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Electronic Supplementary Information (ESI)

for

Superior Proton Conductivity and Selectivity in Sulfonated Ionomer Biocomposites Containing Renewably Processed and Fractionated Lignin

Xueting Wang[1], Mayura Silva[2], Colleen Clarke[1], Bronson Lynn[1], Mark Robertson[3], Aidan J. Leopold[1], Oreoluwa Agede[1], Lilin He[4], Stephen Creager[2], Mark E. Roberts[1], Mark C. Thies[1], and Eric M. Davis[1,]*

[1]Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29631

[2]Department of Chemistry, Clemson University, Clemson, SC 29631

[3]School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, MS 39406

[4]Oak Ridge National Laboratory, Oak Ridge, TN 37830

* To whom correspondence should be addressed: ericd@clemson.edu

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1. Nuclear Magnetic Resonance (NMR) Spectroscopy Analysis

1.1. Proton (^1H) NMR

Proton nuclear magnetic resonance (^{1}H NMR, 500 MHz, DMSO-d_6) spectroscopy was utilized to obtain the degree of sulfonation (DS) of the neat SPEEK(72%) and SPEEK(80%) samples. The chemical structure of SPEEK, as well as the ^{1}H NMR spectra for SPEEK(72%) and SPEEK(80%) are shown in **Figures S1**a and **S1**b, respectively. The sulfonation reaction of PEEK is an electrophilic substitution reaction, where the incorporated -SO_3H groups result in a down field shift of the nearest neighboring proton (H4'). The peaks at 7.01 ppm and 7.17 ppm are assigned to hydrogens H5, H6, H11, and H12, as shown in the polymer structure in **Figure S1**, while the peaks at 7.10 ppm and 7.22 ppm are assigned to hydrogens H3' and H1', respectively. The peak located at 7.27 ppm is assigned to hydrogens H1, H2, H3, and H4, while peaks ranging from 7.70-7.90 ppm are assigned to hydrogens H7, H8, H9, and H10. The amount of sulfonic acid groups can therefore be determined from their nearest neighboring proton (H4'), which can be assigned to the peak at 7.52 ppm in **Figures S1**a,b. As such, the peak area of this neighboring proton, relative to areas of all other peaks in the NMR spectrum, can be used in the following equation to determine the degree of sulfonation (DS)

$$\frac{peak\ area\ of\ \delta = 7.52}{\sum peak\ area\ of\ rest\ of\ peaks} = \frac{DS}{12 - 2(DS)} \quad , \qquad \text{(S1)}$$

where DS is degree of sulfonation of the SPEEK. From analysis of the ^{1}H NMR spectra, the vales of the DS of the SPEEK(72%) and SPEEK(80%) samples were determined to be approximately 72% and 80%, respectively.

1.2. Phosphorous (^{31}P) NMR

Phosphorus nuclear magnetic resonance (^{31}P NMR) was used to determine the hydroxyl group and carboxylic acid group contents of the LMW lignin and HMW lignin. The ^{31}P NMR spectra of LMW lignin and HMW lignin are shown in **Figures S2**a,b and **Figures S2**c,d, respectively. Note that the quantitative values obtained from this analysis can be found in **Table 2** of the manuscript.

