

## Supporting Information

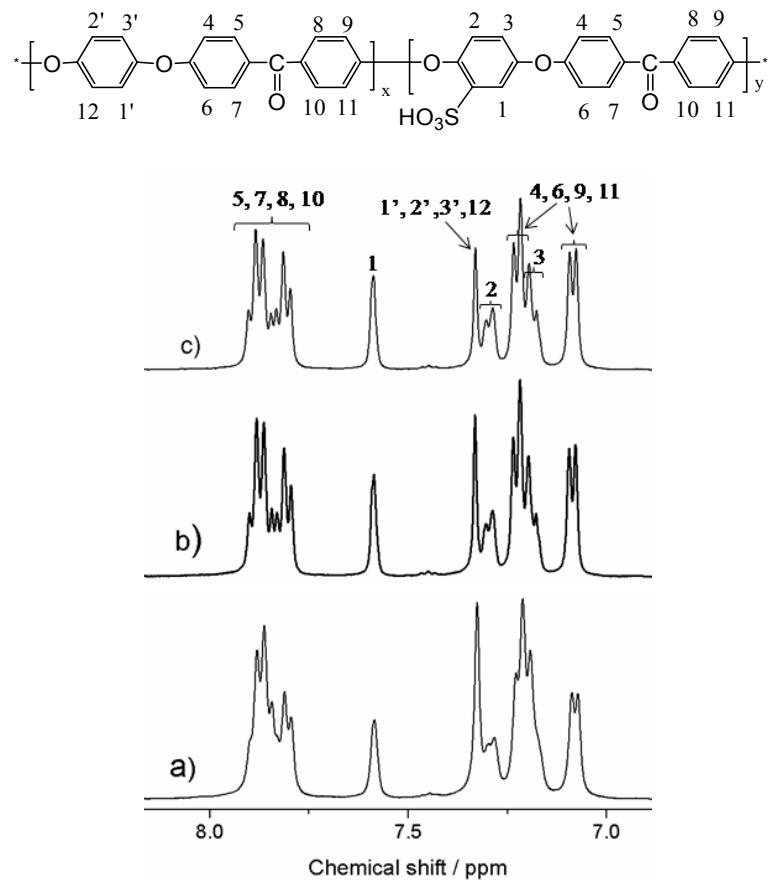
# Degradation Mechanism of Sulfonated Poly(ether ether ketone) (SPEEK) Ion Exchange Membranes under the Vanadium Flow Battery Medium

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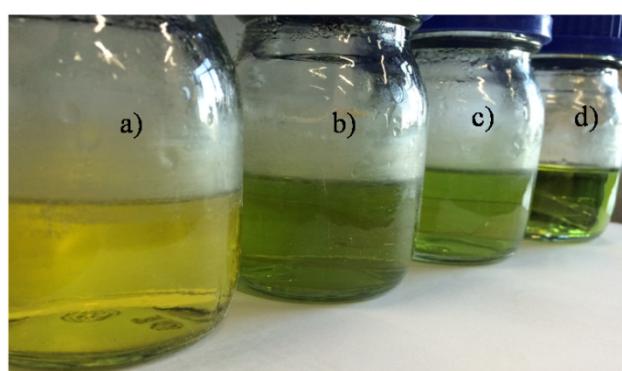
**Figure S1.** Chemical structure and  $^1\text{H}$  NMR spectra of SPEEK in DMSO-d<sub>6</sub>: a) SP1;

b) SP2; c) SP3

DS can be calculated from the proton integration (Eq. (1)):

$$\frac{DS}{12 - 2DS} = \frac{A_{H_1}}{\sum A_{H_N}} \quad \text{Eq. (1)}$$

Where  $A_{H_1}$  represents the integration area of H<sub>1</sub> peak,  $\sum A_{H_N}$  indicates the integration area of all proton peaks.



