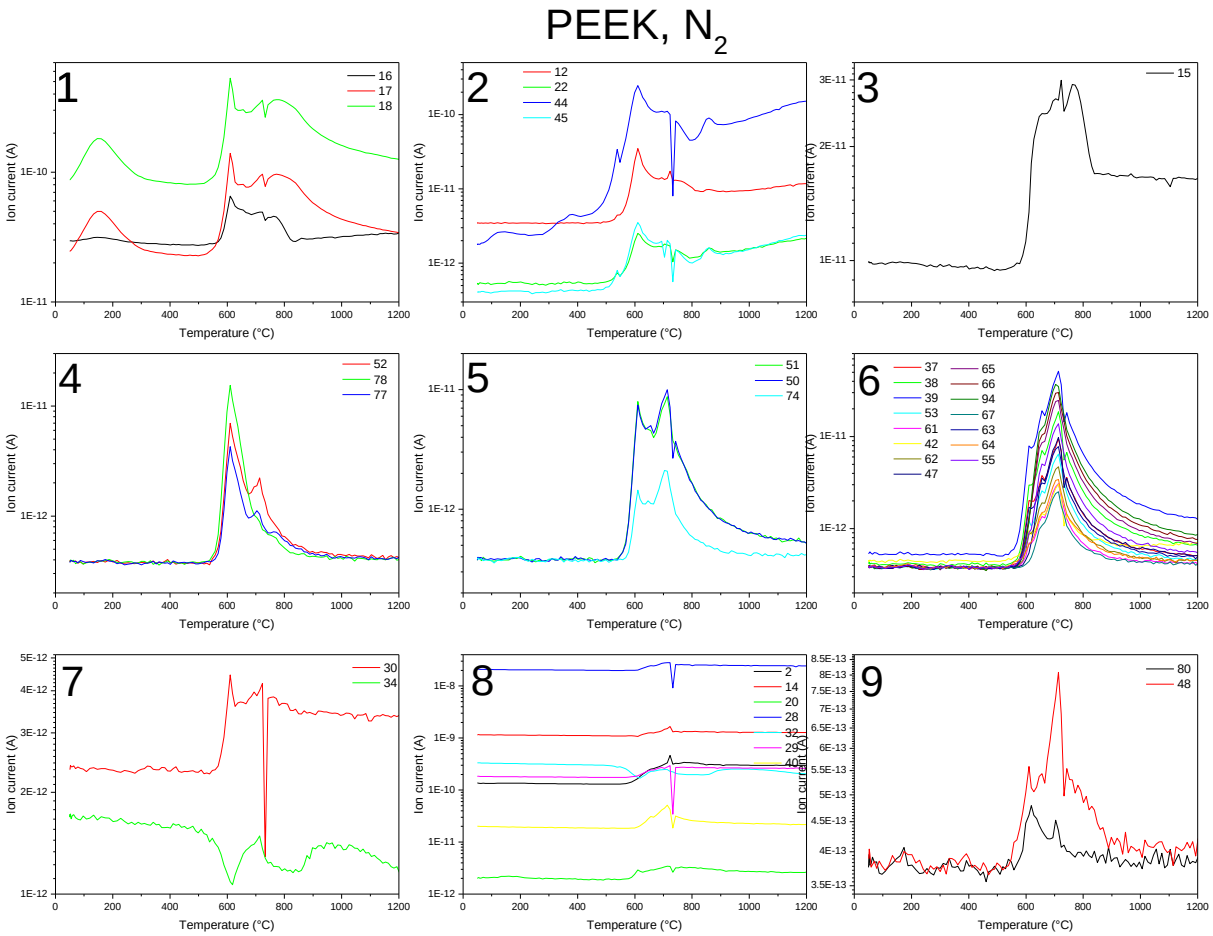

Figure S12: Overview of all the detected MS-signals during the TGA-MS measurement of PEEK

References

(1) Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds. Tables of Spectral Data.*; 4th, revis.; Springer: Heidelberg, 2009.

(2) Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K.; Kaliaguine, S. *J. Membr. Sci.* **2004**, *229*, 95–106.

(3) Maranesi, B.; Hou, H.; Polini, R.; Sgreccia, E.; Alberti, G.; Narducci, R.; Knauth, P.; Di Vona, M. L. *Fuel Cells* **2013**, *13*, 107–117.