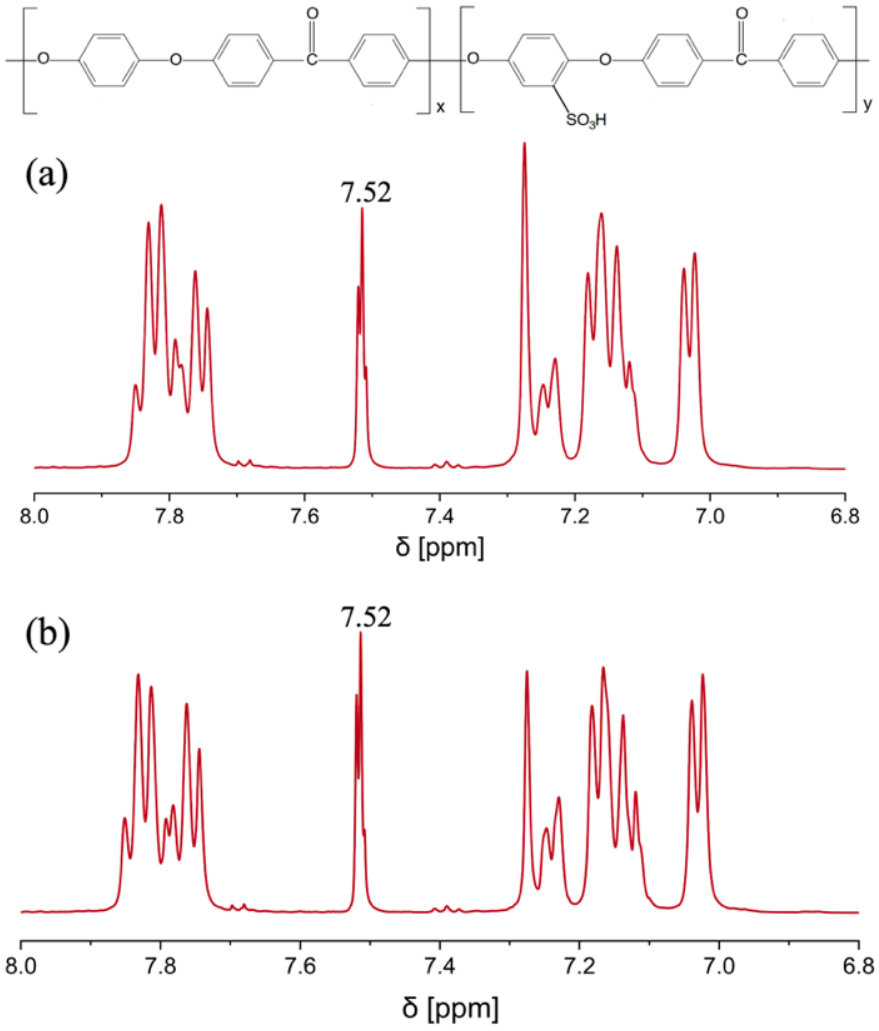

Figure S1. ^{1}H NMR spectra for (a) 3h SPEEK and (b) 4h SPEEK.

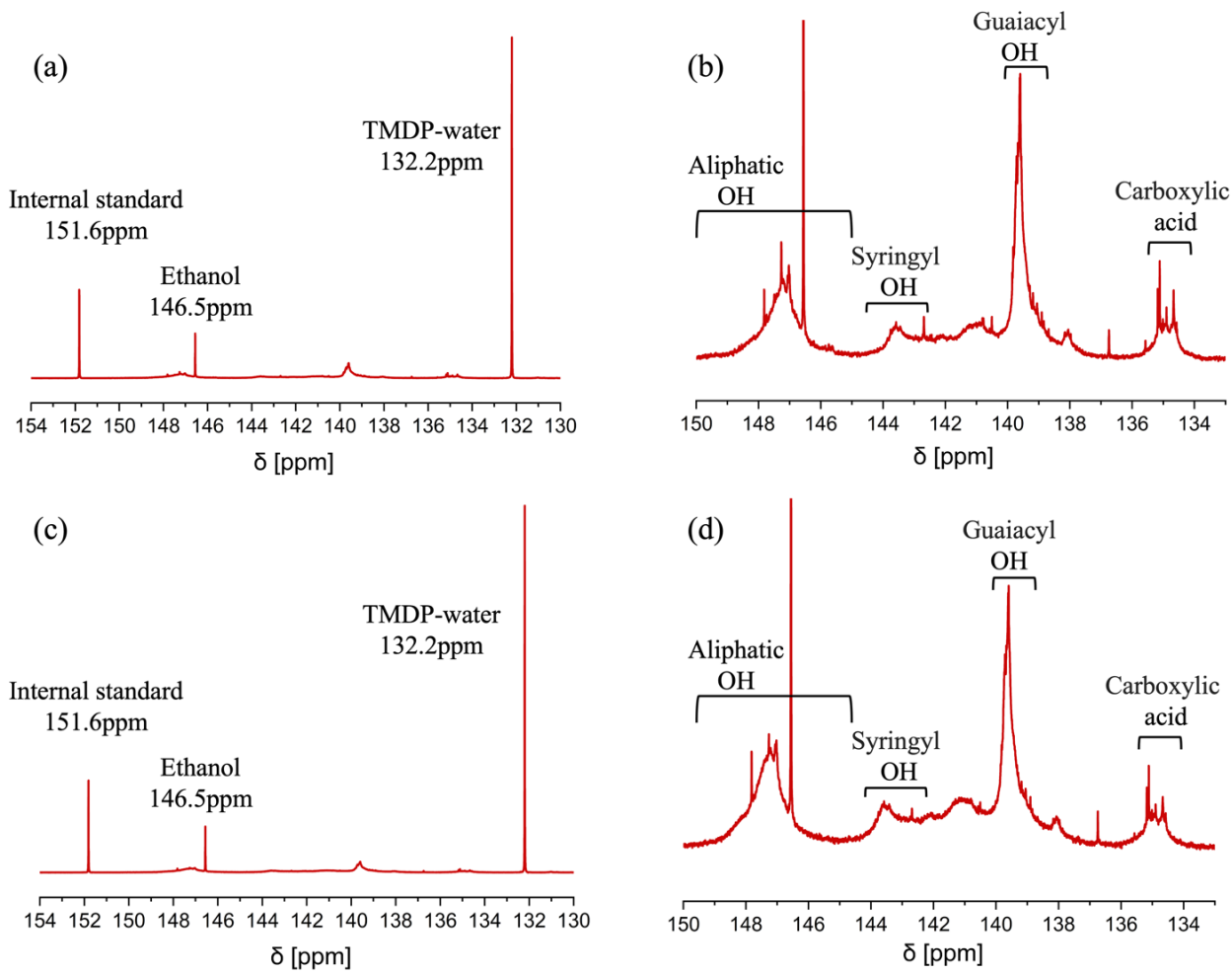

Figure S2. ^{31}P NMR spectra for (a & b) LMW lignin and (c & d) HMW lignin. Note that spectra shown in (b) and (d) exclude the region that contains the TMDP-water peak, making it easier for the reader to see the peaks associated with the lignin functional groups.