**Figure S2.** Membrane samples after immersion in electrolyte (0.15 M  $\text{VO}_2^+$  in 3 M

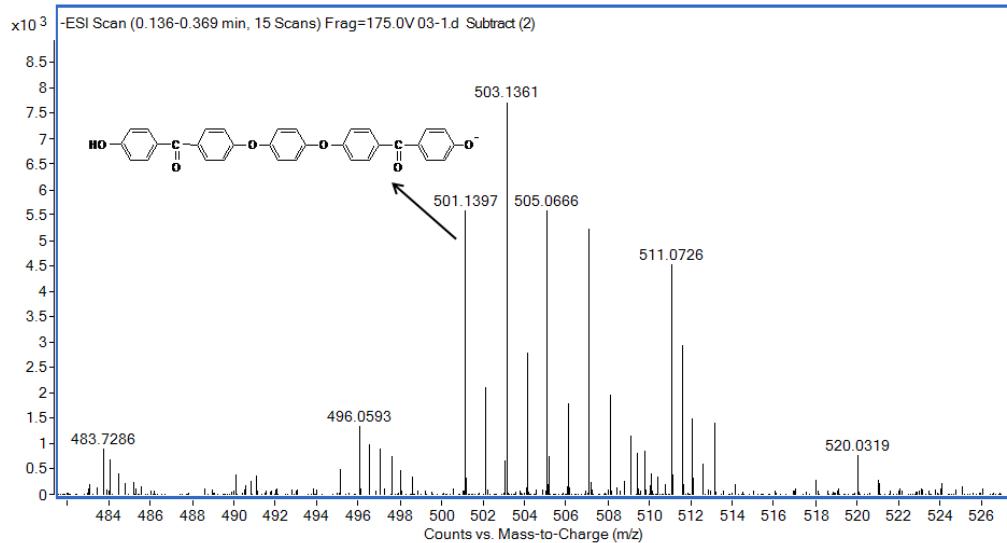
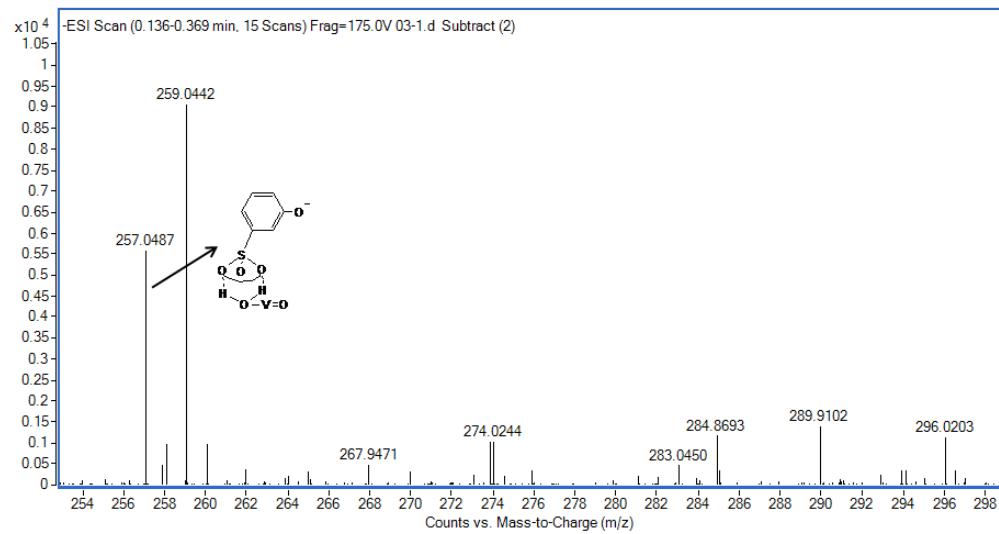
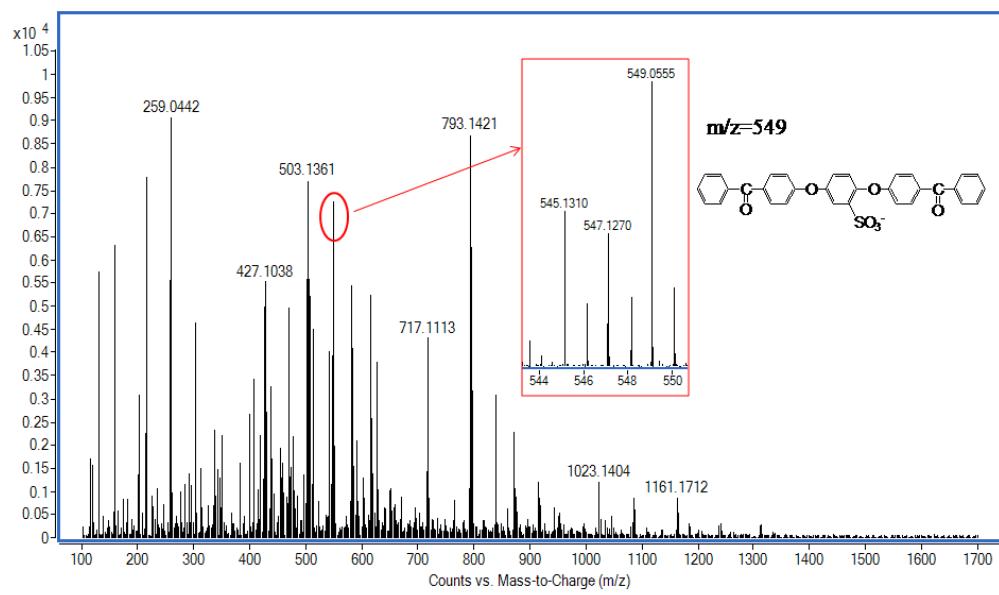
total sulfate) solutions at 40 °C for 30 d: a) Blank solution; b) Solution containing SP1 membrane; c) Solution containing SP2 membrane; d) Solution containing SP3 membrane