2. Lignin Molecular Weight Analysis

The weight-average molecular weights of the feed lignin, as well as of the LMW and HMW lignin fractions were determined via GPC. The GPC chromatograms of the polystyrene standard and the various lignin fractions, along with the polystyrene calibration curve, are provided in

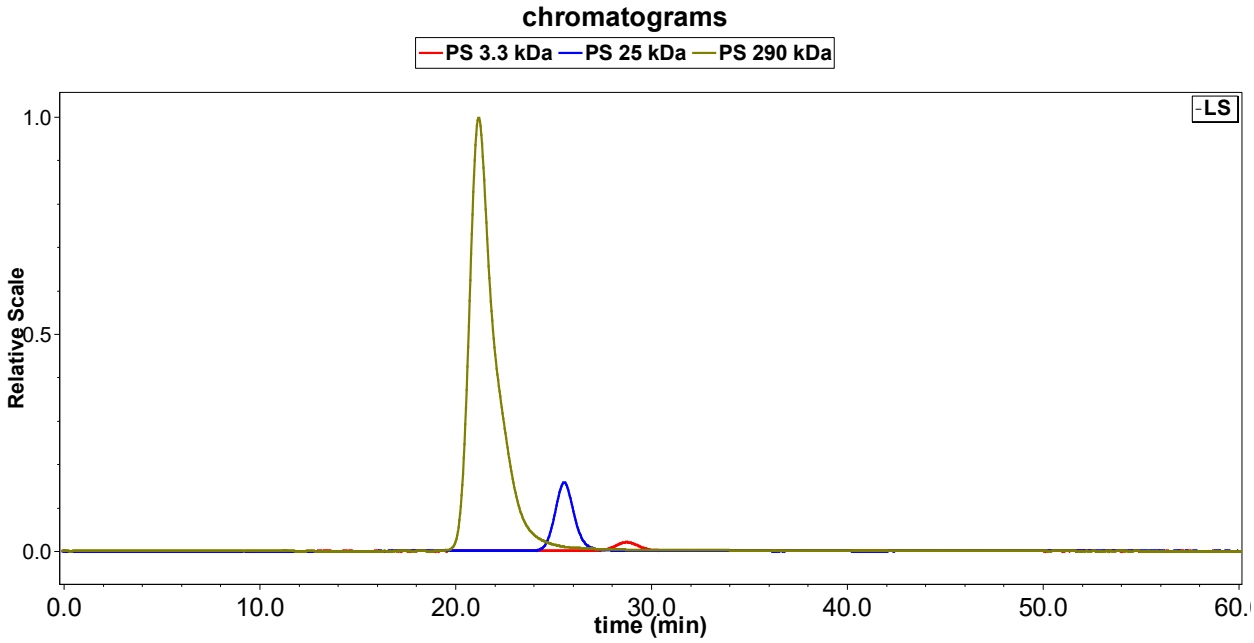

Figure S3. GPC chromatograms of the polystyrene standard at 3,300 g mol^{-1} (solid red line), 25,000 g mol^{-1} (solid blue line), and 290,000 g mol^{-1} (solid green line).

Figures S3, **S4**, and **S5**, respectively.

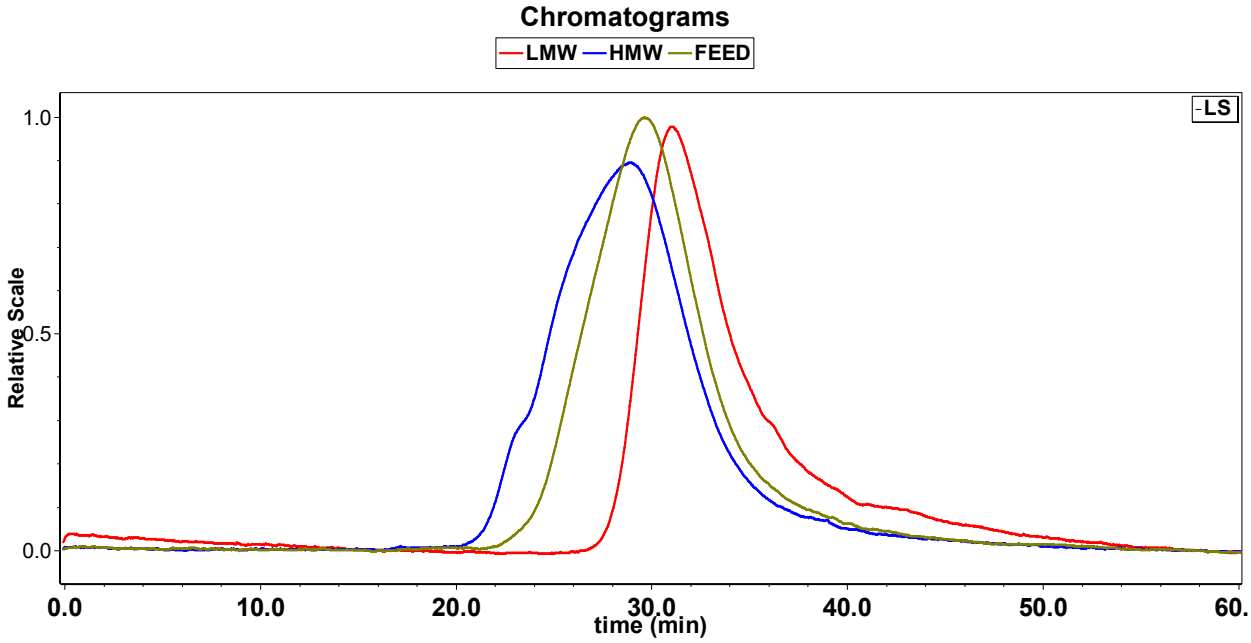

Figure S4. GPC chromatograms of the feed lignin (referred to as BCL in the manuscript; solid green line) and the LMW (solid red line) and HMW (solid blue line) lignin fractions.