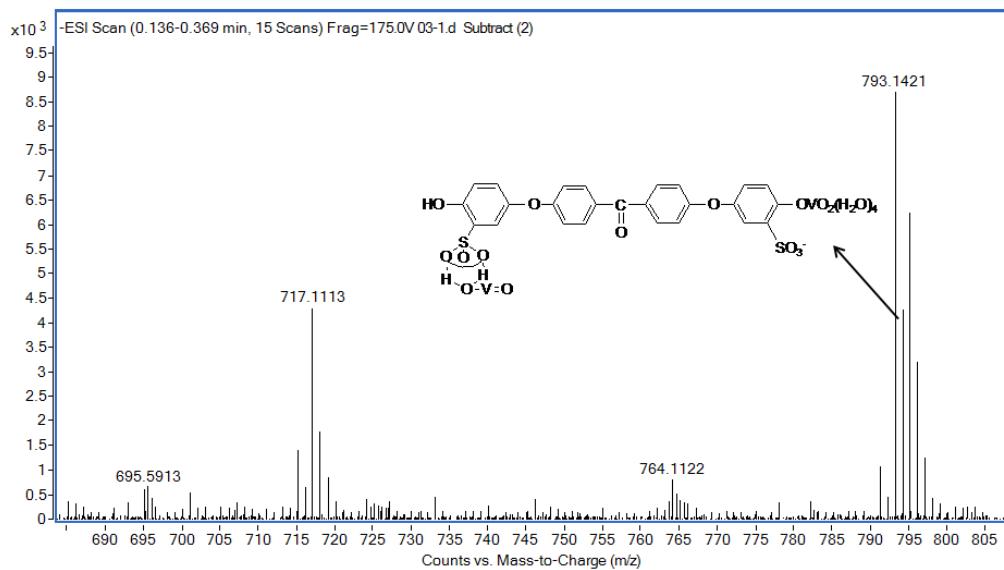
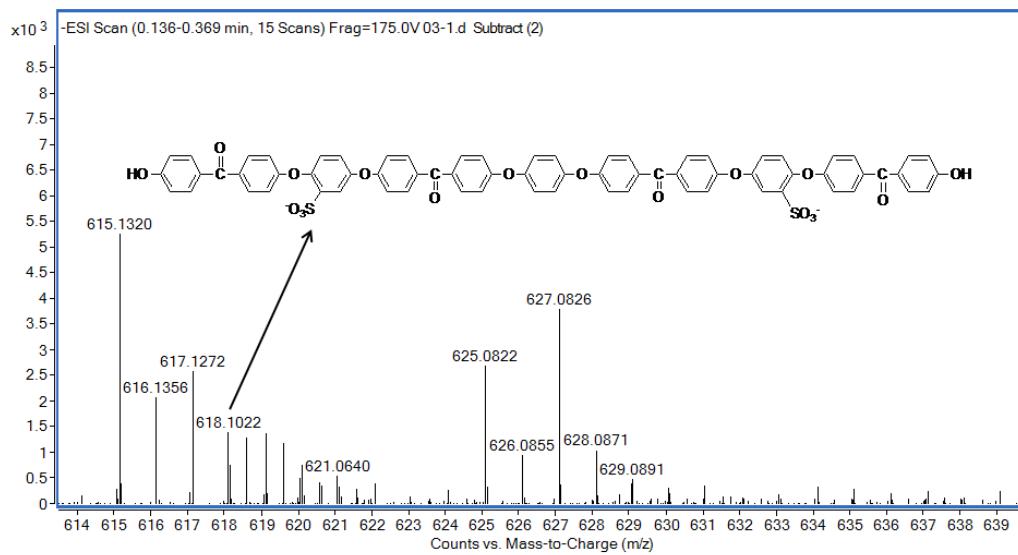
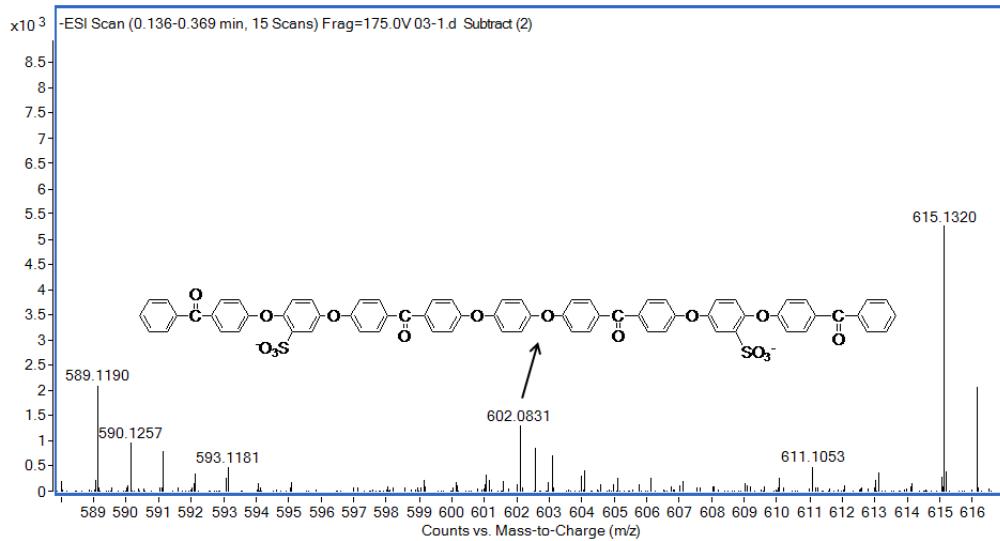


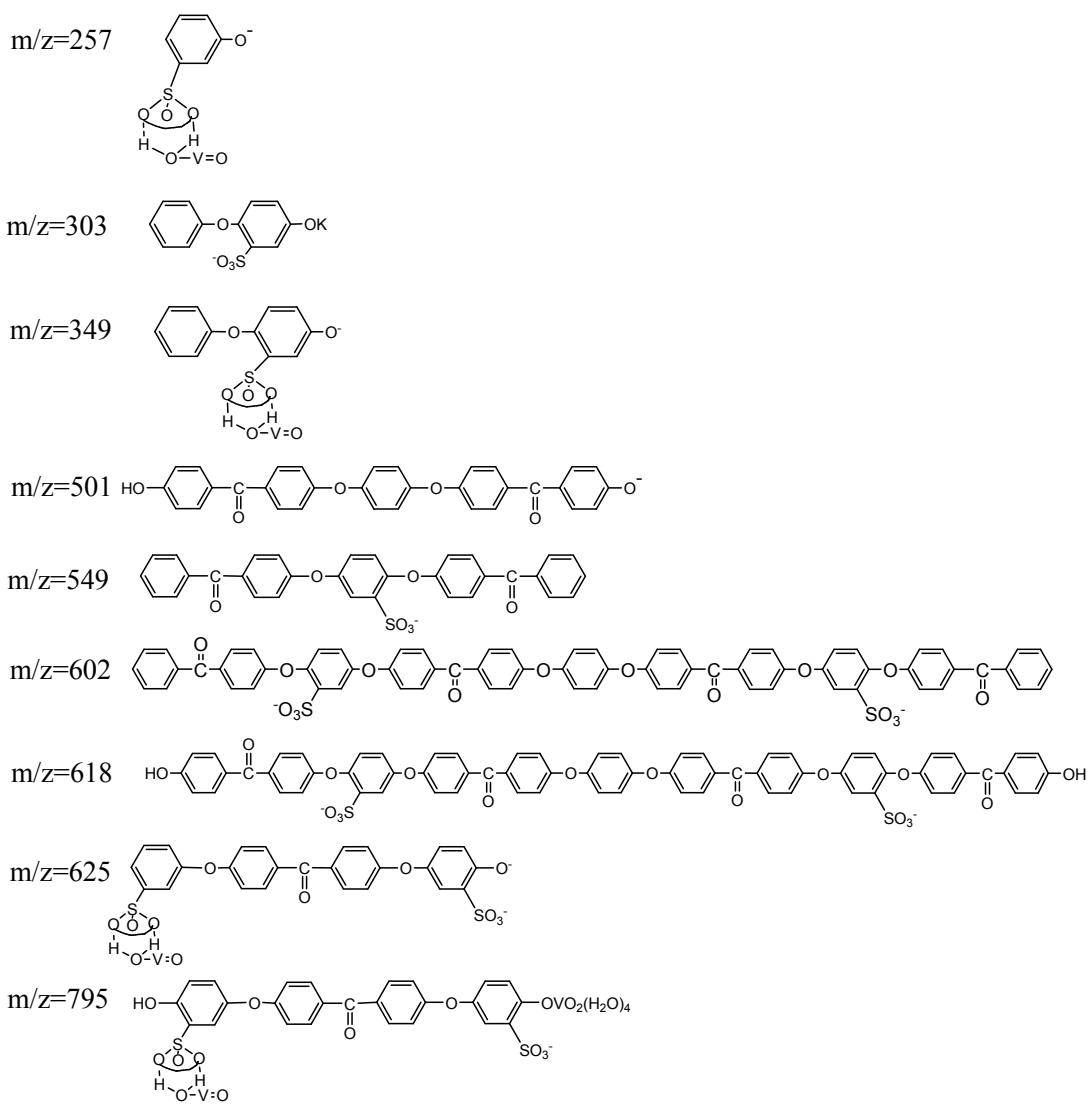
**Figure S3.** SP3 membrane fragments (after soaked in 1.5 M  $\text{VO}_2^+$  at 40 °C for 30 h)