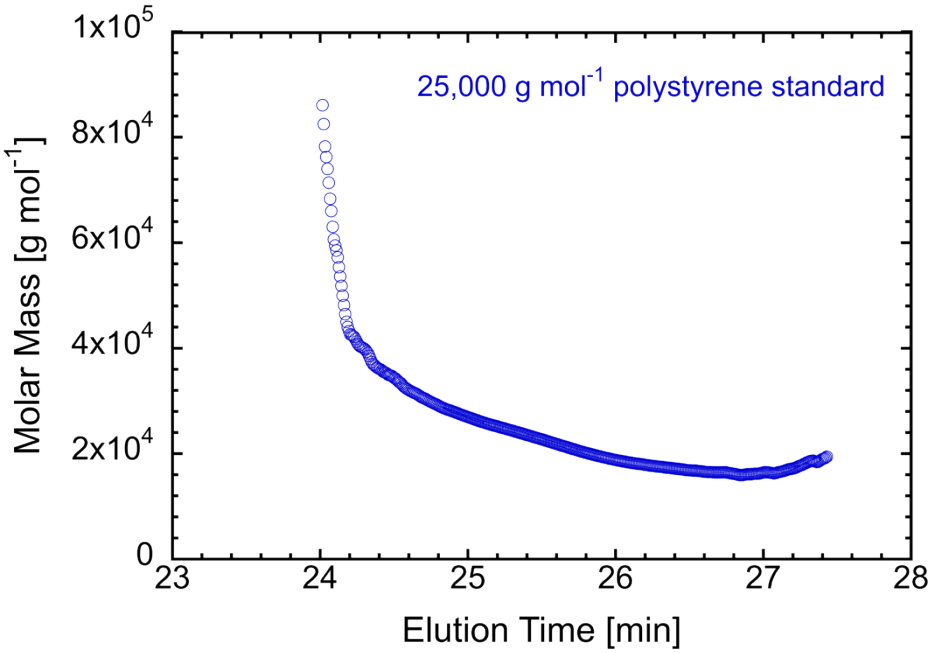

Figure S5. GPC retention time data of the 25,000 g mol^{-1} polystyrene standard, which was used to generate the calibration curve for molecular weight analysis of the lignin fractions.

3. Transmission Electron Microscopy (TEM) Analysis

Figure S6 shows the transmission electron microscopy (TEM) images of SPEEK(80%)–lignin