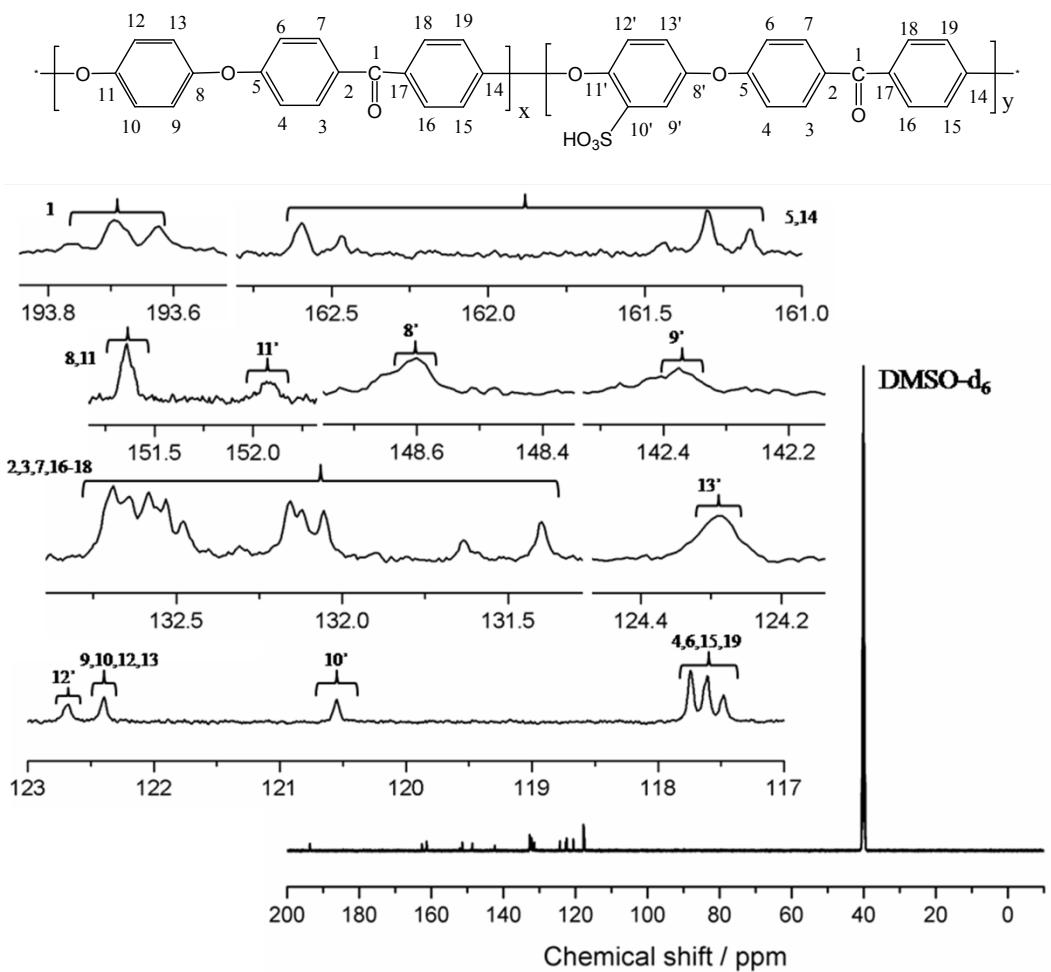
**Figure S4.** Homogeneous solution containing SP3 membrane fragments after immersing in 1.5M  $\text{VO}_2^+$  at 40 °C for 54 h.