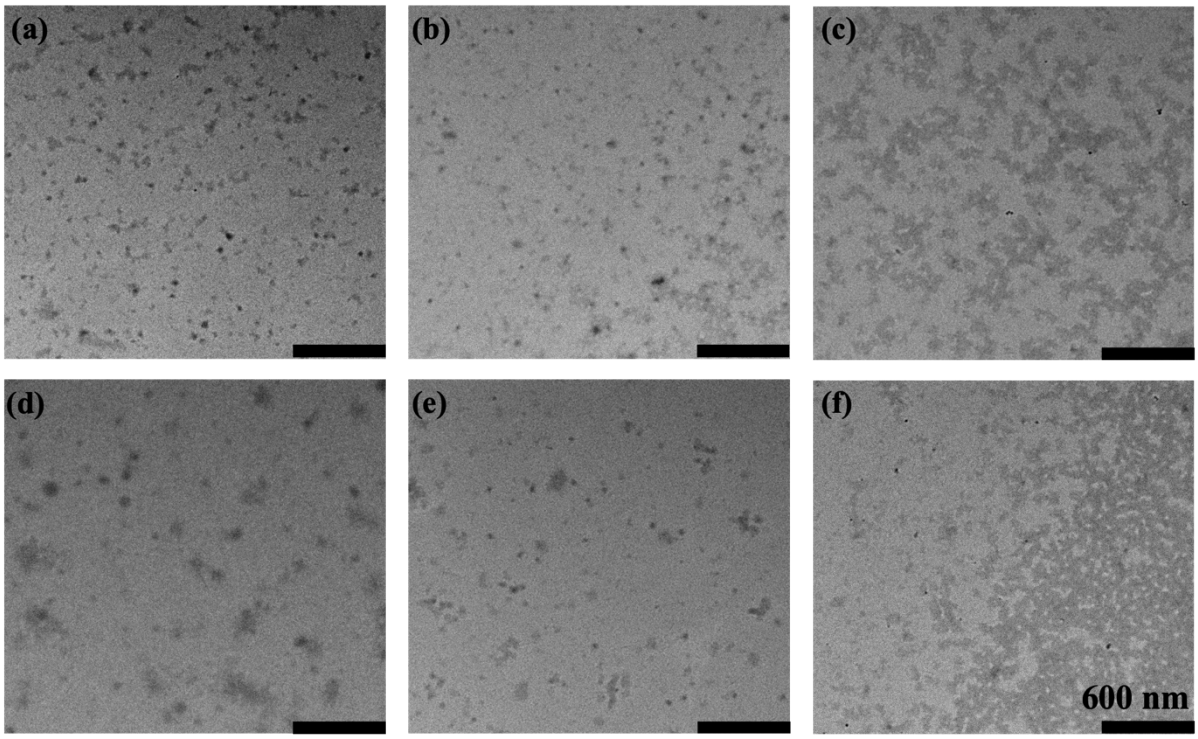

Figure S6. Transmission electron microscopy (TEM) images of 4h SPEEK containing (a) 5 mass%, (b) 15 mass%, and (c) 25 mass% LMW lignin, as well as TEM images of 4h SPEEK containing (d) 5 mass %, (e) 15 mass %, and (f) 25 mass % HMW lignin.

composites. Specifically, **Figures S6**a-c show the TEM images of SPEEK(80%) containing 5 mass %, 15 mass %, and 25 mass % LMW lignin, respectively, while **Figures S6**d-f show the TEM images of SPEEK(80%) containing 5 mass %, 15 mass %, and 25 mass % HMW lignin, respectively. Note that the scale bars in all TEM images shown in **Figure S6** are identical and are equal to 600 nm.

As seen in **Figure 5** of the manuscript, the lignin dispersion state of SPEEK(72%) containing 15 mass % HMW was unique when compared to those ionomers containing 5 and 25 mass %

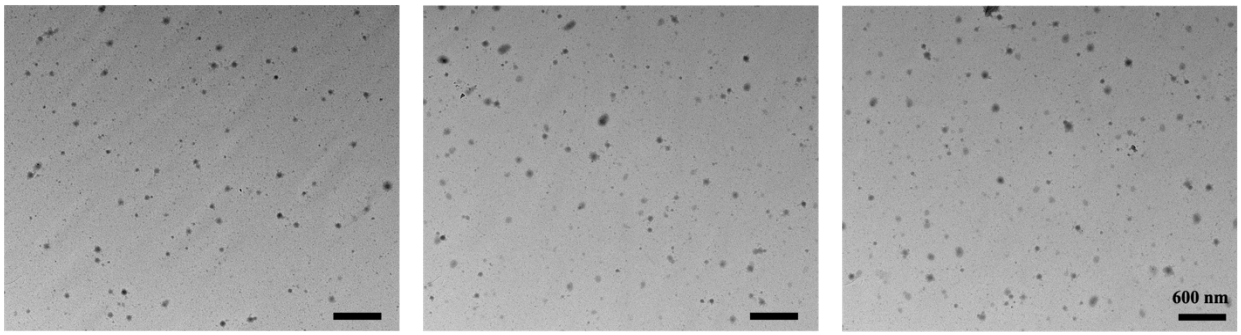

Figure S7. Transmission electron microscopy (TEM) of 3h SPEEK containing 15 mass % HMW lignin.

lignin. To ensure that this was not an artifact of image selection bias, additional TEM images of these samples have been provided in **Figure S7**. As seen from the TEM images in Figure S4, analogous aggregation behavior – i.e., lignin dispersion state – to that shown in **Figure 5** was observed.

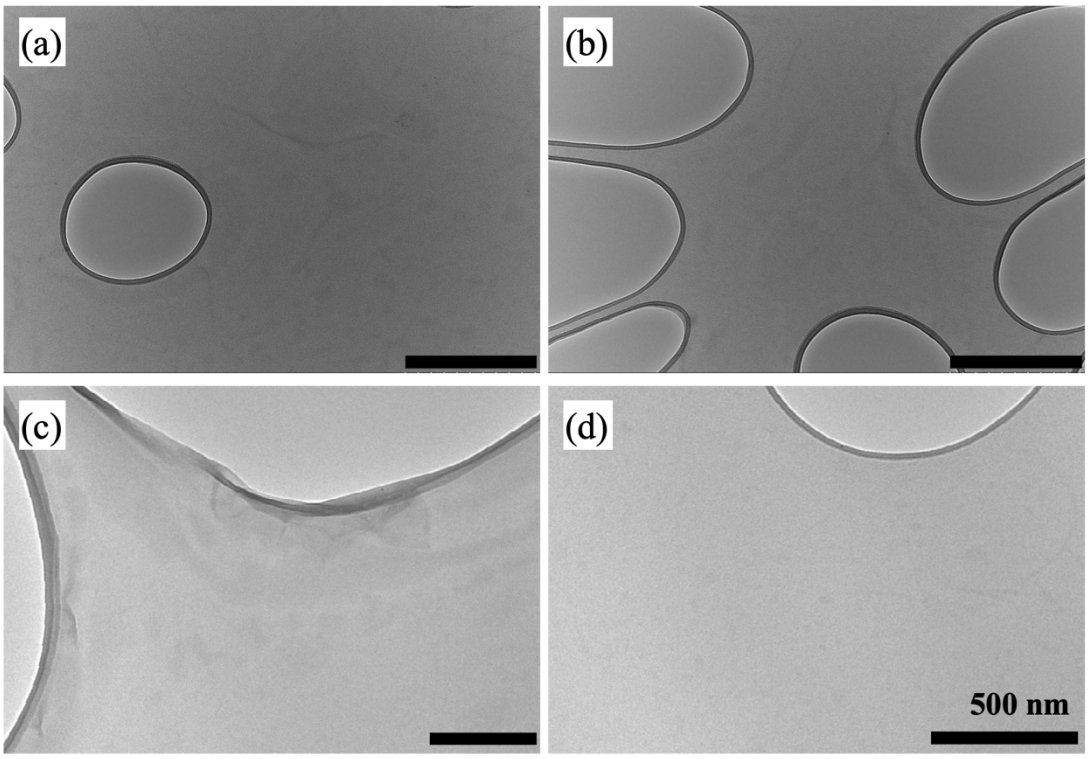

Figure S8. Transmission electron microscopy (TEM) of (a)-(b) neat SPEEK(72%), and (c)-(d) neat SPEEK(80%)

Finally, to confirm that the dark areas in the TEM images of the SPEEK–lignin composites were in fact lignin, TEM was used to image both the neat SPEEK(72%) and SPEEK(80%) membranes. For SPEEK(72%), these results are shown in **Figures S8**a,b, while the results for SPEEK(80%) are shown in **Figures S8**c,d. Similar to how the SPEEK – lignin samples were prepared for TEM, a SPEEK in DMAc solution, with a polymer concentration between 0.05 mass % to 0.1 mass %, was used to cast a thin film onto 300 mesh copper grid with lacey carbon support for TEM experiment. Note that the scale bars in all TEM images shown in **Figure S8** are identical and are equal to 500 nm. Comparing the TEM images of neat SPEEK membrane and their lignin containing counterparts, the dark aggregated phases in the lignin containing samples are further confirmed to be a result of the lignin fillers.

4. Quantitative Analysis of the SANS Data

The ionomer peak of the 3h SPEEK-based composites containing LMW and HMW lignin are shown in **Figures S9**a and **S9**b, respectively, while the ionomer peak of the SPEEK(80%)-based composites containing LMW and HMW lignin are shown in **Figures S9**c and **S9**d, respectively.