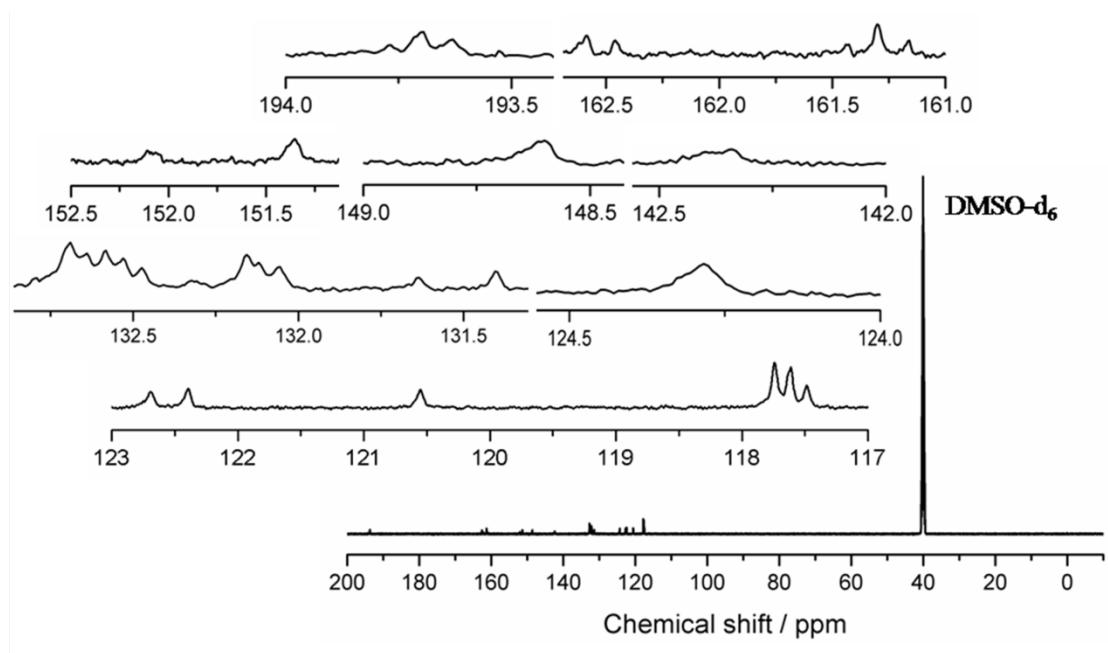




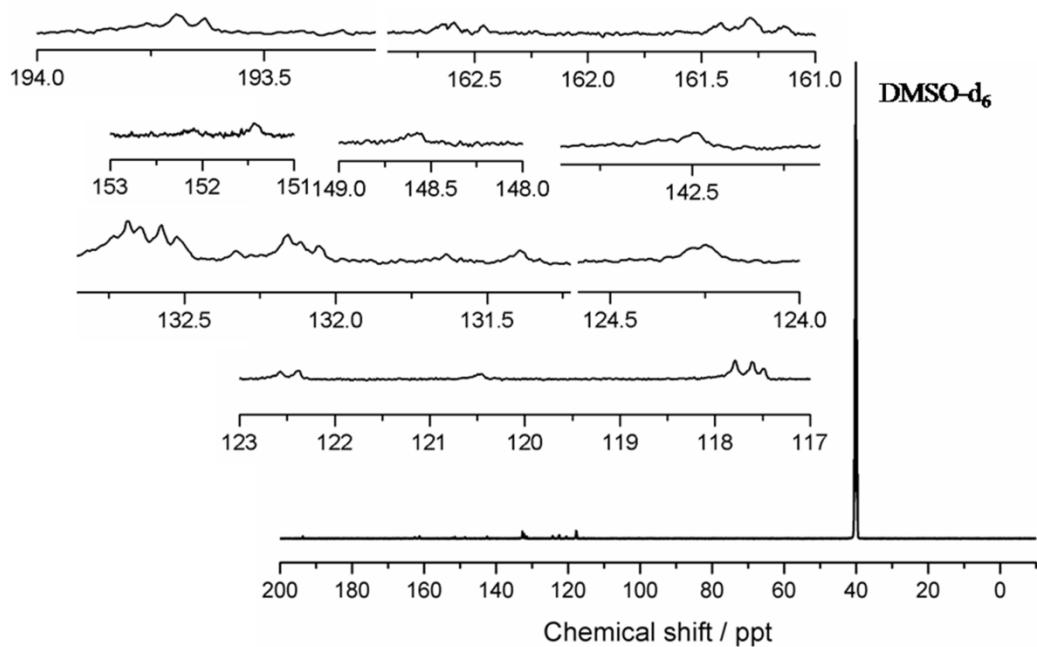
**Figure S5.** LC/MS spectrogram of aqueous solution with negative mode and parts of fragment ion peaks. Insert shows proposed fragmentation products based on degradation mechanism.



**Figure S6.**  $^{13}\text{C}$  NMR spectra of initial SP3 membrane in DMSO-d<sub>6</sub>. Inserts show enlargement of the aromatic region of the spectra.



**Figure S7.**  $^{13}\text{C}$  NMR spectra of degraded SP3 membrane (30 h) in DMSO-d<sub>6</sub>. Inserts show enlargement of the aromatic region of the spectra.



**Figure S8.**  $^{13}\text{C}$  NMR spectra of degraded SP3 membrane (54 h) in DMSO-d<sub>6</sub>. Inserts show enlargement of the aromatic region of the spectra.