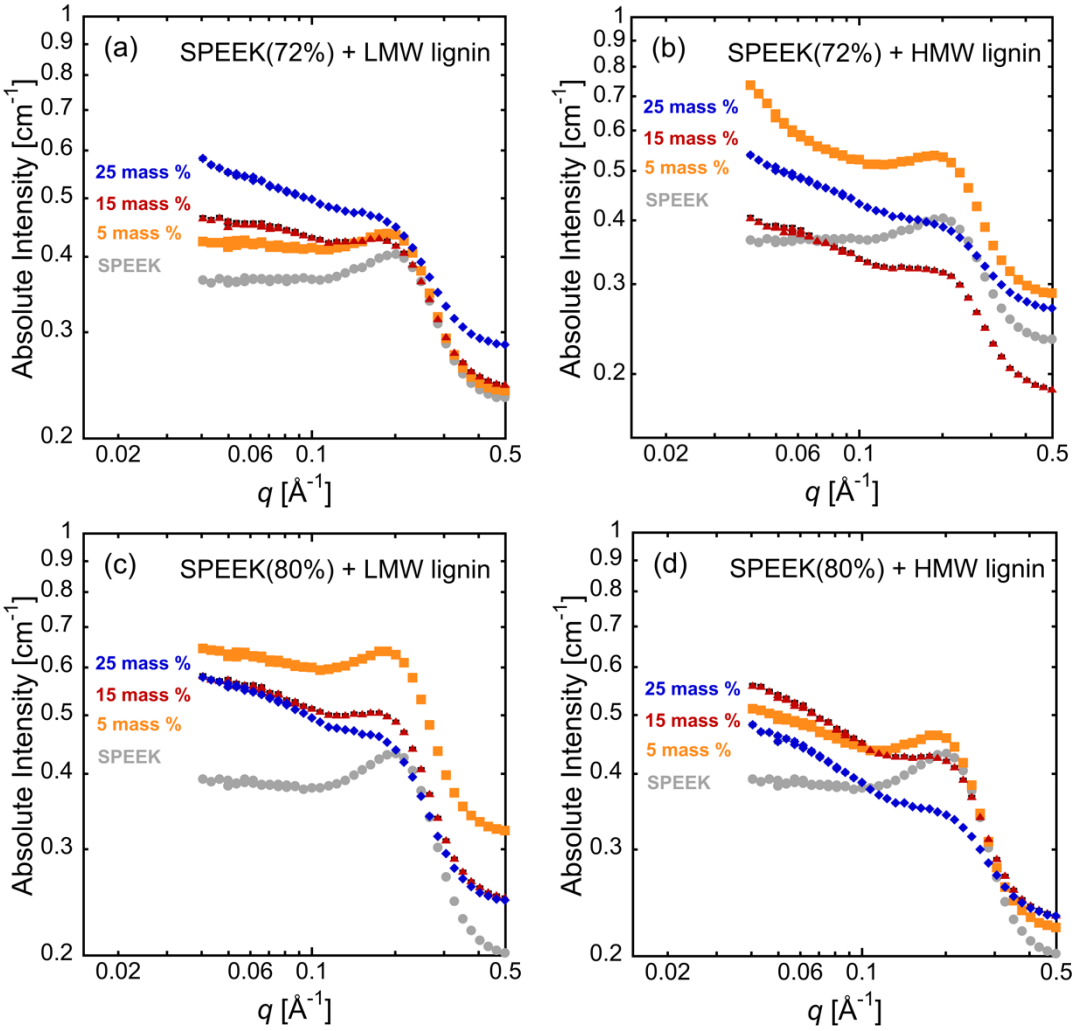

Figure S9. Ionomer peak of SPEEK(72%) containing (a) 0 mass % (solid gray circles), 5 mass % (solid orange squares), 15 mass % (solid red triangles), and 25 mass % (solid blue diamonds) LMW lignin and (b) 0 mass % (solid gray circles), 5 mass % (solid orange squares), 15 mass % (solid red triangles), and 25 mass % (solid blue diamonds) HMW lignin. Ionomer peak of SPEEK(80%) containing (c) 0 mass % (solid gray circles), 5 mass % (solid orange squares), 15 mass % (solid red triangles), and 25 mass % (solid blue diamonds) LMW lignin and (d) 0 mass % (solid gray circles), 5 mass % (solid orange squares), 15 mass % (solid red triangles), and 25 mass % (solid blue diamonds) HMW lignin.

First, there is a noticeable shift towards a lower wave vector with the introduction of lignin –which indicates that the presence of lignin increases the periodic spacing between hydrophilic domains in SPEEK. For ionomer composites containing 15 mass % and 25 mass % lignin, both the LMW and HMW lignin fractions display a new peak around $q \approx$ 0.05 Å^{-1}. Further, the scattering intensity in this q range increases with increasing lignin concentration. A similar scattering peak, located around $q \approx$ 0.04–0.05 Å^{-1}, was observed in a structural study of SPEEK membranes by Gebel and co-workers,[1] where this peak was assigned to crystalline domain formed by the aromatic backbone. However, the IEC values of the membranes in that work were lower than 1.3 mmol g^{-1}, indicating a relatively low values of DS, and likely, little to no crystallinity in these membranes.

As a semicrystalline polymer, the crystallinity of SPEEK membranes is highly dependent on the DS of the ionomer. Noto et al.[2] used differential scanning calorimetry (DSC) to investigate the crystallinity of neat SPEEK membranes with various values of DS. They found that the SPEEK membranes were completely amorphous for DS >62%. However, the lack of a peak in this region does not directly prove that our membranes are completely amorphous, as this may be because the material lacks large-scale, ordered structures that are detectable by SANS. Some other measurement, such as wide-angle X-ray scattering, and DSC would need to be employed to confirm our membranes are completely amorphous at these high values of DS (70% and 80% for 3h SPEEK and 4h SPEEK, respectively).

To extract the d-spacing between hydrophilic clusters, the ionomer peak in the SANS data of each sample were fit to a Gaussian function using the equation shown below

$$I(Q) = Ae^{-\frac{(Q-\mu)^2}{2\sigma^2}}, \qquad \text{(S2)}$$

where A is a pre-exponential factor, σ is the standard deviation (also known as Gaussian root mean square width), which describes the width (spread) of the peak, and μ is the position of the peak center, which was used as the peak location for the ionomer peak. The best-fit Gaussian curves from the analysis of each sample are provided in **Figure S10**. The fitting parameters (i.e., peak location and the spread of the peak) obtained from the regression are shown in **Table S1**.

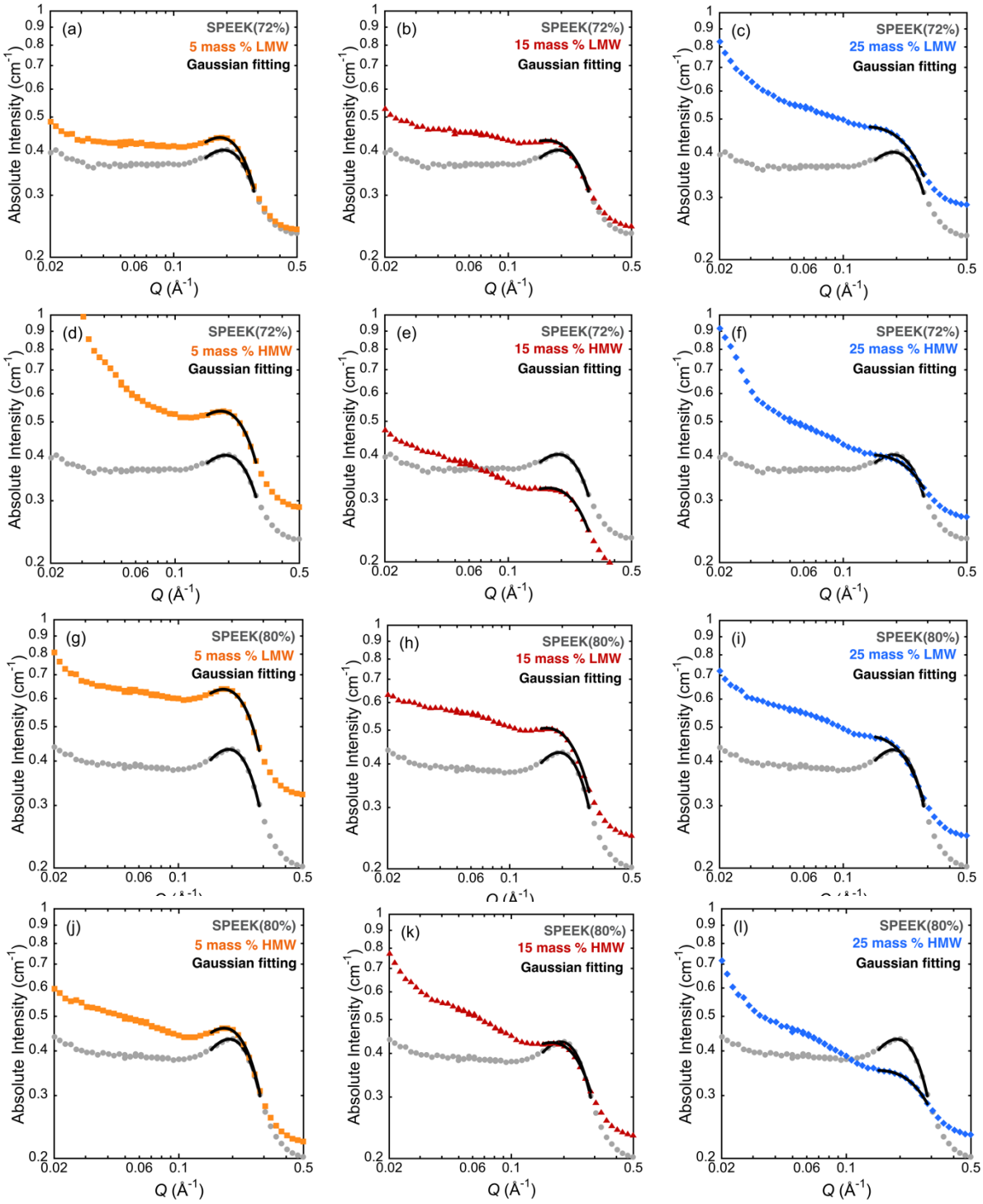

Figure S10. Ionomer peak of SPEEK(72%) containing (a) 5 mass %, (b) 15 mass %, (c) 25 mass % LMW lignin and (d) 5 mass %, (e) 15 mass %, (f) 25 mass % HMW lignin, along with ionomer peak of neat SPEEK(72%) and the Guassian fitting of these ionomer peaks. Ionomer peak of SPEEK(80%) containing (g) 5 mass %, (h) 15 mass %, (i) 25 mass % LMW lignin and (j) 5 mass %, (k) 15 mass %, (l) 25 mass % HMW lignin, along with ionomer peak of neat SPEEK(80%) and the Guassian fitting of these ionomer peaks.

Table S1. Fitting parameters from Gaussian regression of ionomer peaks for each sample.

Sample	Peak Location (μ) [$Å^{-1}$]	Peak Spread (σ) [-]
SPEEK(72%)	0.1920 ± 0.0010	0.1267 ± 0.0022
5LMW-SPEEK(72%)	0.1825 ± 0.0016	0.1257 ± 0.0028
15LMW-SPEEK(72%)	0.1649 ± 0.0030	0.1501 ± 0.0044
25LMW-SPEEK(72%)	0.1318 ± 0.0056	0.1915 ± 0.0069
5HMW-SPEEK(72%)	0.1804 ± 0.0001	0.1280 ± 0.0020
15HMW-SPEEK(72%)	0.1686 ± 0.0028	0.1560 ± 0.0044
25HMW-SPEEK(72%)	0.1404 ± 0.0036	0.2192 ± 0.0052
SPEEK(80%)	0.1919 ± 0.0012	0.1086 ± 0.0022
5LMW-SPEEK(80%)	0.1789 ± 0.0021	0.1188 ± 0.0032
15LMW-SPEEK(80%)	0.1622 ± 0.0036	0.1336 ± 0.0045
25LMW-SPEEK(80%)	0.1361 ± 0.0001	0.1624 ± 0.0051
5HMW-SPEEK(80%)	0.1793 ± 0.0020	0.1146 ± 0.0030
15HMW-SPEEK(80%)	0.1700 ± 0.0021	0.1425 ± 0.0032
25HMW-SPEEK(80%)	0.1499 ± 0.0024	0.2057 ± 0.0037

REFERENCES

(1) Gebel, G. Structure of Membranes for Fuel Cells: SANS and SAXS Analyses of Sulfonated PEEK Membranes and Solutions. *Macromolecules* **2013**, *46* (15), 6057–6066. https://doi.org/10.1021/ma400314c.
(2) Di Noto, V.; Piga, M.; Giffin, G. A.; Pace, G. Broadband Electric Spectroscopy of Proton Conducting SPEEK Membranes. *Journal of Membrane Science* **2012**, *390–391*, 58–67. https://doi.org/10.1016/j.memsci.2011.10.049.